

Hence for spherical  $\text{LiMPO}_4$  particles of 40 nm average diameter and a continuous dense carbon coating of 1 nm mean thickness 10 wt% carbon with respect to the mass of  $\text{LiMPO}_4$  would be required. The necessary amount would be higher for non-spherical particles since a sphere has the smallest surface area for a given volume. It would be lower for bigger  $\text{LiMPO}_4$  particles or a thinner or discontinuous or less dense carbon coating.

Carbon exhibits good electric conductivity only in its graphite modification ( $\text{sp}^2$  hybridized carbon) and only within the two-dimensional basal graphene planes. Hence for good electric conductivity of the carbon network in the nanocomposite a large fraction and sufficient extension of these graphitic domains with  $\text{sp}^2$  carbon is required. Since the low heat treatment temperature of 350-600°C is not sufficient to cause any graphitization a high graphene fraction must already be present in the carbon additive before milling. According to the present invention this is achieved by employing electro-conductive carbon black of high surface area, such as Printex XE 2 (Degussa), Black Pearls 2000 (Cabot) or Ketjenblack (Akzo Nobel), carbon nanotubes (SWCNT or MWCNT), graphite, expanded graphite or graphene. The fraction and size of well conducting graphene domains in the nanocomposite obtained by milling can be determined by different analytical techniques, such as Raman spectroscopy (ratio of graphene G-band around 1580  $\text{cm}^{-1}$  and disorder D-band around 1360  $\text{cm}^{-1}$ )<sup>57, 58</sup>, X-ray and neutron diffraction, as well as electron microscopy (TEM).

## EXAMPLES

### Example 1: Synthesis of $\text{LiMnPO}_4/\text{C}$ nanocomposite

A mixture of 3.45 g  $\text{MnCO}_3$  (Aldrich 99.9%) + 3.12 g  $\text{LiH}_2\text{PO}_4$  (Aldrich 99%) + 1 g Ketjenblack EC600JD (Akzo Nobel) was milled in a hardened steel container of 250 mL capacity with 12 hardened steel balls of 20 mm diameter in a planetary ball mill (Retsch PM 100) at 500 rpm for 2 hours. The obtained powder was heated up to 450°C within 30 minutes and maintained at this temperature for 1 hour under a stream of argon + 8% hydrogen.

### Example 2: Synthesis of $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$ nanocomposite (18% Ketjenblack)

A mixture of 3.105 g  $\text{MnCO}_3$  (Aldrich 99.9%) + 0.54 g  $\text{FeC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$  (Fluka 99%) + 3.12 g  $\text{LiH}_2\text{PO}_4$  (Aldrich 99%) + 1 g Ketjenblack EC600JD was milled as described in Example 1 and heated at 350, 450 or 550°C for 1 hour under argon + 8% hydrogen.

Figure 1 shows a scanning electron microscope picture of the nanocomposite obtained at 450°C, indicating a primary particle size in the order of 50 nm for the brighter  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$  component.

Figure 2 shows the X-ray diffraction patterns of the three samples, indicating poor crystallization after 1 hour at 350°C, while the sample heated for the same time at 450°C is well crystallized  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$  without any apparent impurities. From the line broadening an average crystallite size of 60 nm with negligible strain was calculated with the Warren-Averbach method. This agrees with the primary particle size in the order of 50 nm observed in the SEM picture (Figure 1).

**Example 3:** Synthesis of  $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/10\%\text{C}$  nanocomposites with different carbon materials

A mixture of 2.76 g  $\text{MnCO}_3$  (Aldrich 99.9%) + 1.08 g  $\text{FeC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$  (Fluka 99%) + 3.12 g  $\text{LiH}_2\text{PO}_4$  (Aldrich 99%) + 0.5 g carbon was milled and heat treated as described in Example 1.

Following carbon materials were compared:

Ketjenblack EC-300J (Akzo Nobel, 800  $\text{m}^2/\text{g}$ )

Ketjenblack EC-600JD (Akzo Nobel, 1400  $\text{m}^2/\text{g}$ )

Printex XE 2 (Degussa, 950  $\text{m}^2/\text{g}$ )

Black Pearls 2000 (Cabot, 1500  $\text{m}^2/\text{g}$ )

Shawinigan acetylene black C-55 (70  $\text{m}^2/\text{g}$ )

Multi walled carbon nanotubes (MWCNT)

High surface graphite Timrex HSAG300 (Timcal, 280  $\text{m}^2/\text{g}$ )

Timrex KS4 graphite (Timcal, 26  $\text{m}^2/\text{g}$ )

Timrex KS6 graphite (Timcal, 20  $\text{m}^2/\text{g}$ )

Timrex SFG6 graphite (Timcal, 17  $\text{m}^2/\text{g}$ )

Timrex MB15 graphite (Timcal, 9.5  $\text{m}^2/\text{g}$ )

**Example 4:** Synthesis of  $\text{LiFePO}_4/3\%\text{C}$  nanocomposite

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A mixture of 5.4 g  $\text{FeC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$  + 3.12 g  $\text{LiH}_2\text{PO}_4$  + 0.15 g SFG6 graphite (Timcal) was milled and heat treated as described in Example 1.

10 **Example 5:** Synthesis of  $\text{LiFe}_{0.9}\text{Mn}_{0.1}\text{PO}_4/3\%\text{C}$  nanocomposite

A mixture of 4.86 g  $\text{FeC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$  + 0.345 g  $\text{MnCO}_3$  + 3.12 g  $\text{LiH}_2\text{PO}_4$  + 0.15 SFG6 graphite (Timcal) was milled and heat treated as described in Example 1.

15 **Example 6:** Preparation of a  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$  cathodes and secondary lithium batteries with such cathodes

1 g of  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$  nanocomposite as obtained in Example 1 to 5 was mixed with 20 mg graphite powder and 75 mg PVdF (polyvinylidene difluoride) in NMP (N-methyl-2-pyrrolidinon). This dispersion was doctor bladed on a carbon coated aluminum foil and dried at  $120^\circ\text{C}$  under vacuum. The electrodes were compressed into  $\varnothing$  23 mm disks with a thickness of about 30  $\mu\text{m}$  and an active material loading of about  $3.0 \text{ mg/cm}^2$ . Cells were assembled in Swagelok<sup>TM</sup> fittings using Li metal foil as counter electrode with a microporous polymer separator (Celgard 2400<sup>TM</sup>) and an electrolyte of 1M  $\text{LiPF}_6$  in propylene carbonate (PC), ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1:3 by volume). The electrochemical properties of the  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$  electrodes were measured by galvanostatic charge/discharge and cyclic voltammetry with Arbin BT 2000. Figures 3, 5, 7 and 8 show the electrochemical performance at different discharging rates. Figures 4 and 6 show the stability on cycling at a charge/discharge rate of 1 C.

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**BRIEF DISCRIPTION OF THE DRAWINGS**

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**Figure 1** shows a scanning electron microscope (SEM) picture of the  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$  nanocomposite (18% Ketjenblack EC600JD) according to Example 2 after heating for 1 hour under argon/8% hydrogen at 450°C. The primary particle size is in the order of 50 nm for the brighter  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$  component.

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**Figure 2** shows the X-ray diffraction (XRD) patterns of the  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$  nanocomposite (18% Ketjenblack EC600JD) according to Example 2 after heating for 1 hour under argon/8% hydrogen at different temperatures. Only weak XRD peaks are observed after 1 hour at 350°C indicating poor crystallization, while the sample heated for the same time at 450°C is well crystallized  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$  without any apparent impurities. Heating at 550°C leads to a further increase in the peak intensities and slight reduction in the peak widths. From the line broadening at 450°C an average crystallite size of 60 nm with negligible strain was calculated with the Warren-Averbach method. This agrees with the primary particle size in the order of 50 nm observed in the SEM picture (Figure 1).

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**Figure 3** represents the electrochemical performance of two different lithium batteries with  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$  nanocomposite cathode (18% Ketjenblack EC600JD) at different discharge rates on cycling between 2.7 and 4.4 V against lithium. A capacity of 150 mAh/g of active material is achieved at D/10. Even at a discharge rate of 5D a capacity as high as 130

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**Figure 4** shows the cycling stability (at 1 C and C/10 each 10th cycle, charged up to 4.25 V) of the lithium batteries from Figure 3 with  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$  nanocomposite cathode (18% Ketjenblack EC600JD).

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**Figure 5** shows the electrochemical performance of a lithium battery with  $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$  nanocomposite cathode (10% Ketjenblack EC600JD) at different discharge rates on cycling between 2.7 and 4.4 V against lithium. A capacity of 145 mAh/g of active material is obtained at D/10. At a discharge rate of 5D the capacity is still higher than 110 mAh/g.

**Figure 6** shows the cycling stability (at 1 C and C/10 each 10th cycle, charged up to 4.25 V) of two lithium batteries according to Figure 5 with  $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$  nanocomposite cathode (10% Ketjenblack EC600JD).

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**Figure 7** shows the electrochemical performance of lithium batteries with  $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/10\%\text{C}$  nanocomposite cathodes prepared from different carbon sources on cycling between 2.7 and 4.4 V against lithium:

- △ Ketjenblack EC-300J (Akzo Nobel, 800  $\text{m}^2/\text{g}$ )
  - 10 □ Ketjenblack EC-600JD (Akzo Nobel, 1400  $\text{m}^2/\text{g}$ )
  - ▲ Black Pearls 2000 (Cabot, 1500  $\text{m}^2/\text{g}$ )
  - ◆ Multi walled carbon nanotubes (MWCNT)
  - High surface graphite Timrex HSAG300 (Timcal, 280  $\text{m}^2/\text{g}$ )
- Ketjenblack EC-600JD and high surface graphite Timrex HSAG300 show the best
- 15 performance with a capacity of 145 mAh/g at D/10 and more than 110 mAh/g at 5D.

**Figure 8** shows the electrochemical performance of lithium batteries with  $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/10\%\text{C}$  nanocomposite cathodes prepared from different carbon sources on cycling between 2.7 and 4.4 V against lithium:

- 20 ▲ Ketjenblack EC-600JD (Akzo Nobel, 1400  $\text{m}^2/\text{g}$ )
  - ◆ Timrex KS4 graphite (Timcal, 26  $\text{m}^2/\text{g}$ )
  - ◇ Timrex SFG6 graphite (Timcal, 17  $\text{m}^2/\text{g}$ )
  - Timrex MB15 graphite (Timcal, 9.5  $\text{m}^2/\text{g}$ )
  - △ Shawinigan acetylene black C-55 (70  $\text{m}^2/\text{g}$ )
- 25 The three different graphites yield comparable performance to Ketjenblack EC-600JD. Shawinigan acetylene black C-55 gives much lower capacity, especially at higher discharge rates.

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## CLAIMS

- 10 1. A lithium metal phosphate/carbon nanocomposite as cathode material for rechargeable electrochemical cells with the general formula  $\text{Li}_x\text{M1}_y\text{M2}_{1-y}\text{PO}_4/\text{C}$  where M1 is Fe, Mn, Co, Ni, VF and M2 is Fe, Mn, Co, Ni, VF, Mg, Ca, Al, B, Cr, Zn, Cu, Nb, Zr, V, Ti and  $x = 0.8-1.0$  and  $y = 0.5-1.0$ , with a carbon content of 0.5 to 20% by weight.
- 15 2. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average crystallite size of the  $\text{Li}_x\text{M1}_y\text{M2}_{1-y}\text{PO}_4$  domains as determined by X-ray diffraction is not larger than 300 nm.
- 20 3. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average crystallite size of the  $\text{Li}_x\text{M1}_y\text{M2}_{1-y}\text{PO}_4$  domains as determined by X-ray diffraction is not larger than 200 nm.
- 25 4. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average crystallite size of the  $\text{Li}_x\text{M1}_y\text{M2}_{1-y}\text{PO}_4$  domains as determined by X-ray diffraction is not larger than 100 nm.
5. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average crystallite size of the  $\text{Li}_x\text{M1}_y\text{M2}_{1-y}\text{PO}_4$  domains as determined by X-ray diffraction is not larger than 80 nm.
- 30 6. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average crystallite size of the  $\text{Li}_x\text{M1}_y\text{M2}_{1-y}\text{PO}_4$  domains as determined by X-ray diffraction is not larger than 60 nm.

7. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average crystallite size of the  $\text{Li}_x\text{M}_1\text{yM}_2\text{1-yPO}_4$  domains as determined by X-ray diffraction is not larger than 50 nm.
- 5
8. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average crystallite size of the  $\text{Li}_x\text{M}_1\text{yM}_2\text{1-yPO}_4$  domains as determined by X-ray diffraction is not larger than 40 nm.
- 10
9. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average cross-sectional dimension of the  $\text{Li}_x\text{M}_1\text{yM}_2\text{1-yPO}_4$  domains as determined by electron microscopy is not larger than 300 nm.
- 15
10. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average cross-sectional dimension of the  $\text{Li}_x\text{M}_1\text{yM}_2\text{1-yPO}_4$  domains as determined by electron microscopy is not larger than 200 nm.
- 20
11. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average cross-sectional dimension of the  $\text{Li}_x\text{M}_1\text{yM}_2\text{1-yPO}_4$  domains as determined by electron microscopy is not larger than 100 nm.
- 25
12. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average cross-sectional dimension of the  $\text{Li}_x\text{M}_1\text{yM}_2\text{1-yPO}_4$  domains as determined by electron microscopy is not larger than 80 nm.
- 30
13. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average cross-sectional dimension of the  $\text{Li}_x\text{M}_1\text{yM}_2\text{1-yPO}_4$  domains as determined by electron microscopy is not larger than 60 nm.
14. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average cross-sectional dimension of the  $\text{Li}_x\text{M}_1\text{yM}_2\text{1-yPO}_4$  domains as determined by electron microscopy is not larger than 50 nm.

15. A lithium metal phosphate/carbon nanocomposite according to claim 1, wherein the average cross-sectional dimension of the  $\text{Li}_x\text{M}_1\text{yM}_2\text{1-yPO}_4$  domains as determined by electron microscopy is not larger than 40 nm.
- 5 16. A lithium metal phosphate/carbon nanocomposite according to claims 1 to 15, wherein the integrated peak intensity ratio  $R = D/G$  of the D-band around  $1360\text{ cm}^{-1}$  and the G-band around  $1580\text{ cm}^{-1}$  in the Raman spectrum due to disordered and graphene carbon is not larger than 1.0. (comment: Sony claims the opposite: D/G not smaller than 0.3, but for the precursor carbon material, not the product).<sup>7, 30-34</sup>
- 10 17. A lithium metal phosphate/carbon nanocomposite according to claims 1 to 15, wherein the integrated peak intensity ratio  $R = D/G$  of the D-band around  $1360\text{ cm}^{-1}$  and the G-band around  $1580\text{ cm}^{-1}$  in the Raman spectrum due to disordered and graphene carbon is not larger than 0.8.
- 15 18. A lithium metal phosphate/carbon nanocomposite according to claims 1 to 15, wherein the integrated peak intensity ratio  $R = D/G$  of the D-band around  $1360\text{ cm}^{-1}$  and the G-band around  $1580\text{ cm}^{-1}$  in the Raman spectrum due to disordered and graphene carbon is not larger than 0.6.
- 20 19. A lithium metal phosphate/carbon nanocomposite according to claims 1 to 15, wherein the integrated peak intensity ratio  $R = D/G$  of the D-band around  $1360\text{ cm}^{-1}$  and the G-band around  $1580\text{ cm}^{-1}$  in the Raman spectrum due to disordered and graphene carbon is not larger than 0.5.
- 25 20. A lithium metal phosphate/carbon nanocomposite according to claims 1 to 15, wherein the integrated peak intensity ratio  $R = D/G$  of the D-band around  $1360\text{ cm}^{-1}$  and the G-band around  $1580\text{ cm}^{-1}$  in the Raman spectrum due to disordered and graphene carbon is not larger than 0.4.
- 30 21. A lithium metal phosphate/carbon nanocomposite according to claims 1 to 15, wherein the integrated peak intensity ratio  $R = D/G$  of the D-band around  $1360\text{ cm}^{-1}$  and the G-band around  $1580\text{ cm}^{-1}$  in the Raman spectrum due to disordered and graphene carbon is not larger than 0.3.

22. A lithium metal phosphate/carbon nanocomposite according to claims 1 to 21, wherein  
the carbon is covalently bound to the lithium metal phosphate through carbon-oxygen-  
metal (C-O-M) and/or carbon-oxygen-phosphor (C-O-P) bridges.
23. A lithium metal phosphate/carbon nanocomposite according to claims 1 to 22, wherein  
M1 = Mn and M2 = Fe.
24. A lithium metal phosphate/carbon nanocomposite according to claims 1 to 22, wherein  
M1 = Fe and M2 = Mn.
25. A lithium metal phosphate/carbon nanocomposite according to claims 1 to 22, wherein  
M1 = M2 = Fe.
26. A process for the production of lithium metal phosphate/carbon nanocomposites  
according to claims 1 to 25, in which the precursors for the lithium metal phosphate  
are milled with a carbon material and subsequently heated for crystallization.
27. A process for the production of lithium metal phosphate/carbon nanocomposites  
according to claim 26, in which the metal precursors for lithium metal phosphate are  
metal carbonates or oxalates or oxides (e.g. MnO, Mn<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>),  
hydroxides, salts with carboxylic acids (e.g. acetates) or hydroxyl carboxylic acids  
(e.g. glycolates, lactates, citrates, tartrates), or any other metal compound that  
produces no byproducts which degrade the main product.
28. A process for the production of lithium metal phosphate/carbon nanocomposites  
according to claim 26, in which the lithium precursor for lithium metal phosphate is  
LiH<sub>2</sub>PO<sub>4</sub> or LiPO<sub>3</sub>, or Li<sub>2</sub>O, LiOH, Li<sub>2</sub>CO<sub>3</sub> or any other lithium compound that  
produces no byproducts which degrade the main product.
29. A process for the production of lithium metal phosphate/carbon nanocomposites  
according to claim 26, in which the phosphate precursor for lithium metal phosphate is  
LiH<sub>2</sub>PO<sub>4</sub> or LiPO<sub>3</sub>, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, phosphoric acid (HPO<sub>3</sub> or H<sub>3</sub>PO<sub>4</sub>), or any phosphate  
compound that produces no byproducts which degrade the main product.

- 5 30. A process for the production of lithium metal phosphate/carbon nanocomposites according to claim 27, in which the metal precursors for lithium metal phosphate are added in stoichiometric excess with respect to the phosphate precursor in order to favor formation of a metal oxide bonding layer (C-O-M) between carbon and lithium metal phosphate.
- 10 31. A process for the production of lithium metal phosphate/carbon nanocomposites according to claim 29, in which the phosphate precursor for lithium metal phosphate is added in stoichiometric excess with respect to the metal precursor in order to favor formation of a phosphate bonding layer (C-O-P) between carbon and lithium metal phosphate.
- 15 32. A process for the production of lithium metal phosphate/carbon nanocomposites according to claim 26 to 31, in which the carbon material is a high surface area electro-conductive carbon black, such as Printex XE 2 (Degussa), Black Pearls 2000 (Cabot) or Ketjenblack EC-300J or EC-600JD (Akzo Nobel).
- 20 33. A process for the production of lithium metal phosphate/carbon nanocomposites according to claim 26 to 31, in which the carbon material is single or multi walled carbon nanotubes (SWCNT or MWCNT).
- 25 34. A process for the production of lithium metal phosphate/carbon nanocomposites according to claim 26 to 31, in which the carbon material is natural or synthetic graphite, such as high surface graphite Timrex HSAG300 (Timcal), Timrex KS4 or KS 6 or KS44 graphite (Timcal), Timrex SFG6 or SFG44 graphite (Timcal), or Timrex MB15 graphite (Timcal).
- 30 35. A process for the production of lithium metal phosphate/carbon nanocomposites according to claim 26 to 31, in which the carbon material is expanded graphite.
36. A process for the production of lithium metal phosphate/carbon nanocomposites according to claim 26 to 31, in which the carbon material is exfoliated graphite or graphite oxide or graphene.

37. A process for the production of lithium metal phosphate/carbon nanocomposites according to claim 26 to 36, in which milling is carried out in a ball mill, shaker mill, vibration mill, roller mill, attrition mill, jet mill or any other suitable mill.
- 5 38. A process for the production of lithium metal phosphate/carbon nanocomposites according to claim 26 to 37, in which milling is carried out under air or inert gas atmosphere, preferably in dry conditions or alternatively in the presence of a solvent.
- 10 39. A process for the production of lithium metal phosphate/carbon nanocomposites according to claim 26 to 38, in which the product of milling is heated for crystallization to 300-600°C, preferably to 400-500°C, for a sufficient time.
- 15 40. A process for the production of lithium metal phosphate/carbon nanocomposites according to claim 39, in which heat treatment is carried out under vacuum or inert gas atmosphere, such as nitrogen or argon, with or without addition of reducing gases, such as hydrogen or carbon monoxide/dioxide mixtures, or just under the exclusion of oxygen excess from the atmosphere.
- 20 41. A rechargeable battery comprising a cathode, an anode and an electrolyte, said cathode comprising a metal phosphate/carbon nanocomposite according to claims 1 to 40.
- 25 42. A rechargeable battery according to claim 41, wherein the cathode further comprises a conductive additive.
43. A rechargeable battery according to claim 41, wherein the cathode further comprises a polymeric binder.

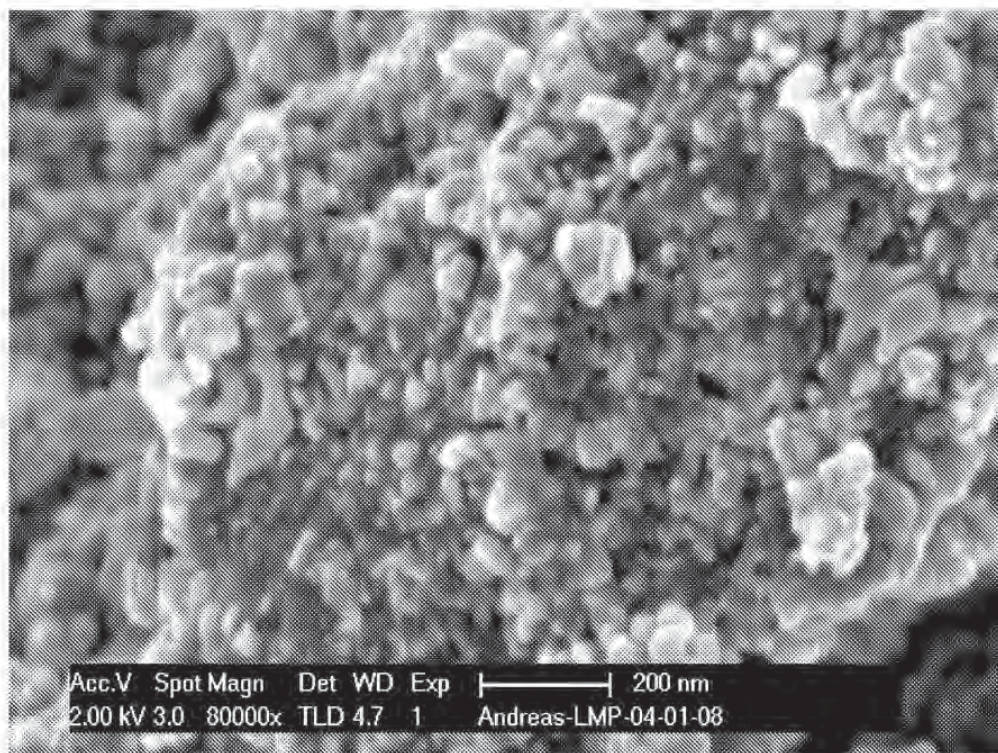


**Figure 1**

SEM picture of LiMn<sub>0.9</sub>Fe<sub>0.1</sub>PO<sub>4</sub>/C nanocomposite (18% Ketjenblack EC600JD) after heating for 1 hour under argon/8% hydrogen at 450°C

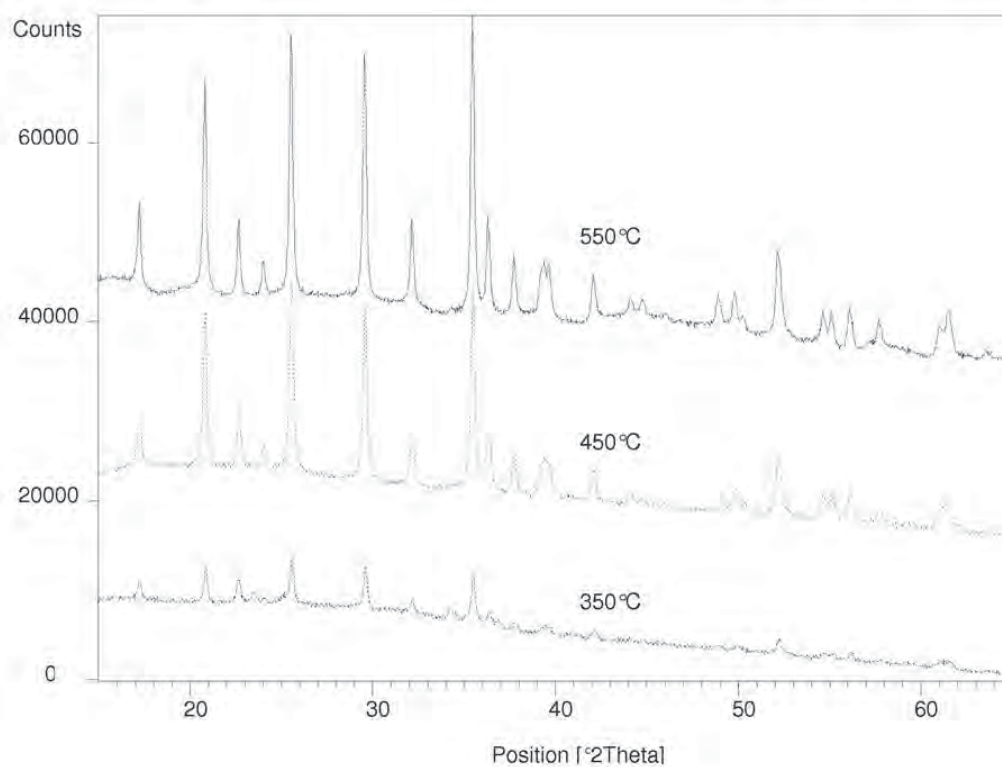
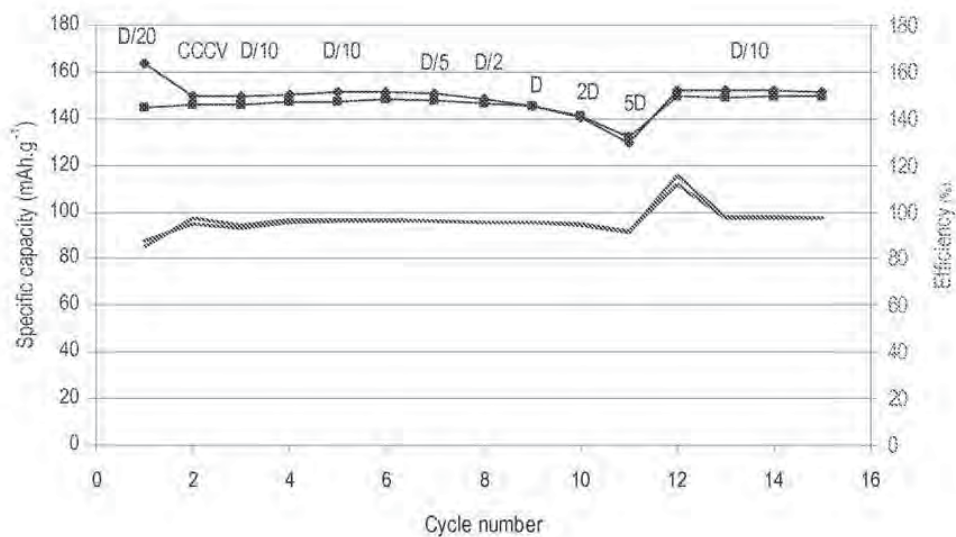
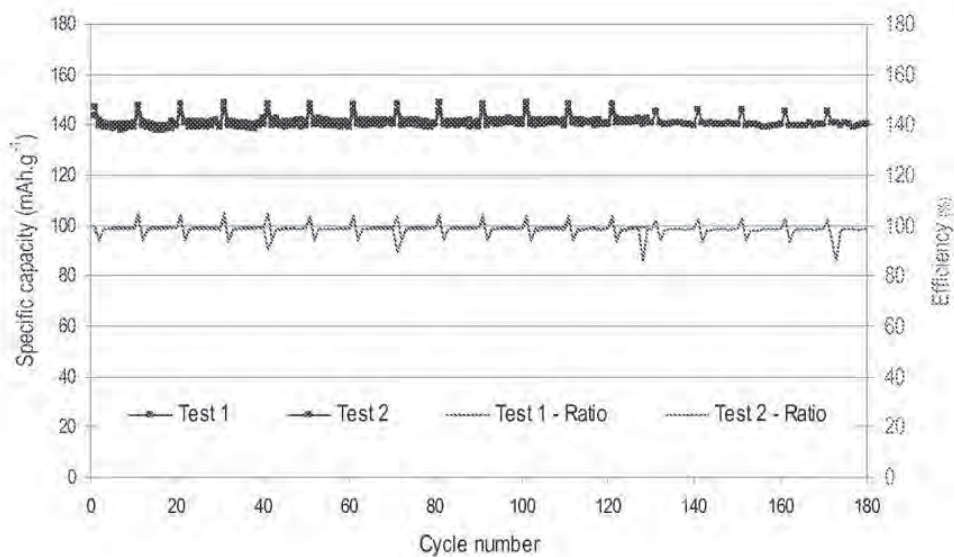


**Figure 2**

XRD patterns of  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$  nanocomposite (18% Ketjenblack EC600JD) after heating for 1 hour under argon/8% hydrogen at different temperatures

**Figure 3**

Electrochemical performance of two lithium batteries with  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$  nanocomposite cathode (18% Ketjenblack EC600JD) at different discharge rates

**Figure 4**

Cycling stability (at 1 C and C/10 each 10th cycle, charged up to 4.25 V) of two lithium batteries with  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$  nanocomposite cathode (18% Ketjenblack EC600JD)

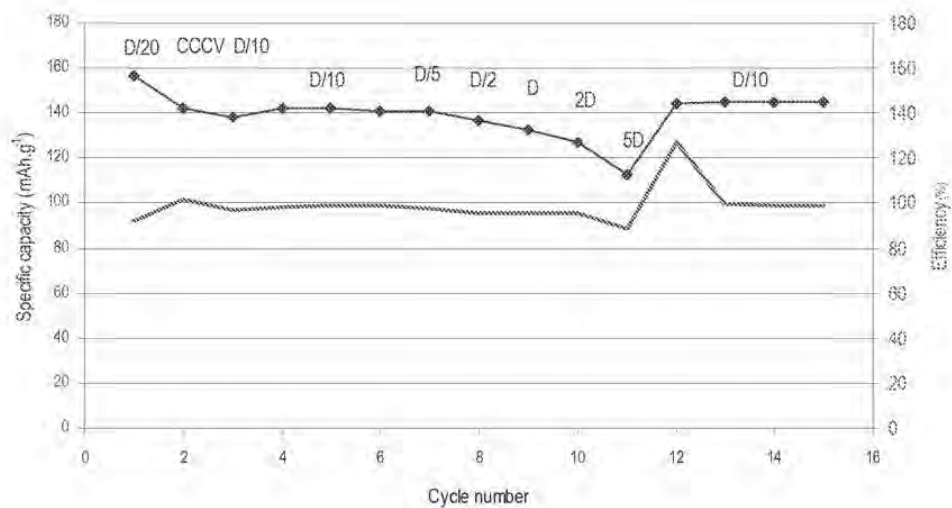
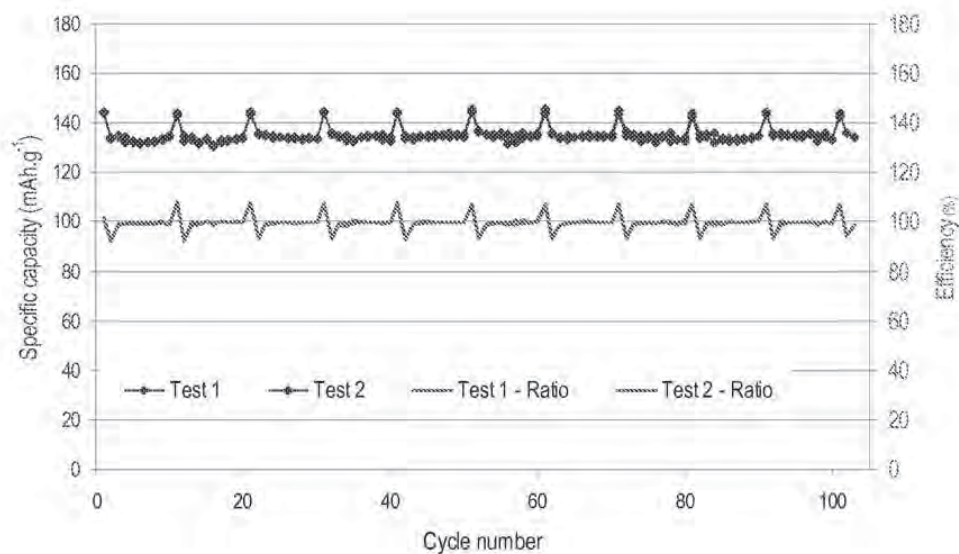
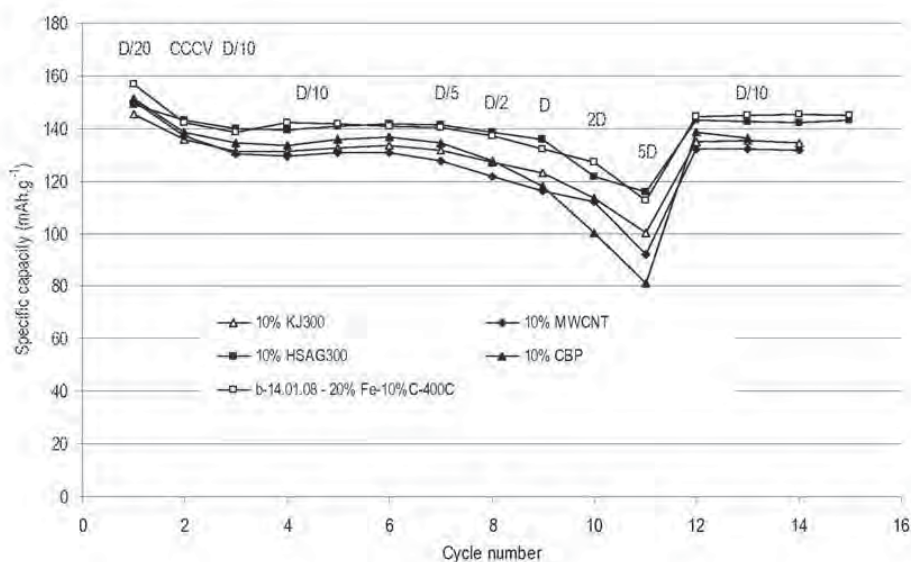


**Figure 5**

Electrochemical performance of lithium battery with  $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$  nanocomposite cathode (10% Ketjenblack EC600JD) at different discharge rates

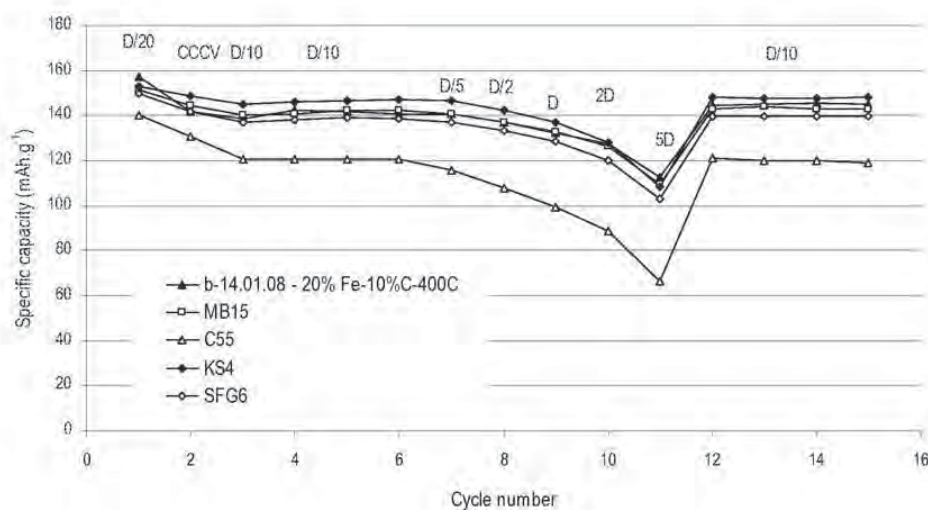
**Figure 6**

Cycling stability (at 1 C and C/10 each 10th cycle, charged up to 4.25 V) of two lithium batteries with  $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$  nanocomposite cathode (10% Ketjenblack EC600JD)

**Figure 7**

Electrochemical performance of lithium batteries with  $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/10\%\text{C}$  nanocomposite cathodes prepared from different carbon sources:

- $\Delta$  Ketjenblack EC-300J (Akzo Nobel,  $800 \text{ m}^2/\text{g}$ )
- $\square$  Ketjenblack EC-600JD (Akzo Nobel,  $1400 \text{ m}^2/\text{g}$ )
- $\blacktriangle$  Black Pearls 2000 (Cabot,  $1500 \text{ m}^2/\text{g}$ )
- $\blacklozenge$  Multi walled carbon nanotubes (MWCNT)
- $\blacksquare$  High surface graphite Timrex HSAG300 (Timcal,  $280 \text{ m}^2/\text{g}$ )

**Figure 8**

Electrochemical performance of lithium batteries with  $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/10\%\text{C}$  nanocomposite cathodes prepared from different carbon sources:

- ▲ Ketjenblack EC-600JD (Akzo Nobel,  $1400 \text{ m}^2/\text{g}$ )
- ◆ Timrex KS4 graphite (Timcal,  $26 \text{ m}^2/\text{g}$ )
- ◇ Timrex SFG6 graphite (Timcal,  $17 \text{ m}^2/\text{g}$ )
- Timrex MB15 graphite (Timcal,  $9.5 \text{ m}^2/\text{g}$ )
- △ Shawinigan acetylene black C-55 ( $70 \text{ m}^2/\text{g}$ )

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2008/051418

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C01B25/37 C01B25/45 H01M4/62

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                  | Relevant to claim No. |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | LEI WANG ET AL: "Nano-LiFePO <sub>4</sub> /MWCNT cathode materials prepared by room-temperature solid-state reaction and microwave heating"<br>JOURNAL OF THE ELECTROCHEMICAL SOCIETY<br>ELECTROCHEMICAL SOCIETY INC. USA,<br>vol. 154, no. 11, November 2007 (2007-11),<br>pages A1015-A1019, XP002513827<br>ISSN: 0013-4651<br>the whole document<br>-----<br>-/- | 1-38,<br>41-43        |

☒ Further documents are listed in the continuation of Box C.

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Date of the actual completion of the international search

6 February 2009

Date of mailing of the international search report

17/02/2009

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Rigondaud, Bernard

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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2008/051418

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                                                                       |                           |
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Information on patent family members

International application No

PCT/IB2008/051418

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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US 20110104551A1

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**YANG et al.**

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(43) **Pub. Date: May 5, 2011**

(54) **NANOTUBE COMPOSITE ANODE  
MATERIALS SUITABLE FOR LITHIUM ION  
BATTERY APPLICATIONS**

*H01M 4/58* (2010.01)  
*H01M 4/56* (2006.01)  
*H01M 4/60* (2006.01)  
*H01M 4/525* (2010.01)  
*H01M 4/54* (2006.01)  
*H01M 4/583* (2010.01)  
*H01M 6/42* (2006.01)  
*B82Y 30/00* (2011.01)

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Chicago, IL (US)

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(22) Filed: **Nov. 3, 2010**

(52) **U.S. CL.** ..... **429/149; 429/207; 429/231.95;  
429/226; 429/229; 429/222; 429/231.6; 429/212;  
429/223; 429/219; 429/220; 429/221; 429/231.5;  
429/231.8; 977/742; 977/750; 977/752**

**Related U.S. Application Data**

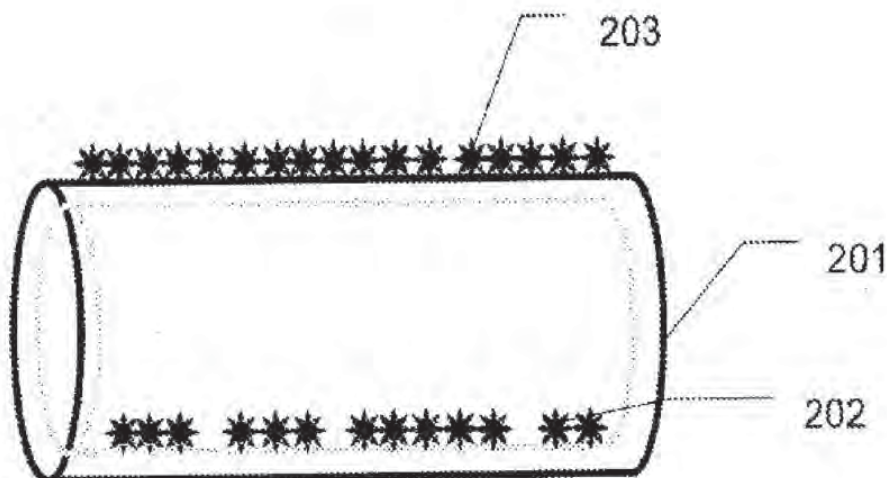
(60) Provisional application No. 61/280,627, filed on Nov.  
5, 2009.

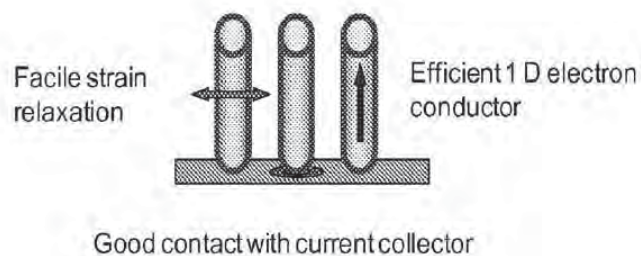
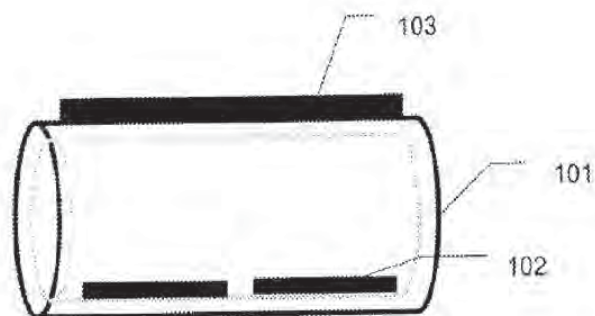
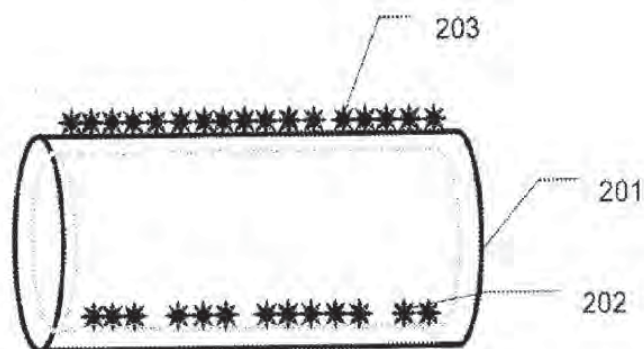
**Publication Classification**

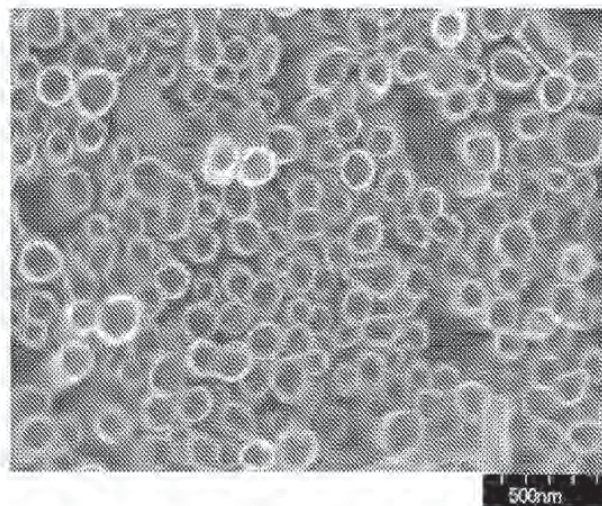
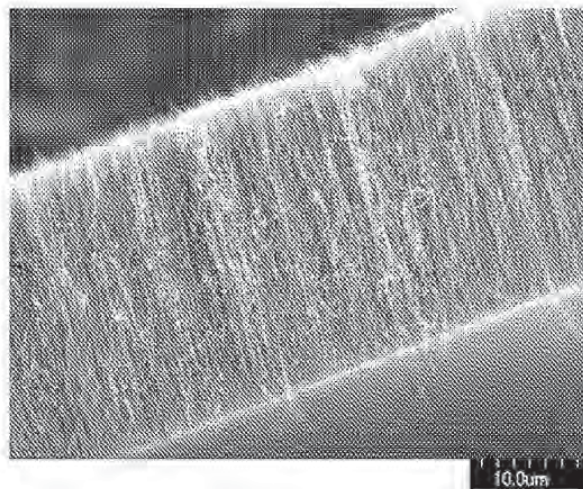
(51) **Int. Cl.**  
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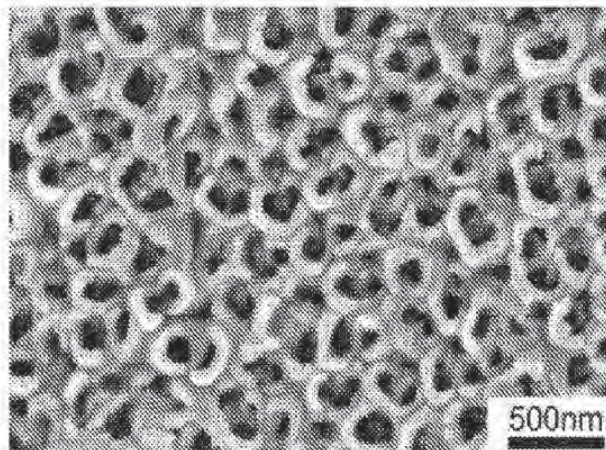
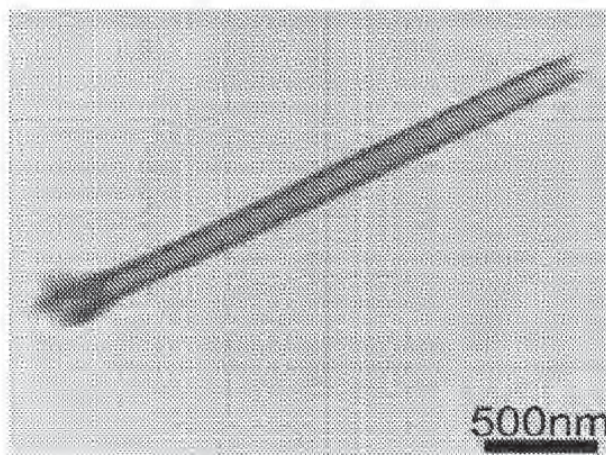
(57) **ABSTRACT**

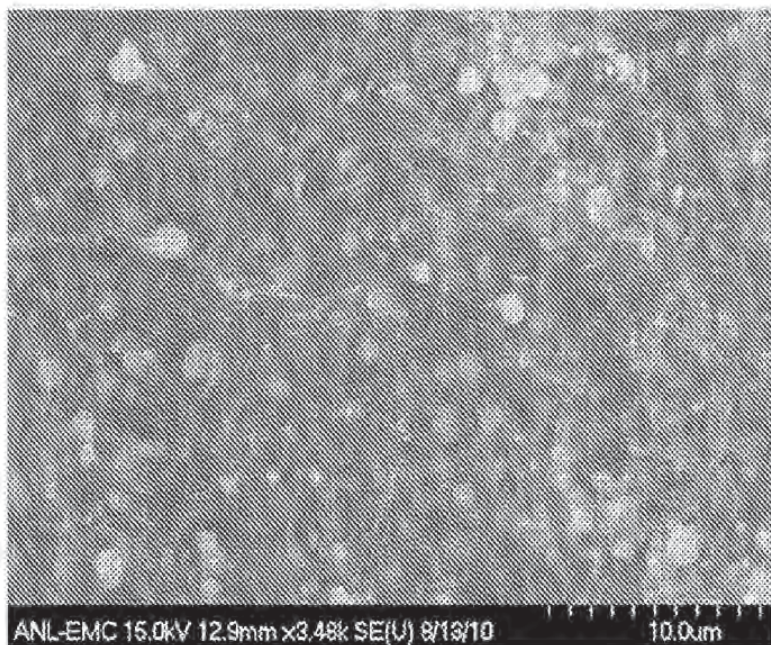
The present invention provides a composite material suitable for use in an anode for a lithium ion battery. the composite material comprising a layer of a lithium-alloying material on the walls of an aligned nanotubular base material. Preferably, the lithium-alloying material comprises a material selected from the group consisting of Si, Sn, Pb, Al, Au, Pt, Zn, Cd, Ag, Mg, and a combination of two or more of the foregoing.



**FIG. 1****FIG. 2****FIG. 3**

**A****B****FIG. 4**

**A****B****FIG. 5**

**FIG. 6**

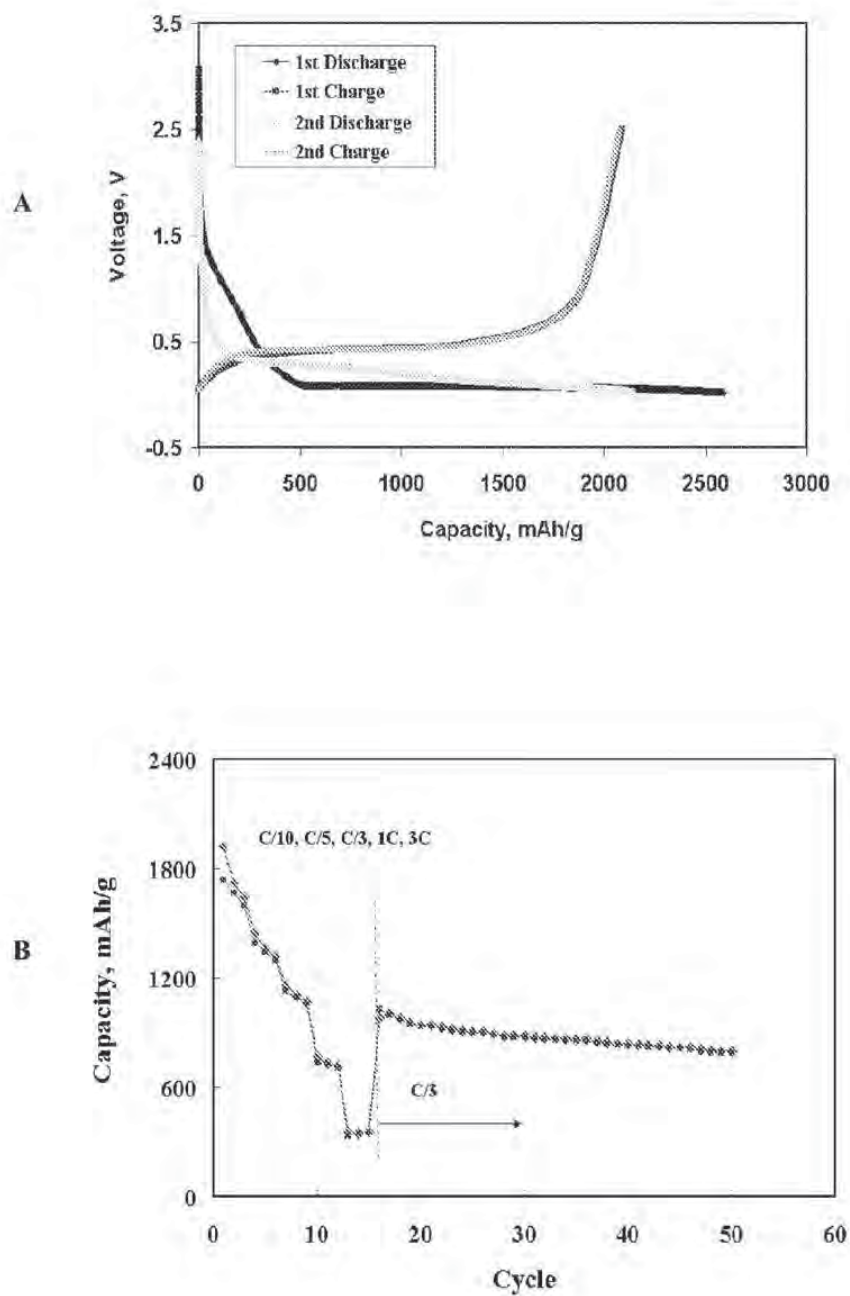
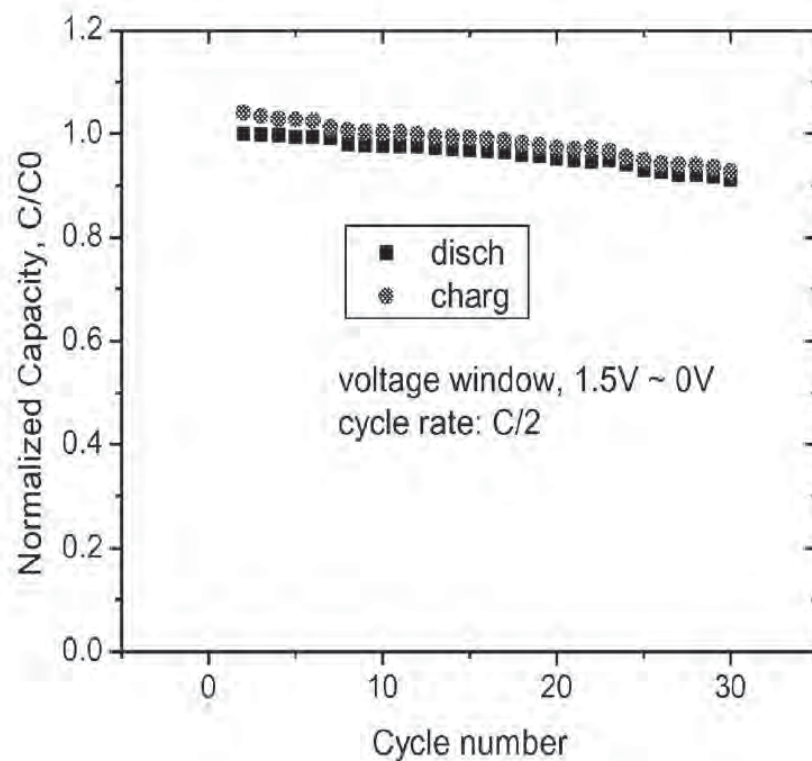


**FIG. 7**

**FIG. 8**

# NANOTUBE COMPOSITE ANODE MATERIALS SUITABLE FOR LITHIUM ION BATTERY APPLICATIONS

## CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Ser. No. 61/280,627, filed on Nov. 5, 2009, which is incorporated herein by reference in its entirety.

## CONTRACTUAL ORIGIN OF THE INVENTION

[0002] The United States Government has rights in this invention pursuant to Contract No. DE-AC02-06CH11357 between the United States Government and UChicago Argonne, LLC representing Argonne National Laboratory.

## FIELD OF THE INVENTION

[0003] This invention relates to anode materials for lithium ion batteries. More particularly, the invention relates to nanotube composite materials suitable for use as anode materials in lithium ion batteries.

## BACKGROUND OF THE INVENTION

[0004] The use of Li-ion batteries as rechargeable power sources represents a promising technology for use in the development of consumer electronics and electric-based vehicles. Lithium ion batteries (LIBs) with high energy density are in increasing demand. Since Sony commercialized lightweight LIBs for electronics in 1991, these batteries have been used widely in laptops, mobile phones, and other devices. However, there are substantial technical challenges to use this battery for automobile applications. The existing LIB technology uses  $\text{LiCoO}_2$  as the cathode material, graphite as the anode material, and a lithium salt such as  $\text{LiPF}_6$  in an organic solvent (e.g., organic carbonates) as the electrolyte. Since its commercialization, LIB capacity has increased about 1.7 times due to improvements in battery structure and enhancement in the capacity of the anode/cathode/electrolyte materials. In terms of battery manufacturing technology, the battery capacity typically has been increased by increasing the amount of the active materials in the cathode, anode and electrolyte, and by decreasing the thickness of the current collector, separator, and cell case. These efforts appear to have approached their limits in terms of improving battery capacity. Current LIB capacity also has been improved by utilizing new cathode materials, such as layered  $\text{Li}[\text{Ni}_x\text{CO}_y\text{Mn}_z]\text{O}_2$ ,  $\text{Li}-\text{Mn}-\text{O}$  spinels,  $\text{LiFePO}_4$  (olivine), and related materials. Use of such new materials has provided about 9 to about 18% increase in total mAh/g capacity over today's commercial cells, which is still insufficient to satisfy the requirements of plug-in hybrid electric vehicles (PHEVs). [0005] Current anode materials for LIBs typically fall into one of two types of materials: intercalation materials and alloy-forming materials. Graphite is a material based on intercalating lithium ion into its carbon layers for storage of lithium. Graphite exhibits good charge/discharge cycle stability, but low capacity (theoretical capacity is 372 mAh/g based on a theoretical Li-to-C ratio (Li:C) of about 1:6 (i.e.,  $\text{LiC}_6$ ). Other materials, including Si, Sn, Pb, Al, Au, Pt, Zn, Cd, Ag, and Mg, can be used as an alternative to graphite. These materials store lithium via formation of a lithium alloy. Among known lithium-alloying materials, silicon is one of the most attractive, since it has a relatively low discharge

potential, the highest known theoretical capacity (about 4200 mAh/g based on  $\text{Li}_{4.4}\text{Si}$ ), and a large natural availability reserve (silicon is the second most abundant element on earth). A disadvantage of alloy-forming materials such as silicon is that capacity typically fades quickly due to a very large volume expansion upon alloy formation, which can result in disruption (e.g., pulverization) of the electrode and loss of electric contact between electrode materials. For example, silicon undergoes up to 400% volume change during the alloying and de-alloying process. Silicon also possesses a relatively low electrical conductivity, which has a negative effect on the power capacity of the battery.

[0006] In view of the foregoing, there is an ongoing need for new, relatively high specific capacity anode materials.

## SUMMARY OF THE INVENTION

[0007] The present invention provides a composite material suitable for use in an anode for a lithium ion battery. The composite material comprises a layer of lithium-alloying material on the walls of an aligned nanotubular base material.

[0008] The lithium-alloying material preferably is selected from the group consisting of Si, Sn, Pb, Al, Au, Pt, Zn, Cd, Ag, Mg, and a combination of two or more of the foregoing. Silicon is particularly preferred.

[0009] The aligned nanotubular base material preferably comprises a material selected from the group consisting of a conductive organic polymer, a conductive or semiconductive inorganic material, or a combination thereof. In some preferred embodiments the aligned nanotubular base material comprises at least one material selected from the group consisting of polyaniline, polypyrrole, and polythiophene. In other preferred embodiments the aligned nanotubular base material comprises at least one material selected from the group consisting of a metal (e.g., Ni, Ag, Cu, Te, Co, Fe, Bi), a chalcogenide (e.g.,  $\text{MoS}_2$ ,  $\text{WS}_2$ ,  $\text{MoSe}_2$ ,  $\text{WSe}_2$ ,  $\text{NbS}_2$ ,  $\text{NbSe}_2$ ,  $\text{HfS}_2$ ,  $\text{ZrS}_2$ ,  $\text{TiS}_2$ ,  $\text{TiSe}_2$ ), an oxide (e.g.,  $\text{TiO}_2$ ,  $\text{H}_2\text{Ti}_2\text{O}_7$ ,  $\text{ZrO}_2$ ,  $\text{VO}_2$ ,  $\text{SiO}_2$ ,  $\text{IrO}_2$ ,  $\text{ZnO}$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{K}_4\text{Nb}_6\text{O}_{17}$ ), a nitride (e.g., BN, AlN, GaN), a phosphide (e.g., InP), a halide (e.g.,  $\text{NiCl}_2$ ), and carbon. In a preferred embodiment, the aligned nanotubular base material comprises aligned carbon nanotubes (ACNT). The aligned nanotubular base material can include single-walled carbon nanotube, multi-walled carbon nanotubes, or both; and can be open-ended nanotubes, close-ended nanotubes, or both.

[0010] Preferably, the aligned nanotubular base material comprises nanotubes having diameters of not more than about 100 nm, e.g., diameters in the range of about 2 to about 100 nm. The aligned nanotubular base material preferably comprises nanotubes having an average spacing between any two adjacent nanotubes in the range of about 5 to about 300 nm.

[0011] In some embodiments, the lithium-alloying material is present on the surface of the aligned nanotubular base material in a layer having an average thickness in the range of about 1 to about 200 nm. The layer of lithium-alloying material on the surface of the aligned nanotubular base material can be comprises a film or can comprise particles of the lithium-alloying material, or both. The lithium-alloying material can be coated on the exterior tubular surfaces of the aligned nanotubular base material, the interior tubular surfaces of the aligned nanotubular base material, or both.

[0012] In another aspect, the present invention provides an electrochemical cell comprising a cathode, an anode and a lithium ion-containing electrolyte therebetween, wherein the

anode comprises the composite material of the present invention. In some embodiments cathode comprises one or more of a lithium metal oxide, a phosphate, a spinel, and the like. Preferably, the lithium ion-containing electrolyte comprises a lithium salt in an organic solvent (e.g., an organic carbonate solvent).

[0013] In yet another aspect, the present invention provides a battery comprising a plurality of the electrochemical cells of the invention arranged in series, parallel, or both.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 shows an exemplary structure and mechanism for the use of a Si-ACNT composite as an anode material for Li-ion battery.

[0015] FIG. 2 schematically illustrates a nanotube including thin films of a lithium-alloying material on the interior and exterior of the nanotube.

[0016] FIG. 3 illustrates a similar nanotube to the one shown in FIG. 2 except that the lithium-alloying material is present in the form of particles rather than thin films.

[0017] FIG. 4 provides scanning electron microscope (SEM) images of aligned carbon nanotubes (ACNT) along the nanotube alignment axis (Panel A), and in a side-view (Panel B).

[0018] FIG. 5 provides SEM image of aligned conducting polymer nanotubes along the nanotube alignment axis (Panel A), and a side-view transmission electron microscope (TEM) image of conducting polymer nanotube (Panel B).

[0019] FIG. 6 provides a SEM image of silicon-coated ACNTs of the invention.

[0020] FIG. 7 provides electrochemical cycling data for the Si-ACNT material shown in FIG. 6; Panel A provides a plot of Voltage versus Capacity; Panel B provides a plot of Capacity versus cycle number.

[0021] FIG. 8 shows a plot of stability versus cycling number of a silicon-aligned carbon nanotube (ACNT) composite material of the present invention.

#### DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0022] The present invention relates to improved anode materials for a Li-ion battery that provide increased dimensional stability during lithiation and delithiation. The anode materials of the present invention afford a significant increase in specific capacity together with significant improvements in long term stability.

[0023] The new materials of the invention comprise a composite structure of a lithium-alloying material coated on the wall surfaces of an aligned nanotubular base material. The lithium-alloying material preferably is selected from Si, Sn, Pb, Al, Au, Pt, Zn, Cd, Ag, Mg, and a combination of two or more of the foregoing. Silicon is a preferred lithium-alloying material. The silicon can comprise crystalline silicon, amorphous silicon, silicon compounds such as silicon carbide and silicon oxide, or any combination of two or more of the foregoing.

[0024] The lithium-alloying material (e.g., Si) is present on at least a portion of the wall surfaces of the nanotubes as a relatively thin layer which can be a film, a particulate layer, or a combination thereof. The layer of lithium-alloying material can be present on the exterior wall-surfaces of the nanotubes, and in the case of open-ended nanotubes, the lithium-alloying material can be present on the interior wall surfaces, as well.

The layer of lithium-alloying material (e.g., Si) can have a thickness in the range of about 1 to about 200 nm, more preferably about 10 to about 100 nm.

[0025] Preferably, the aligned nanotubular base material comprises nanotubes with a diameter not more than about 100 nm. The nanotubes preferably have a diameter in the range of about 2 to about 100 nanometers, and a pitch (spacing) between any two adjacent carbon nanotubes in the range of about 5 to about 300 nanometers. The nanotubes can comprise open ended nanotubes, sealed nanotubes, or both. Preferably, the nanotubes comprise predominately open-ended nanotubes. The nanotubes can comprise organic materials, inorganic materials, or a combination thereof. The nanotube material can comprise single-walled nanotubes, multi-walled nanotubes, or a combination thereof.

[0026] In one embodiment, the nanotubes comprise a conductive polymer such as polyaniline, polypyrrole or polythiophene. In other embodiments of the present invention the nanotubes comprise various inorganic conductive or semi-conductive materials such as metals (e.g., Ni, Ag, Cu, Te, Co, Fe, Bi), chalcogenides (e.g., MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub>, WSe<sub>2</sub>, NbS<sub>2</sub>, NbSe<sub>2</sub>, HfS<sub>2</sub>, ZrS<sub>2</sub>, TiS<sub>2</sub>, TiSe<sub>2</sub>, TiS<sub>2</sub>, TiSe<sub>2</sub>), oxides (e.g., TiO<sub>2</sub>, H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>, ZrO<sub>2</sub>, VO<sub>2</sub>, SiO<sub>2</sub>, IrO<sub>2</sub>, ZnO, Ga<sub>2</sub>O<sub>3</sub>, BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, K<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub>), nitrides (e.g., BN, AlN, GaN), phosphides (e.g., InP), halides (e.g., NiCl<sub>2</sub>), carbon, and any combination of such materials. Carbon nanotubes are particularly preferred. The aligned nanotubular base material serves as support material for the lithium-alloying material, and provides dimensional stability for the lithium alloy formed during the lithiation and delithiation process, as well as establishing an electronic conducting pathway within the electrode.

[0027] As used herein the term "carbon nanotubes" and grammatical variations thereof refers to nanotubular materials that comprise predominately carbon, and can optionally include lesser amounts of other materials such as nitrogen and metals (e.g., Fe). Methods of preparing such aligned carbon nanotubes are well known in the art. The term "aligned" when used in reference to nanotube materials means that the nanotubes are substantially parallel to one another and are substantially perpendicular to a substrate material on which they are formed or coated (e.g., a conductive metal foil).

[0028] In some embodiments, the stability of the lithium-alloying material—nanotube composite of the invention is improved by modification of the nanotube wall surfaces to facilitate formation of chemical bonds between the lithium-alloying material and the nanotube walls, leading to improved structural stability. Non-limiting examples of surface modifications of nanotubes (e.g., ACNT) include incorporation of oxygen, nitrogen, sulfur, and/or metal containing functional groups on the wall surfaces.

[0029] A schematic of a Si-ACNT composite anode configuration is shown in FIG. 1. The ACNTs are grown directly on the metallic current collector substrate. The Si-ACNT materials provide a synergistic capacity contribution during charge and discharge from both Si and carbon nanotubes. A higher stability of silicon during cycling is provided due to bonding between the silicon coating and aligned carbon nanotube base material, and the outstanding elastic deformability of carbon nanotubes, which serve as a buffer layer for the silicon and compensates for the large volume expansion exhibited by Si when it is alloyed with lithium. Inside the Si-ACNT anode electrode, ACNTs offer many voids into which Si can expand without being in physical contact with

the current collector, thus avoiding the problem of delamination that can occur with silicon electrodes in the absence of the carbon nanotubes. Delamination jeopardizes the integrity of the negative electrode, as has been observed in the case of  $\text{Li}_{4.4}\text{Si}$ . In addition, fast charge and discharge rates can be achieved because of the unique aligned structure of carbon nanotubes, their mesoporosity, and their relatively high electronic conductivity. A significant weight reduction and a longer lifetime are also provided by the composite materials of the invention as the result of integrating a high capacity anode within highly ordered aligned nanotube base material, which offers facile pathways for lithium ion insertion and de-insertion, as well as alloy formation between lithium and an alloying material such as Si. In particular, Si-ACNT provides a long-life negative electrode material with much improved energy and power densities for lithium ion batteries.

**[0030]** FIG. 2 schematically illustrates a nanotube having a coating of a lithium-alloying material on the interior and exterior surfaces thereof. Nanotube 101 (e.g., a carbon nanotube, conductive organic polymer nanotube, or inorganic nanotube), includes thin films 102, 103 of a lithium-alloying material (e.g., Si, Sn, Sb and Ge) on the interior and exterior surfaces, respectively, of nanotube 101.

**[0031]** FIG. 3 illustrates a similar embodiment to that shown in FIG. 2, except the lithium alloying material is present as particles 202, 203 on the interior and exterior surfaces, respectively, of nanotube 201.

#### Selected Advantages of the Composite Materials of the Present Invention

**[0032]** The nanotube component of the composite materials of the present invention provides dimensional stability for lithium alloying materials such as silicon by serving as a buffer layer. Specifically, the nanotubes provide elastic deformability, which makes it possible to absorb the volume changes of the lithium alloying material when lithium is inserted therein and removed therefrom.

**[0033]** Nanotubes with an open-ended structure, such as certain open-ended aligned carbon nanotubes, possess a mesoporous structure, which provides fast access of electrolyte to electrode surface, and thus leading to fast charge and discharge rates.

**[0034]** Carbon nanotubes are a preferred aligned nanotubular base material in the present invention. Silicon, which possesses the highest known theoretical lithium ion charge capacity, is a preferred lithium-alloying material. The Si-aligned carbon nanotube (Si-ACNTs) composite materials of the invention provide a higher lithium ion capacity than traditional graphite materials or ACNT materials alone. In addition, the carbon nanotube component provides high electronic conductivity and helps improve the electrochemical performance of the lithium alloying material incorporated therein. Si-CNTs composite structure can be used as both an active material and a current collector, amplifying the weight savings associated with its high specific activity.

**[0035]** In addition, ACNT and Si-ACNT can be grown on the surface of a current collector (e.g., a Cu foil) and can be employed directly as working electrode without the need for binders and conductivity additives. ACNT growth and Si deposition can be carried out in the same reactor through sequential CVD processes, which further simplifies the fabrication process.

**[0036]** The following non-limiting examples are provided to further illustrate certain aspects and features of the present invention.

#### EXAMPLE 1

##### Synthesis of Carbon Nanotubes

**[0037]** Carbon nanotubes (CNT) can be synthesized according to procedures that are known in the art. For example, carbon nanotubes were prepared by a chemical vapor deposition process inside a quartz tube inserted through a low-temperature heating section (Zone I, about 200° C.) and a high-temperature heating section (Zones II, about 750° C.). About 0.34 g of ferrocene was dissolved in about 22.63 mL of xylene and used as the precursor for the CNT synthesis. The solution was injected into and vaporized in Zone I. A hydrogen and argon mixture (60 mL/min and 90 mL/min, respectively) was used to transport the vaporized ferrocene and xylene mixture from Zone I to Zone II. The CNTs were formed over a polished quartz plate inside Zone II. After about 30 minutes, the solution injection was stopped and the furnaces heating Zones I and II were cooled down to room temperature with the argon and hydrogen gas mixture still flowing. FIG. 4 shows SEM images of a typical ACNT material useful in the composites of the present invention. Panel A of FIG. 4 shows a view along the alignment axis of the nanotubes, while Panel B shows a side view.

#### EXAMPLE 2

##### Conducting Polymer Nanotubes

**[0038]** Conductive polymer nanotubes have been fabricated by various methods known in the art. Such methods can be divided into at least three categories: template (or hard template) methods, pseudotemplate (or soft template) methods, and template-free methods. Template methods have been widely used because of their simplicity, versatility, and controllability. The hard template is usually a thin porous film of aluminum oxide or polycarbonate. Different kinds of conducting polymers have been deposited in the cylindrical pores of such films to form nanotubes or nanowires. The deposition has been performed by methods such as pressure injection, vapor deposition, chemical deposition, and electrodeposition; the last two of these methods being the most popular in recent research. For purposes of illustration, FIG. 5 provides SEM and TEM images of poly(3,4-ethylenedioxythiophene) nanotube material (from Cho, S. I. and Lee, S. B., 2008, "Fast Electrochemistry of Conductive Polymer Nanotubes: Synthesis, Mechanism, and Application", *Accounts of Chemical Research*, 41 (6): 699-707) which is suitable for use in the present invention. Panel A of FIG. 5 shows a view along the alignment axis of the nanotubes, while Panel B shows a TEM side view of one of the nanotubes.

#### EXAMPLE 3

##### Surface Modification of Aligned Carbon Nanotubes

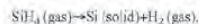
**[0039]** The as-synthesized ACNTs were steam oxidized to introduce a surface functional group in order to deposit a Pt catalyst on the surface. This steam oxidation was achieved in the same CVD reactor as was used to synthesize the ACNT according to Example 1, using the following procedure: Zone I and Zone II were heated and kept at about 500° C. and about 800° C., respectively. Deionized water was injected into the

quartz tube at the middle sites of Zone I at the rate of about 0.225 mL/min to generate steam. Flowing argon (about 140 mL/min) was used to carry the steam to Zone II and react with ACNTs that were synthesized in the reactor using the CVD process described in Example 1. The water injection was continued for about 50 minutes, after which time the heating was terminated and the contents of the reactor were cooled to room temperature with flowing argon.

#### EXAMPLE 4

##### Deposition of Silicon on Carbon Nanotubes

[0040] Following the formation of the carbon nanotubes, a film of nanoscale silicon particles is deposited at the surface of the nanotubes. This deposition may be carried out, for example, by chemical vapor deposition (CVD) starting from silylated precursors, such as the silane ( $\text{SiH}_4$ ), which makes it possible to obtain a uniform distribution of the silicon, which thus forms a sheath around each nanotube. For example, the gaseous silyl precursors, such as silanes (e.g.,  $\text{SiH}_4$ ), can be deposited on carbon nanotubes, which are pre-heated at about 600° C. to give a uniform coating of silicon on carbon nanotubes according to a reaction such as the following:



Alternatively, another gaseous silicon precursor material, such as trichlorosilane can be used in place of silane.

[0041] In a specific example, ACNTs were prepared through a one-step, chemical vapor deposition (CVD) process using inexpensive aromatic hydrocarbons and transition metal compounds. Briefly, a liquid mixture of xylene and ferrocene was injected into the low-temperature zone of a CVD reactor and was fully vaporized. The vapor mixture was carried downstream to the high temperature zone by hydrogen and inert gas and was subsequently decomposed over a copper foil substrate.

[0042] For CVD of silicon deposition, the same reactor as ACNT synthesis was used. Briefly, liquid trichlorosilane (TCS) was injected into the low-temperature zone (100° C.) of the reactor and was fully vaporized. The vapor mixture was carried downstream to the high temperature zone by hydrogen and was subsequently decomposed over the ACNT material, which was preheated to 800° C. At this temperature, TCS decomposed to finely dispersed, equally sized silicon nanoparticles outside and inside the graphene layers of the ACNTs. FIG. 6 show the SEM image of Si-ACNTs supported on copper foil, which is the current collect normally used in lithium ion batteries. The ACNTs typically have diameters in the range of 2 to 50 nm and length in the range of 5 to 50  $\mu\text{m}$ , which fall in the typical thickness of a battery electrode. The silicon nanoparticles are uniformly dispersed inside the ACNT bundles.

[0043] The as prepared Si-ACNT material supported on copper foil was used directly as the anode for a lithium ion battery. The performance was evaluated in a 2032-type coin cells. The cell was configured with lithium foil as negative electrode, a 25  $\mu\text{m}$  Microporous Trilayer Membrane (Celgard 2325) as separator, the above prepared electrode as positive electrode, and an appropriate amount of electrolyte. The electrolyte was 10 wt % of fluoroethylene carbonate (FEC) combined with 1.2M  $\text{LiPF}_6$  dissolved in the mixture solvent of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with an EC:EMC volume ratio of about 3:7. The electrochemical performance of the Si-ACNT composite material

was investigated by cycling the cell between 0.02 to 1.5 V with a constant current of different rates using a computerized battery test system manufactured by Maccor, Inc.

[0044] FIG. 7 shows the cycling performance of this Si-ACNT material. The first cycle efficiency is about 80%, which is mainly due to the reaction of electrolyte with carbon/silicon surfaces to form solid-electrolyte-interface (SEI) layer. A plot of Voltage versus Capacity is shown in Panel A, and a plot of Capacity versus Cycle number is shown in Panel B. The reversible capacity of this Si coated CNT is determined to be over 840 mAh/g after 50 cycles at room temperature. For comparison, silicon powder (~10  $\mu\text{m}$  average diameter) lost over 90% of its capacity after 10 cycles, as reported in the literature [Ryu et al., *Electrochemical and Solid-State Letters*, 2004; 7:A306]. In the Si-ACNT material, the ACNTs served as support materials and buffer layer for silicon, therefore, Si can expand without being in physical contact with the current collector where a problem of delamination usually occurs—a process that would jeopardize the integrity of the negative electrode. Higher stability of silicon during cycling is achieved due to the outstanding elastic deformability of carbon nanotubes, which accommodate the tensions caused by the huge silicon volume change. The results demonstrate that CNTs stabilized silicon during repeated alloying and de-alloying processes and possessed over 2 times the reversible capacity of state-of-the-art graphite materials. This is the first demonstration of synthesizing aligned carbon nanotubes on copper foil and followed by in-situ CVD deposition of silicon of which the inventors are aware.

[0045] This Example demonstrates the following benefits: (1) ACNT and Si-ACNT can be grown on the surface of a current collector (e.g. Cu foil) and can be employed directly as working electrode without the need for binders and conductive additives; (2) ACNT growth and Si deposition will be carried out in the same reactor through sequential CVD processes, which simplify the fabrication process; (3) a Si-ACNT hybrid structure can be used as both an active material and a current collector, amplifying the weight savings associated with its high specific capacity, and (4) higher stability of silicon during cycling is achieved due to the outstanding elastic deformability of carbon nanotubes.

#### EXAMPLE 5

##### Si-ACNT Composite Prepared Through Magnetron Sputtering Method and its Battery Performance

[0046] A thin layer of silicon was deposited onto ACNTs prepared as in Example 1 using magnetron sputtering, and the capacity resulting composite in a half cell configuration was tested. The reversible capacity of this Si-coated ACNT composite was determined to be over 750 mAh/g. FIG. 8 shows the cycling performance of this Si-ACNT material. Surprisingly, over 90% capacity retention was observed after 30 cycles at room temperature. For comparison, silicon powder (about 10  $\mu\text{m}$  average diameter) lost over 90% of its capacity after 10 cycles, as reported by Ryu Ji Heon et al., "Failure Modes of Silicon Powder Negative Electrode in Lithium Secondary Batteries," *Electrochemical and Solid-State Letters* 2004; 7 (10): A306-A309. The present result demonstrates that the silicon-coated ACNTs surprisingly stabilized the silicon during repeated alloying and de-alloying processes, and exhibited almost 2 times the reversible capacity of state-of-the-art graphite materials.

[0047] The use of the terms “a” and “an” and “the” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (i.e., meaning “including, but not limited to,”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0048] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composite material suitable for use in an anode for a lithium ion battery, the composite material comprising a layer of a lithium-alloying material on the wall surfaces of an aligned nanotubular base material.
2. The composite material of claim 1 wherein the lithium-alloying material comprises a material selected from the group consisting of Si, Sn, Pb, Al, Au, Pt, Zn, Cd, Ag, Mg, and a combination of two or more of the foregoing.
3. The composite material of claim 1 wherein the lithium-alloying material comprises silicon.
4. The composite material of claim 1 wherein the aligned nanotubular base material comprises a material selected from the group consisting of a conductive organic polymer, a conductive or semiconductive inorganic material, or a combination thereof.
5. The composite material of claim 1 wherein the aligned nanotubular base material comprises at least one material selected from the group consisting of polyaniline, polypyrrole, and polythiophene.
6. The composite material of claim 1 wherein the aligned nanotubular base material comprises at least one material selected from the group consisting of a metal (e.g., Ni, Ag,

Cu, Te, Co, Fe, Bi), a chalcogenide (e.g., MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub>, WSe<sub>2</sub>, NbS<sub>2</sub>, NbSe<sub>2</sub>, HfS<sub>2</sub>, ZrS<sub>2</sub>, TiS<sub>2</sub>, TiSe<sub>2</sub>), an oxide (e.g., TiO<sub>2</sub>, H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>, ZrO<sub>2</sub>, VO<sub>x</sub>, SiO<sub>2</sub>, IrO<sub>2</sub>, ZnO, Ga<sub>2</sub>O<sub>3</sub>, BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>), a nitride (e.g., BN, AlN, GaN), a phosphide (e.g., InP), a halide (e.g., NiCl<sub>2</sub>), and carbon.

7. The composite material of claim 1 wherein the aligned nanotubular base material comprises aligned carbon nanotubes (ACNT).

8. The composite material of claim 1 wherein the aligned nanotubular base material comprises nanotubes having diameters of not more than about 100 nm.

9. The composite material of claim 1 wherein the aligned nanotubular base material comprises nanotubes having diameters in the range of about 2 to about 100 nm.

10. The composite material of claim 1 wherein the aligned nanotubular base material comprises nanotubes having an average spacing between any two adjacent nanotubes in the range of about 5 to about 300 nm.

11. The composite material of claim 1 wherein the aligned nanotubular base material comprises a open-ended nanotubes, close-ended nanotubes, or both.

12. The composite material of claim 1 wherein the lithium-alloying material is present on the surface of the aligned nanotubular base material in a layer having an average thickness in the range of about 1 to about 200 nm.

13. The composite material of claim 1 wherein the layer of lithium-alloying material on the surface of the aligned nanotubular base material comprises a film.

14. The composite material of claim 1 wherein the layer of lithium-alloying material on the surface of the aligned nanotubular base material comprises particles of the lithium-alloying material.

15. The composite material of claim 1 wherein lithium-alloying material is present on the exterior tubular surfaces of the aligned nanotubular base material.

16. The composite material of claim 1 wherein lithium-alloying material is present on the interior tubular surfaces of the aligned nanotubular base material.

17. The composite material of claim 1 wherein the aligned nanotubular material comprises single-walled carbon nanotubes, multi-walled carbon nanotubes, or both.

18. An electrochemical cell comprising an cathode, an anode, and a lithium ion-containing electrolyte therebetween, wherein the anode comprises the composite material of claim 1.

19. The electrochemical cell of claim 18 wherein the cathode comprises one or more material selected from a lithium metal oxide, a phosphate, and a spinel.

20. The electrochemical cell of claim 18 wherein the lithium ion-containing electrolyte comprises a lithium salt in an organic solvent.

21. A battery comprising a plurality of the electrochemical cells of claim 1 arranged in series, parallel, or both.

\* \* \* \* \*



European Patent Office  
80298 MUNICH  
GERMANY

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Date  
06.10.16

|                                                     |                                                           |
|-----------------------------------------------------|-----------------------------------------------------------|
| Reference<br>P100028EP00                            | Application No./Patent No.<br>12731264.3 - 1360 / 2724403 |
| Applicant/Proprietor<br>Molecular Rebar Design, LLC |                                                           |

#### Transmission of the certificate for a European patent pursuant to Rule 74 EPC

The certificate for a European patent is herewith transmitted.

The European patent specification can be downloaded from the EPO publication server  
<https://data.epo.org/publication-server/> (see OJ EPO 2005, 126).

#### Note:

A corrected title page of the European patent specification will be published, if the bibliographic data have been changed after completion of the technical preparations.

#### For the Examining Division





European Patent Office  
80298 MUNICH  
GERMANY

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Contact Customer Services at [www.epo.org/contact](http://www.epo.org/contact)



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Date  
08.09.16

|                                                     |                                                           |
|-----------------------------------------------------|-----------------------------------------------------------|
| Reference<br>P100028EP00                            | Application No./Patent No.<br>12731264.3 - 1360 / 2724403 |
| Applicant/Proprietor<br>Molecular Rebar Design, LLC |                                                           |

#### Decision to grant a European patent pursuant to Article 97(1) EPC

Following examination of European patent application No. 12731264.3 a European patent with the title and the supporting documents indicated in the communication pursuant to Rule 71(3) EPC (EPO Form 2004C) or in the information (EPO Form 2004W, cf. Notice from the EPO dated 8 June 2015, OJ EPO 2015, A52) dated 29.04.16 is hereby granted in respect of the designated Contracting States.

Patent No. : 2724403  
Date of filing : 21.06.12  
Priority claimed : 23.06.11/USP201161500560

Designated Contracting States and Proprietor(s) : AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR  
Molecular Rebar Design, LLC  
13477 Fitzhugh Road  
Austin, TX 78736/US

This decision will take effect on the date on which the European Patent Bulletin mentions the grant (Art. 97(3) EPC).

The mention of the grant will be published in European Patent Bulletin 16/40 of 05.10.16.

Examining Division

Kelly M

Cojuhovski O

Ramos Flores C



Registered letter  
EPO Form 2006A 07.15 (01/09/16)

to EPO postal service: 02.09.16  
Page: 1 of 1

ANMERKUNG ZUR ENTSCHEIDUNG ÜBER DIE ERTEILUNG  
EINES EUROPÄISCHEN PATENTS (EPA Form 2006)

1. **EPA Informationsbroschüre "Nationales Recht zum EPÜ"**  
Diese Broschüre enthält nützliche Informationen zu den formalen Erfordernissen und den Handlungen, die vor den Patentbehörden der Vertragsstaaten vorzunehmen sind, um Rechte in diesen Staaten zu erlangen. Da diese Handlungen einem ständigen Wandel unterworfen sind, sollte immer nur die neueste Ausgabe der Broschüre benutzt werden. Nachträgliche Informationen werden im Amtsblatt veröffentlicht.
2. **Übersetzung der europäischen Patentschrift nach Artikel 65 (1) des Europäischen Patentübereinkommens**  
Sie werden erneut darauf hingewiesen, dass bestimmte Vertragsstaaten nach Artikel 65 (1) EPÜ eine Übersetzung der europäischen Patentschrift verlangen; hierauf wird in der Mitteilung gemäß Regel 71 (5) EPÜ verwiesen. Die Nichteinreichung dieser Übersetzung kann zur Folge haben, dass das Patent in dem betreffenden Staat/in den betreffenden Staaten als von Anfang an nicht eingetreten gilt. Weitere Einzelheiten entnehmen Sie bitte der oben genannten Broschüre.
3. **Zahlung von Jahresgebühren für europäische Patente**  
Nach Artikel 141 EPÜ können "nationale" Jahresgebühren für das europäische Patent für die Jahre erhoben werden, die an das Jahr anschließen, in dem der Hinweis auf die Erteilung des europäischen Patents im "Europäischen Patentblatt" bekanntgemacht wird. Weitere Einzelheiten entnehmen Sie bitte der oben genannten Broschüre.

NOTE RELATING TO THE DECISION TO GRANT A  
EUROPEAN PATENT (EPO Form 2006)

1. **EPO Information Brochure "National law relating to the EPC"**  
This brochure provides useful information regarding formal requirements and the steps to be taken before the patent authorities of the Contracting States in order to acquire rights in those states. Since the necessary steps are subject to change the latest edition of the brochure should always be used. Subsequent information is published in the Official Journal.
2. **Translation of the European patent application under Article 65(1) of the European Patent Convention**  
Your attention is again drawn to the requirements regarding translation of the European patent specification laid down by a number of Contracting States under Article 65(1) EPC, to which reference is made in the communication under Rule 71(5) EPC. Failure to supply such translation(s) may result in the patent being deemed to be void "ab initio" in the State(s) in question. For further details you are recommended to consult the above-mentioned brochure.
3. **Payment of renewal fees for European patents**  
Under Article 141 EPC "national" renewal fees in respect of a European patent may be imposed for the years which follow that in which the mention of the grant of the European patent is published in the "European Patent Bulletin". For further details you are recommended to consult the above-mentioned brochure.

REMARQUE RELATIVE A LA DECISION DE DELIVRANCE  
D'UN BREVET EUROPEEN (OEB Form 2006)

1. **Brochure d'information de l'OEB "Droit national relatif à la CBE"**  
Cette brochure fournit d'utiles renseignements sur les conditions de forme requises et sur les actes à accomplir auprès des offices de brevet des Etats contractants aux fins d'obtenir des droits dans les Etats contractants. Etant donné que les actes indispensables sont susceptibles de modifications, il serait bon de toujours consulter la dernière édition de la brochure. Toute information ultérieure est publiée au Journal Officiel.
2. **Traduction du fascicule du brevet européen en vertu de l'article 65(1) de la Convention sur le brevet européen**  
Votre attention est de nouveau attirée sur l'obligation faite par certains Etats contractants, en vertu de l'article 65(1) CBE, de fournir une traduction du fascicule du brevet européen, à laquelle il est fait référence dans la notification établie conformément à la règle 71(5) CBE. Si la(les) traduction(s) n'est(ne sont) pas fournie(s), le brevet européen peut, dès l'origine, être réputé sans effet dans cet(ces) Etat(s). Pour plus de détails, nous vous renvoyons à la brochure susmentionnée.
3. **Paiement des taxes annuelles pour le brevet européen**  
Conformément à l'article 141 CBE des taxes annuelles "nationales" dues au titre du brevet européen peuvent être perçues pour les années suivant celle au cours de laquelle la mention de la délivrance du brevet européen est publiée au "Bulletin européen des brevets". Pour plus de détails, nous vous renvoyons à la brochure susmentionnée.



## Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

|                                 |                                                                                                                            |                                                                                                |
|---------------------------------|----------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| Submission number               | 4601037                                                                                                                    |                                                                                                |
| Application number              | EP12731264.3                                                                                                               |                                                                                                |
| Date of receipt                 | 29 August 2016                                                                                                             |                                                                                                |
| Receiving Office                | European Patent Office, The Hague                                                                                          |                                                                                                |
| Your reference                  | P100028EP00                                                                                                                |                                                                                                |
| Applicant                       | All applicants as on file                                                                                                  |                                                                                                |
| Documents submitted             | <div>package-data.xml</div> <div>epf1038.pdf (2 p.)</div> <div>CLMSTRAN-DE-1.pdfP100028EP00<br/>De claims.pdf (3 p.)</div> | <div>ep-sfd-request.xml</div> <div>CLMSTRAN-FR-1.pdfP100028EP00<br/>Fr claims.pdf (2 p.)</div> |
| Submitted by                    | CN=Yi Li 43825                                                                                                             |                                                                                                |
| Method of submission            | Online                                                                                                                     |                                                                                                |
| Date and time receipt generated | 29 August 2016, 11:44 (CEST)                                                                                               |                                                                                                |
| Message Digest                  | AB:E2:0F:EE:AB:8A:F2:9C:F6:03:53:37:C6:30:D6:74:F1:D9:64:3F                                                                |                                                                                                |

### Correction by the EPO of errors in debit instructions filed by eOLF

Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

/European Patent Office/



## Letter accompanying subsequently filed items

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The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number

12731264.3

Applicant's or representative's reference

P100028EP00

|   | Description of document           | Original file name        | Assigned file name |
|---|-----------------------------------|---------------------------|--------------------|
| 1 | French translations of the claims | P100028EP00 Fr claims.pdf | CLMSTRAN-FR-1.pdf  |
| 2 | German translations of the claims | P100028EP00 De claims.pdf | CLMSTRAN-DE-1.pdf  |

|      | Fees                                                                                                   | Factor applied | Fee schedule | Amount to be paid |
|------|--------------------------------------------------------------------------------------------------------|----------------|--------------|-------------------|
| 15-1 | 007 Fee for grant and printing (not more than 35 pages) or fee for grant including fee for publication | 1              | 925.00       | 925.00            |
|      | Total:                                                                                                 |                | EUR          | 925.00            |

|   | Payment                                                                                                                                        |                            |
|---|------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------|
| 1 | Mode of payment                                                                                                                                | Debit from deposit account |
|   | Currency:                                                                                                                                      | EUR                        |
|   | The European Patent Office is hereby authorised, to debit from the deposit account with the EPO any fees and costs indicated on the fees page. |                            |
|   | Deposit account number:                                                                                                                        | 28090002                   |
|   | Account holder:                                                                                                                                | V.O.                       |
| 2 | Refund/Reimbursement                                                                                                                           |                            |
|   | Reimbursement (if any) to be made to EPO deposit account:                                                                                      | 28090002                   |
|   | Account holder:                                                                                                                                | V.O.                       |

### Annotations

Communication under Rule 71(3) EPC(V.O.; 29.08.2016)

1. Remark(Annotate)

I refer to the communication under Rule 71(3) EPC and enclose herewith the following documents :

P100028EP00

1. Translations of claims :

and

2. Payment in settlement of the granting and printing fees.

I herewith authorize the European Patent Office to deduct all necessary fees that are involved in this specific action from my deposit-account No. 2809.0002

**Signatures**

|                      |                  |
|----------------------|------------------|
| Place:               | Den Haag         |
| Date:                | 29 August 2016   |
| Signed by:           | /C.M. Jansen/    |
| Association:         | V.O.             |
| Representative name: | C.M. Jansen      |
| Capacity:            | (Representative) |

P100028EP00

REVENDEICATIONS

1. Une composition utile pour des batteries lithium-ion, comprenant:  
des nanotubes de carbone discrets, ces nanotubes de carbone discrets comportant des  
5 cristaux ou des couches de matériau actif lithium-ion attachés à leur surface,  
composition dans laquelle les nanotubes de carbone discrets ont un rapport d'aspect  
de 10 à 500 et des niveaux d'oxydation de 1% à 15% en poids des nanotubes de  
carbone.
2. La composition selon la revendication 1, dans laquelle les cristaux ou les  
10 couches de matériau actif lithium-ion comprennent un sel métallique de lithium et un  
élément choisi dans le groupe constitué par: le fer, le manganèse, le cobalt, le cuivre,  
le nickel, le vanadium, le titane et leurs mélanges.
3. La composition selon la revendication 2, dans laquelle le sel métallique  
de lithium présente une structure cristalline d'olivine.
- 15 4. La composition selon la revendication 1, dans laquelle les cristaux ou les  
couches de matériau actif lithium-ion comprennent l'étain, le silicium, le cuivre,  
l'antimoine, l'aluminium, le germanium, le titane ou leurs mélanges.
5. La composition selon l'une quelconque des revendications 1-4,  
comportant en outre du graphène ou du graphène oxygéné.
- 20 6. La composition selon la revendication 5, dans laquelle le rapport  
pondéral graphène/nanotube de carbone se situe dans l'intervalle de 0,1/99,9 à  
99,9/0,1.
7. La composition selon l'une quelconque des revendications 1-6, dans  
laquelle les nanotubes de carbone présentent un rapport pondéral nanotubes de  
25 carbone/sels de lithium de 0,1% à 10%.
8. La composition selon l'une quelconque des revendications 1-7,  
comportant des nanotubes de carbone oxydé comportant des cristaux ou couches de  
matériau actif lithium-ion attachés à leur surface, dans laquelle les nanotubes de  
carbone sont uniformément dispersés sans formation de grappes sur une échelle de  
30 dimension inférieure à 1 micromètre.
9. La composition selon l'une quelconque des revendications 1-8,  
comportant des nanotubes de carbone oxydés uniformément dispersibles comportant  
des cristaux ou couches de matériau actif lithium-ion attachés à leur surface.
10. La composition selon la revendication 9, dans laquelle les cristaux ou  
35 couches de matériau actif lithium-ion sont chimiquement attachés à la surface des  
nanotubes de carbone oxydés dispersibles.

11. Un procédé pour la production de nanotubes de carbone discrets présentant des cristaux ou des couches de matériaux actifs lithium-ion attachés à leur surface tels que définis dans la revendication 3, comprenant les étapes de:

- 5 a) sélection des nanotubes de carbone de rapport d'aspect de 10 à 500 et un niveau d'oxydation de 1% à 15% en poids;
- b) mélange des nanotubes de carbone avec un liquide de point d'ébullition élevé;
- c) addition des réactifs dans un équilibre correct pour synthétiser un sel de lithium;
- d) réaction du mélange à une température pour former le sel de lithium pendant la sonication du mélange;
- 10 e) séparation du liquide des nanotubes de carbone discrets solides avec les sels de lithium qui leur sont attachés; et
- f) séchage et recuit des nanotubes de carbone discrets solides avec les sels de lithium qui leur sont attachés sous une atmosphère inerte à une température suffisante pour obtenir une structure cristalline d'olivine.

15 12. Un procédé pour la production de nanotubes de carbone discrets présentant des cristaux ou des couches de matériaux actifs lithium-ion attachés à leur surface, tels que définis dans la revendication 3, comprenant les étapes de:

- a) sélection des nanotubes de carbone de rapport d'aspect compris entre 10 et 500 et un niveau d'oxydation de 1% à 15% en poids;
- 20 b) mélange des nanotubes de carbone et d'un sel de lithium dans un liquide avec un agent tensio-actif;
- c) sonication du mélange liquide de nanotubes de carbone/sel de lithium;
- d) séparation du liquide des nanotubes de carbone discrets solides avec les sels de lithium qui leur sont attachés; et
- 25 e) séchage et recuit des nanotubes de carbone discrets solides avec les sels de lithium qui leur sont attachés sous une atmosphère inerte à une température suffisante pour obtenir une structure cristalline d'olivine.

Ansprüche

1. Zusammensetzung, verwendbar für Lithiumionenbatterien,  
5 umfassend:  
diskrete Kohlenstoffnanoröhren, wobei die diskreten  
Kohlenstoffnanoröhren Kristalle oder Schichten von Lithiumionen-aktivem  
Material, befestigt auf ihrer Oberfläche aufweisen, wobei die diskreten  
Kohlenstoffnanoröhren ein Aspektverhältnis von 10 bis 500 und  
10 Oxidationsstufen von 1 Gew.-% bis 15 Gew.-% des Kohlenstoffnanorohrs  
aufweisen.
2. Zusammensetzung nach Anspruch 1, wobei die Kristalle oder  
Schichten von Lithiumionen-aktivem Material ein Lithiummetallsalz und ein  
15 Element, ausgewählt aus der Gruppe bestehend aus: Eisen, Mangan, Cobalt,  
Kupfer, Nickel, Vanadium, Titan und Gemischen davon, umfassen.
3. Zusammensetzung nach Anspruch 2, wobei das Lithiummetallsalz  
eine Olivin-Kristallstruktur hat.  
20
4. Zusammensetzung nach Anspruch 1, wobei die Kristalle oder  
Schichten von Lithiumionen-aktivem Material Zinn, Silikon, Kupfer, Antimon,  
Aluminium, Germanium, Titan oder Gemische davon umfassen.
- 25 5. Zusammensetzung nach einem der Ansprüche 1-4, ferner umfassend  
Graphen oder oxygeniertes Graphen.
6. Zusammensetzung nach Anspruch 5, wobei das Gewichtsverhältnis  
von Graphen zum Kohlenstoffnanoröhren im Bereich von 0,1:99,9 bis 99,9:0,1  
30 liegt.

2

7. Zusammensetzung nach einem der Ansprüche 1-6, wobei die Kohlenstoffnanoröhren in einem Gewichtsverhältnis von Kohlenstoffnanoröhren zu Lithiumsalzen von 0,1 % bis 10 % vorliegen.

5        8. Zusammensetzung nach einem der Ansprüche 1-7, umfassend oxidierte Kohlenstoffnanoröhren mit Kristallen oder Schichten von Lithiumionen-aktiven Materialien, befestigt auf ihrer Oberfläche, wobei die Kohlenstoffnanoröhren gleichförmig ohne Clusterbildung auf einer Dimensionsskala von weniger als 1 Mikrometer dispergiert sind.

10       9. Zusammensetzung nach einem der Ansprüche 1-8, umfassend gleichförmig dispergierbare oxidierte Kohlenstoffnanoröhren mit Kristallen oder Schichten von Lithiumionen-aktiven Materialien, befestigt auf ihrer Oberfläche.

15       10. Zusammensetzung nach Anspruch 9, wobei die Kristalle oder Schichten von Lithiumionen-aktiven Materialien chemisch auf der Oberfläche der dispergierbaren oxidierten Kohlenstoffnanoröhren befestigt sind.

20       11. Verfahren zur Herstellung diskreter Kohlenstoffnanoröhren mit Kristallen oder Schichten von Lithiumionen-aktiven Materialien, befestigt auf ihrer Oberfläche, wie in Anspruch 3 definiert, umfassend die Schritte von:

      a) Auswählen von Kohlenstoffnanoröhren mit einem Aspektverhältnis von 10 bis 500 und Oxidationsstufen von 1 % bis 15 % nach Gewicht;

25       b) Mischen der Kohlenstoffnanoröhren mit einer Flüssigkeit mit hohem Siedepunkt;

      c) Hinzufügen von Reagenzien im korrekten Gleichgewicht zum Synthetisieren eines Lithiumsalzes;

30       d) Reagieren des Gemischs bei einer Temperatur, um das Lithiumsalz zu bilden, während das Gemisch im Ultraschallbad behandelt wird;

e) Trennen der festen, diskreten Kohlenstoffnanoröhren mit befestigten Lithiumsalzen von der Flüssigkeit; und

f) Trocknen und Härten der festen, diskreten Kohlenstoffnanoröhren mit befestigten Lithiumsalzen unter einer inerten Atmosphäre bei  
5 ausreichender Temperatur, um eine Olivin-Kristallstruktur zu erhalten.

12. Verfahren zur Herstellung diskreter Kohlenstoffnanoröhren mit Kristallen oder Schichten von Lithiumionen-aktiven Materialien, befestigt auf ihrer Oberfläche, wie in Anspruch 3 definiert, umfassend die Schritte von:

10 a) Auswählen von Kohlenstoffnanoröhren mit einem Aspektverhältnis von 10 bis 500 und Oxidationsstufen von 1 Gew.-% bis 15 Gew.-%;

b) Mischen der Kohlenstoffnanoröhren und eines Lithiumsalzes in einer Flüssigkeit mit Tensid;

c) Ultraschallbad-Behandlung des flüssigen  
15 Kohlenstoffnanorohrs/Lithiumsalz-Gemischs;

d) Trennen der festen, diskreten Kohlenstoffnanoröhren mit befestigten Lithiumsalzen von der Flüssigkeit; und

e) Trocknen und Härten der festen, diskreten Kohlenstoffnanoröhren mit befestigten Lithiumsalzen unter einer inerten Atmosphäre bei  
20 ausreichender Temperatur, um eine Olivin-Kristallstruktur zu erhalten.

**Annex to EPO Form 2004, Communication pursuant to Rule 71(3) EPC**

Bibliographical data of European patent application No. 12 731 264.3

For the intended grant of the European patent, the bibliographical data are set out below, for information:

**Title of invention:**

- LITHIUMIONENBATTERIEN MIT DISKRETEN KOHLENSTOFFNANORÖHRCHEN, HERSTELLUNGSVERFAHREN DAFÜR UND DARAUS GEWONNENE PRODUKTE
- LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
- BATTERIES LITHIUM-ION QUI UTILISENT DES NANOTUBES DE CARBONE DISCRETS, PROCÉDÉS DE PRODUCTION DE CES DERNIÈRES ET PRODUITS AINSI OBTENUS

**Classification:** INV. H01M4/62 H01M4/134 H01M10/0525 H01M4/1395 H01M4/505 H01M4/525 H01M4/131 H01M4/133 H01M4/1391 H01M4/1393

**Date of filing:** 21.06.2012

**Priority claimed:** US / 23.06.2011 / USP201161500560

**Contracting States\***  
for which fees have been paid:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

**Extension States\***  
for which fees have been paid:

**Validation States\***  
for which fees have been paid:

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- \*) If the time limit for the payment of designation fees according to Rule 39(1) EPC has not yet expired and the applicant has not withdrawn any designation, **all Contracting States/Extension States/Validation States** are currently still deemed to be designated. See also Rule 71a(3) EPC and, if applicable, the above Note to users of the automatic debiting procedure.
- \*\*) If two or more applicants have designated different Contracting States, this is indicated here.



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|                                          |                     |                    |
|------------------------------------------|---------------------|--------------------|
| Application No.<br>12 731 264.3 - 1360   | Ref.<br>P100028EP00 | Date<br>29.04.2016 |
| Applicant<br>Molecular Rebar Design, LLC |                     |                    |

## Communication under Rule 71(3) EPC

### 1. Intention to grant

You are informed that the examining division intends to grant a European patent on the basis of the above application, with the text and drawings and the related bibliographic data as indicated below.

A copy of the relevant documents is enclosed.

#### 1.1 In the text for the Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT  
RO RS SE SI SK SM TR

#### Description, Pages

1-11 filed in electronic form on 21-05-2015

#### Claims, Numbers

1-12 filed in electronic form on 30-10-2015

#### Drawings, Sheets

1/3-3/3 as published

### 1.2 Bibliographic data

The title of the invention in the three official languages of the European Patent Office, the international patent classification, the designated contracting states, the registered name(s) of the applicant(s) and the other bibliographic data are shown on **EPO Form 2056** (enclosed).

Registered letter

EPO Form 2004C 07/15TRI

**2. Invitation**

You are invited, **within a non-extendable period of four months** of notification of this communication,

**2.1 to EITHER approve the text communicated above and verify the bibliographic data (Rule 71(5) EPC)**

- (1) by filing a translation of the claim(s) in the other two official languages of the EPO

| Fee code | EUR |
|----------|-----|
|----------|-----|

- (2a) by paying the fee for grant including the fee for publication;  
minus any amount already paid (Rule 71a(5) EPC):

|            |        |
|------------|--------|
| <b>007</b> | 925.00 |
|            | 0.00   |

|               |        |
|---------------|--------|
| Total amount: | 925.00 |
|---------------|--------|

- (3) by paying additional claims fees under Rule 71(4) EPC;  
number of claims fees payable: 0  
minus any amount already paid (Rule 71a(5) EPC):

|            |      |
|------------|------|
| <b>016</b> | 0.00 |
|            | 0.00 |

|               |      |
|---------------|------|
| Total amount: | 0.00 |
|---------------|------|

**Important:** If the translations of the claims and fees have already been filed and paid respectively in reply to a previous communication under Rule 71(3) EPC, e.g. in the case of resumption of examination after approval (see Guidelines C-V, 6), **agreement as to the text to be granted** (Rule 71a(1) EPC) must be expressed within the same time limit (e.g. by approving the text and verifying the bibliographic data, by confirming that grant proceedings can go ahead with the documents on file and/or by stating which translations of the claims already on file are to be used).

Note 1: See "Important notes concerning fee payments" below.

Note 2: Any overpaid "minus" amounts will be refunded when the decision to grant (EPO Form 2006A) has been issued.

**2.2 OR, in the case of disapproval, to request reasoned amendments or corrections to the text communicated above or keep to the latest text submitted by you (Rule 71(6) EPC).**

In this case the translations of the claims and fee payments mentioned under point 2.1 above are NOT due.

The terms "amendment(s)" and "correction(s)" refer only to amendments or corrections of the application documents and not of other documents (e.g. bibliographic data, the designation of the inventor, etc.).

If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the examining division requesting that you correct this deficiency (Rule 137(4) EPC).

**2.3 Bibliographic data**

Where you request a change or correction of bibliographic data in response to the Rule 71(3) communication, this will **not** cause the sending of a further communication under Rule 71(3) EPC. You will still have to pay the fees and file translations in reply to the Rule 71(3) communication in the case of 2.1 above, unless you also file a reasoned request for amendments or corrections in response to the Rule 71(3) communication (see case 2.2 above).

**3. Loss of rights**

If neither of the two possible actions above (see points 2.1 or 2.2) is performed in due time, the European patent application will be deemed to be withdrawn (Rule 71(7) EPC).

#### 4. Further procedure

##### 4.1 In the case of point 2.1 above

- 4.1.1 The decision to grant the European patent will be issued, and the **mention of the grant** of the patent will be published in the European Patent Bulletin, if the requirements concerning the translation of the claims and the payment of all fees are fulfilled and there is agreement as to the text to be granted (Rule 71a(1) EPC).

**Note on payment of the renewal fee:**

If a renewal fee becomes due before the next possible date for publication of the mention of the grant of the European patent, publication will be effected only after the renewal fee and any additional fee have been paid (Rule 71a(4) EPC).

Under Article 86(2) EPC, the obligation to pay renewal fees to the European Patent Office terminates with the payment of the renewal fee due in respect of the year in which the mention of the grant of the European patent is published.

**Note on payment of the designation fee(s):**

If the designation fee(s) become(s) due after the communication under Rule 71(3) EPC, the mention of the grant of the European patent will not be published until these fees have been paid (Rule 71a(3) EPC).

- 4.1.2 After publication, the **European patent specification** can be downloaded free of charge from the EPO publication server <https://data.epo.org/publication-server> or ordered from the Vienna sub-office upon payment of a fee (OJ EPO 2005, 126).

##### 4.1.3 Filing of translations in the contracting states

As regards translation requirements prescribed by the contracting states under Article 65(1) EPC, please consult the website of the European Patent Office

[www.epo.org](http://www.epo.org) → Law & practice → Legal texts, National law relating to the EPC

[www.epo.org](http://www.epo.org) → Law & practice → All Legal texts → London Agreement

##### In the case of a valid extension or validation

As regards translation requirements prescribed by the extension or validation states, please consult the website of the European Patent Office

[www.epo.org](http://www.epo.org) → Law & practice → Legal texts, National law relating to the EPC

**Failure to supply a prescribed translation in a contracting state, or in an extension or validation state may result in the patent being deemed to be void *ab initio* in the state concerned (Art. 65(3) EPC).**

##### 4.2 In the case of 2.2 above

If the present communication under Rule 71(3) EPC is based on an auxiliary request and, within the time limit, you maintain the main request or a higher ranking request which is not allowable, the application will be refused (Art. 97(2) EPC).

If the examining division gives its consent to the requested amendments or corrections, it will issue a new communication under Rule 71(3) EPC; otherwise, it shall resume the examination proceedings (Rule 71(6) EPC).

#### 5. Filing of a divisional application

Any divisional application relating to this European patent application must be filed directly with the European Patent Office in Munich, The Hague or Berlin and will be in the language of the proceedings for the present application, or if the latter was not in an official language of the EPO, the divisional application may be filed in the language of the present application as filed (see Article 76(1) and Rule 36(2) EPC). Any such divisional application must be filed while the present application is still pending (Rule 36(1) EPC; Guidelines A-IV, 1.1.1).

**6. Important notes concerning fee payments**

**6.1** For all payments, please refer to the relevant **fee code(s)**.

**6.2 Automatic debiting procedure**

The fee for grant, including the fee for publication, and any additional claims fees due under Rule 71(4) EPC will be debited automatically on the date of filing of the translations of the claims, or on the last day of the period of this communication. However, if the designation fee(s) become(s) due as set out in Rule 71a(3) EPC and/or a renewal fee becomes due as set out in Rule 71a(4) EPC, these should be paid separately by another permitted way of payment in order not to delay the publication of the mention of the grant. The same applies in these circumstances to the payment of extension and validation fees. For further details see the Arrangements for the automatic debiting procedure (AAD) and accompanying information from the EPO concerning the automatic debiting procedure (Annexes A.1 and A.2 to the Arrangements for deposit accounts (ADA) in Supplementary publication - OJ EPO 3/2015).

Note: If a waiver is expressed in response to a Rule 71(3) communication (see OJ EPO 2015, A52), the fee for grant, including the fee for publication/printing, and any additional claims fees will not be debited automatically. These fees must be paid separately by another means of payment allowed under the Rules relating to Fees.

**6.3 Important information relating to fee amounts**

Following any amendment to the Rules relating to Fees, the amount(s) mentioned in this communication may be different from the amount(s) **actually due on the date of payment**. The latest version of the Schedule of fees and expenses, published as a Supplement to the Official Journal of the EPO, is also available on the EPO website ([www.epo.org](http://www.epo.org)) and can be found under [www.epo.org/schedule-of-fees](http://www.epo.org/schedule-of-fees), which allows the viewing, downloading and searching for individual fee amounts, both current and previous. Please note that procedural fees are usually adjusted every two years, on even years, with effect from 1 April.

**Examining Division:**

|                      |                    |
|----------------------|--------------------|
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Enclosures:      Text intended for grant (17 pages)  
EPO Form 2056

Application No.:

12 731 264.3

#### IV.2. Patent classification

The classification indicated on the published patent application remains unchanged. It is as follows:

INV. H01M4/62 H01M4/134 H01M10/0525 H01M4/1395 H01M4/505 H01M4/525  
H01M4/131 H01M4/133 H01M4/1391 H01M4/1393

#### IV.3. Title of the invention

The title indicated on the published patent application remains unchanged. It reads as follows:

LITHIUMIONENBATTERIEN MIT DISKRETEN KOHLENSTOFFNANORÖHRCHEN,  
HERSTELLUNGSVERFAHREN DAFÜR UND DARAUS GEWONNENE PRODUKTE

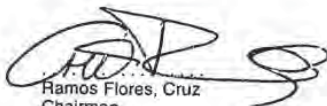
LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS  
FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM

BATTERIES LITHIUM-ION QUI UTILISENT DES NANOTUBES DE CARBONE  
DISCRETS, PROCÉDÉS DE PRODUCTION DE CES DERNIÈRES ET PRODUITS  
AINSI OBTENUS

#### IV.4. Documentation

STIN The file contains technical information submitted after the application was filed and not  
included in this specification.

17.12.15  
Date



Ramos Flores, Cruz  
Chairman



Kelly, Michael  
1st examiner



Cojuhovsky, Oana  
2nd examiner

Enclosure(s):

Title: ~~LITHIUM ION BATTERIES USING DISCRETE CARBON  
NANOTUBES, METHODS FOR PRODUCTION THEREOF AND  
PRODUCTS OBTAINED THEREFROM~~

This application claims priority to U.S. Provisional Patent Application  
Serial No. 61/500,560, entitled "LITHIUM ION BATTERIES USING  
DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION  
THEREOF AND PRODUCTS OBTAINED THEREFROM," filed on June 23,  
5 2011.

#### FIELD OF THE INVENTION

The present invention relates generally to the field of improved  
technologies for lithium batteries. In some embodiments, the invention relates  
to discrete carbon nanotubes having crystals or layers of lithium ion active  
10 materials attached to their surface.

#### BACKGROUND

Lithium batteries are used extensively for portable electronic  
equipment and are increasingly being used to provide electrical back-up for  
wind and solar energy. The commercially used lithium ion (Li-ion) rechargeable  
15 batteries based on cobalt, nickel or manganese oxides for the cathode materials  
are known for their poor electrical conductivity and poor electrochemical  
stability which results in poor cycling (charge/discharge) ability. Olivine  
structures such as lithium iron phosphate,  $\text{LiFePO}_4$  or lithium manganese  
phosphate,  $\text{LiMnPO}_4$ , operate at higher charge and discharge rates, but are  
20 still limited by low electrical conductivity and the kinetics of Li-ion diffusion.

Attempts to overcome the above deficiencies have included synthesis  
of nano-sized crystals, termed nanocrystals, of lithium salts as well as mixtures  
of lithium salts and carbon nanotubes. Even though the mixtures of carbon  
nanotubes and nanocrystals of lithium salts show improvements in

charge/discharge rates, the carbon nanotubes previously employed are not considered to be essentially discrete, i.e., individual uniformly dispersed tubes. Carbon nanotubes as conventionally made by gas phase reaction result in a tangled bundle of tubes with particle diameters ranging from 50 to 200 micrometers. Also, the lithium nanocrystals are not ionically or covalently attached to the surface of the discrete carbon nanotubes to provide for intimate electron transfer and enhanced mechanical strength of the active material. During charging and discharging of conventional lithium ion batteries, the nanocrystals expand and contract. Over a number of cycles, this leads to microcrack formation in the layer of active material and hence to higher internal resistance and decline of the battery performance. With crystals bound to and interconnected with discrete carbon nanotubes the microcrack formation due to severe mechanical vibration, bending, or expansion and contraction will be retarded.

In WO 2010/117392, exfoliated carbon nanotubes are described which may have an aspect ratio of at least 100. Further, it describes that for some embodiments the carbon nanotubes may be further associated or functionalized with an electroactive material, such as  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

US 2011/0104551 teaches a composite material suitable for use in an anode / or a lithium ion battery. Said composite material comprises a layer of a lithium-alloying material on the walls of an aligned nanotubular base material.

Lithium salts have also been carbon coated with very thin coatings on the nanometer scale to enhance inter-particle electrical conductivity, but the carbon coating can slow the lithium ion transport and may also react unfavorably with electrolytes over time. The carbon coating is considered to be amorphous in structure and is more likely to react with electrolyte than the crystalline carbon structure of the carbon nanotubes. Likewise, carbon particles have been added to the crystals of lithium salts to enhance inter-particle conductivity but these generally reduce the mechanical strength of dried pastes in the battery leading to cracking and reduced performance over time.

The present invention overcomes the difficulties of low electrical conduction, particularly due to expansion and contraction of the material during charging and discharging of the battery, improved lithium ion transport and mitigation of potentially damaging chemical side reactions by attaching  
5 nanosized crystals or nanosized layers of lithium ion active material to the surface of discrete, functionalized and well dispersed carbon nanotubes.

Likewise, for the lithium battery anode materials, active anode materials, such as carbon particles, tin oxide or silicon, can be attached to the discrete carbon nanotube surfaces to provide numerous benefits such as  
10 improved capacity, electron and ion conductivity and mechanical strength.

In addition to the discrete carbon nanotube network providing support and spatial stabilization of nanosized particles or layers for cathode or anode material of the lithium battery, other benefits include improved heat transfer media to avoid thermally-induced runaway, structural strength to the paste  
15 during manufacturing and high surface area per weight of lithium ion active material to provide good energy density. The uniform dispersion of discrete tubes will also provide a more uniform voltage gradient across the cathode or anode layer, therefore reducing the probability of locally high electrically resistive regions that can cause accelerated decay of performance in that local  
20 region.

### SUMMARY

One aspect of the invention is a composition useful for lithium ion batteries, comprising discrete carbon nanotubes having attached to their  
25 surface lithium ion active materials in the form of nanometer sized crystals or layers; the discrete carbon nanotubes having an aspect ratio of 10 to 500 and oxidation levels from 1% to 15% by weight of the carbon nanotube. For a cathode, the lithium ion active material comprises a lithium metal salt which may further comprise iron, manganese, cobalt, copper, nickel, vanadium,  
30 titanium, or mixtures thereof. The composition can further comprise the

lithium metal salt with an olivine crystal structure. For an anode, the lithium ion active material may comprise carbon, tin, silicon, copper, antimony, aluminum, germanium, titanium or mixtures thereof. The discrete carbon nanotubes of the composition have an aspect ratio of 10 to 500 and oxidation  
5 levels from 1 to 15 weight percent of the carbon nanotube. The composition can further comprise graphene or oxygenated graphene. In one embodiment, the weight ratio of graphene to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.

Yet another aspect of this invention is a process for the production of  
10 discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers, comprising the steps of:

- a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1 to 15 weight percent,
- 15 b) mixing the carbon nanotubes with a high boiling point liquid, optionally with a non-ionic surfactant,
- c) optionally sonicating the carbon nanotube liquid mixture,
- d) adding reagents in correct balance to synthesize the desired lithium salt,
- 20 e) reacting the mixture at the desired temperature to form the lithium salt while sonicating the mixture,
- f) separating the solid salts from the liquid; and
- g) drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient  
25 temperature to obtain the olivine crystal structure.

A further aspect of the invention is a process for the production of the discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers, comprising the steps of:

- 5
- a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1 to 15 weight percent,
  - b) mixing the carbon nanotubes and desired lithium salt in a liquid with surfactant,
  - c) sonicating the carbon nanotube/lithium salt liquid mixture,
  - d) separating the solid salts from the liquid,
  - e) drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure.

10 An additional aspect of this invention is a composition useful for lithium ion batteries comprising discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.

15 Yet another aspect of this invention useful for lithium ion batteries is a composition comprising oxidized carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers wherein the carbon nanotubes are uniformly dispersed without clustering on a dimension scale less than one micrometer.

20 A further aspect of this invention is a composition useful for lithium ion batteries comprising uniformly dispersible oxidized carbon nanotubes having lithium ion active materials attached to their surface, whether ionically or chemically.

## 25 BRIEF DESCRIPTION OF THE FIGURES

Figure 1 depicts lithium salt coated as a nanolayer on discrete carbon nanotubes.

Figure 2 shows  $\text{LiMnO}_4$  with 5% oxidized carbon nanotubes of this invention.

Figure 3 shows titanium dioxide crystals attached to discrete carbon nanotubes.

#### DETAILED DESCRIPTION

5       The term “carbon nanotubes” as used herein refers to allotropes of carbon with a cylindrical nanostructure. The nanotubes may be single, double or multiwall.

      The term “discrete carbon nanotubes” as used herein refers to carbon nanotubes capable of being separated to give individual tubes.

10       The term “graphene” as used herein refers to individual atomic thickness plates of carbon.

      The term “oxidized graphene” as used herein refers to the products of oxidizing graphene plates. The oxidized species are generally at the edges of the graphene plates.

15       The term “oxidized carbon nanotubes” as used herein refers to the products of oxidizing the carbon nanotubes. Generally the oxidized species are carboxylic, ketone or hydroxyl functionalities.

      The term “weight percent” or “percent weight” or “% by weight” as used herein is calculated by dividing the weight of a reagent by the total weight  
20 of a mixture to which it is added subsequent to the addition of the reagent. For example, adding 1 gram of a reagent A to 99 grams of a reagent B, thereby forming 100 grams of a mixture A+B would constitute adding 1 weight percent of the reagent A to the mixture.

      During the process of making discrete carbon nanotubes (which can be  
25 single, double and multiwall configurations), the nanotubes are cut into segments and residual catalyst particles that are interior to the carbon nanotubes as received from the manufacturer are dissolved. This cutting of the tubes helps with exfoliation. The cutting of the tubes reduces the length of the tubes into carbon nanotube segments that are defined here as Molecular Rebar.  
30 Proper selection of the carbon nanotube feed stock related to catalyst particle

type and distribution in the carbon nanotubes allows more control over the resulting individual tube lengths and overall tube length distribution. A preferred selection is where the internal catalyst sites are evenly spaced and where the catalyst is most efficient. The selection can be evaluated using  
5 electron microscopy and determination of the exfoliated tube distribution. Molecular Rebar gives advantageous mechanical and transport properties when added to other materials compared to materials with no Molecular Rebar.

#### **Types of migratable ions and ion active materials**

The ion active material which can be attached to the discrete carbon  
10 nanotubes is defined here as meaning an ion can migrate into or out of the ion active material thereby exchanging electrons. The migrating ion is preferably lithium ion, and is preferably 50 percent by mole of the available migratable ions, more preferably 75 mole percent or higher, most preferably 95 mole percent or higher and can be as high as 100 mole percent of the total  
15 migratable ions. Other migratable ions can include magnesium, aluminium, iron, zinc, manganese, sodium, potassium, lead, mercury, silver, gold, nickel, cadmium and the like.

Examples of ion active materials are lithium iron phosphate, lithium manganese phosphate, lithium cobalt oxide, silica, manganese dioxide,  
20 cadmium, titanium dioxide and carbon.

The ion active materials can be the same or comprise different active materials. Further, ion species in these ion active materials can be the same, or they can be different. When using a mixture of migratable ions, it preferred that the lithium ions comprise the majority of the ions of the mixture.  
25 Mixtures of migratable ions, when used, can be of 2 different ions, or can be three or more different ions in various proportions. In addition, the ion mixture can be varying valence (or oxidation) states of the same ion, such as  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ .

When mixing ion active materials for attachment to the carbon  
30 nanotubes, the mixture may be merely accidental, such as that resulting from

either natural states of the ion active material compounds, or the mixture can be an intentional mixing of the different ion active materials, including those in differing chemical or physical state. In some cases comprising migratable ion mixture using lithium ion, the lithium ion may comprise the minority ionic component, of the mix, although this is not usually the preferred configuration. When more than one ion is used, then the ratio of Li ion to other total ions is preferably at least 2:1, or 3:1 or 10:1 and can be as high as 25:1 (mole ratios).

The ion active material attached to the discrete carbon nanotubes can also be useful for applications such as fuel cells, sensors, capacitors, photovoltaics and catalysts.

#### **Experimental Examples**

The following experimental examples are included to demonstrate particular aspects of the present disclosure. It should be appreciated by those of ordinary skill in the art that the methods described in the examples that follow merely represent illustrative embodiments of the disclosure.

##### **Example 1**

##### **Discrete carbon nanotubes with attached copper oxide nanoparticles suitable for a lithium ion battery anode material**

102 mg of multi-wall carbon nanotubes (CNano, grade C9000) oxidized to about 8 weight percent and aspect ratio about 60 are added to 100 mg copper sulfate, 640 mg sodium EDTA, 15 mg of polyethylene glycol, 568 mg of sodium sulfate and 60 mL of deionized water. The mixture is sonicated for 10 minutes and then heated to 40°C. 3 mL of formaldehyde (37% solution) and 500 mg of sodium hydroxide is added to bring the pH to 12.2. The mixture is stirred for 30 minutes at 85°C and then filtered using a 5 micron PVDF filter and washed with 200 mL of deionized water. The resultant coated multiwall tubes show a coppery hue color. An electron micrograph shows copper oxide particles of diameter about 50 to 150 nm interconnected by well-dispersed carbon nanotubes.

**Example 2**

**Discrete carbon nanotubes with lithium iron phosphate coated on the surface of the tubes, suitable for a lithium ion battery cathode material**

- 5           0.2 grams of multi-wall carbon nanotubes (CNano, grade C9000) oxidized to about 8 weight percent and aspect ratio about 60 are added to 23.5 grams of diethylene glycol and sonicated for 15 minutes. The solution is grey. 1.16 grams of iron acetate dissolved in 4 ml of deionized water is added and the mixture heated under nitrogen, stirring and sonication. After 1 hour at 140°C
- 10   a solution of 0.65 grams of lithium acetate and 0.74 grams of ammonium phosphate in 4.2 ml of deionized water is added. The temperature is raised to about 185°C over 30 minutes, then held at 185°C for 4 hours. The mixture is cooled to 110°C and sonicated for 5 minutes followed by further cooling to ambient temperature while stirring. The solids are separated from the mixture
- 15   by centrifugation followed by ethanol washing. The resultant powder is dried to constant weight *in vacuo*.

The resultant dried powder is determined to have a resistance of 2,000 ohm-cm compared to a commercially obtained sample determined as 19,000 ohm-cm.

20           **Example 3**

- Lithium iron phosphate obtained commercially is ground with multiwall carbon nanotubes (CNano, grade C9000) oxidized to about 8 weight percent and of aspect ratio about 60, in a mortar and pestle at weight ratios of 5:1 and 1:1 lithium salt to carbon nanotube. Sodium dodecyl sulfate (SDS) is
- 25   then added at a weight ratio of 0.7:1 compared to the carbon nanotube and deionized water added to resultant mixture to give a 0.5 weight percent solution of carbon nanotubes in the presence of lithium salt and surfactant. The mixture is sonicated for 1 hour, then the solids filtered using a polyvinylidene fluoride filter (0.2 micron), washed with deionized water and
- 30   dried. A micrograph of the discrete carbon nanotubes coated with lithium iron

phosphate is shown in Figure 1. The results of the resistance of the powders are given in Table 1, units of resistance are ohm-cm.

Table 1

| Material               | 5:1 Weight ratio Lithium salt:carbon nanotube | 1:1 Weight ratio Lithium salt:carbon nanotube |
|------------------------|-----------------------------------------------|-----------------------------------------------|
| Dry mix                | 860                                           | 26                                            |
| Coated                 | 46.2                                          | 6.9                                           |
| Improvement of coating | 18.6 X                                        | 3.8X                                          |

5

#### Example 4

##### Preparation of lithium manganese phosphate in the presence of five percent by weight oxidized carbon nanotubes

37.439g manganese II acetate is dissolved in 5.0ml of water and added to 589mL of diethylene glycol (DEG) already in the reaction vessel. The mixture is then heated to a target temperature of 140°C, under stirring and gentle nitrogen flow to distill off the water. 1.119g of oxidized carbon nanotubes (originally CNano, grade C9000, average diameter 13 nm) nanotubes having an oxidation of 4% and average aspect ratio of 60 are dispersed in 222.2 mL diethylene glycol (0.5% w/v) using sonication while stirring for 30 minutes. Additionally, 14.4434g lithium acetate and 16.4497g ammonium dihydrogen phosphate are dissolved in 90 mL of water. The dispersion of oxidized carbon nanotubes, lithium acetate and ammonium dihydrogen phosphate are added to the reaction medium while stirring, and with sonication. Heating is increased to maintain a target temperature of 180 degrees centigrade for 3 hours, while maintaining constant nitrogen flow. Following the end of the reaction, heating and sonication are turned off while stirring and nitrogen are maintained as the system cools to room temperature.

The product is a highly viscous, dark-grey colored fluid. The carbon nanotube coated with lithium manganese phosphate is centrifuged and the solids washed with anhydrous ethanol three times. An electron micrograph of the product is shown in Figure 2. In figure 2 the majority of tubes are shown to have coatings of lithium manganese phosphate about 20-40nm thick. The coatings are not smooth as seen in Example 1.

#### Example 5

**A composition useful as an anode active material in lithium batteries - *In situ* synthesis of TiO<sub>2</sub>-oxidized carbon nanotube composition from titanium isopropoxide as a precursor**

0.179g of carbon nanotubes (originally CNano, grade C-9000) oxidized to about 4 % by weight and aspect ratio about 60 is added to 27.3ml NMP and 2.7ml RO water and sonicated for 1 hour to obtain a fully exfoliated solution. A 19% v/v solution is prepared by adding 3.41ml of titanium isopropoxide (Sigma-Aldrich) to 18ml of isopropanol (Ultra Pure Solutions, Inc.) and is added dropwise with stirring to the exfoliated carbon nanotube dispersion while under sonication. The reaction vessel is then sealed and gently heated to slightly above room temperature for 1 hour. Sonication and a medium stirring speed are maintained over the entire duration of the reaction. The reaction products are obtained by filtering with a Buchner filter under vacuum, washing with ethanol to remove NMP and drying *in vacuo* to constant weight. An electron micrograph, Figure 3, shows crystals of titanium dioxide of scale 50-100nm bound to discrete well-dispersed carbon nanotubes.

## Claims

~~What is claimed is the following:~~

1. A composition useful for lithium ion batteries comprising:  
discrete carbon nanotubes, the discrete carbon nanotubes having crystals  
5 or layers of lithium ion active material attached to their surface, wherein  
the discrete carbon nanotubes have an aspect ratio of 10 to 500 and  
oxidation levels from 1% to 15% by weight of the carbon nanotube.
2. The composition of claim 1, wherein the crystals or layers of lithium ion  
10 active material comprise a lithium metal salt and an element selected  
from the group consisting of: iron, manganese, cobalt, copper, nickel,  
vanadium, titanium, and mixtures thereof.
3. The composition of claim 2, wherein the lithium metal salt has an olivine  
15 crystal structure.
4. The composition of claim 1, wherein the crystals or layers of lithium ion  
active material comprise tin, silicon, copper, antimony, aluminum,  
20 germanium, titanium, or mixtures thereof.
5. The composition of any one of claims 1-4, further comprising graphene or  
oxygenated graphene.
6. The composition of claim 5, wherein the weight ratio of graphene to  
25 carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.

7. The composition of any one of claims 1-6, wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.
8. The composition of any one of claims 1-7, comprising oxidized carbon  
5 nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are uniformly dispersed without clustering on a dimension scale less than 1 micrometer.
9. The composition of any one of claims 1-8, comprising uniformly dispersible  
10 oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.
10. The composition of claim 9, wherein the crystals or layers of lithium ion  
15 active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.
11. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface as defined in claim 3, comprising the steps of:  
20
  - a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% by weight;
  - b) mixing the carbon nanotubes with a high boiling point liquid;
  - c) adding reagents in correct balance to synthesize a lithium salt;
  - d) reacting the mixture at a temperature to form the lithium salt while  
25 sonicating the mixture;
  - e) separating the solid discrete carbon nanotubes with attached lithium salts from the liquid; and
  - f) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient  
30 temperature to obtain an olivine crystal structure.

12. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface as defined in claim 3, comprising the steps of:
- a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level of 1% to 15% by weight;
  - b) mixing the carbon nanotubes and a lithium salt in a liquid with surfactant;
  - c) sonicating the liquid carbon nanotube/lithium salt mixture;
  - d) separating the solid discrete carbon nanotubes with attached lithium salts from the liquid; and
  - e) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

1/3

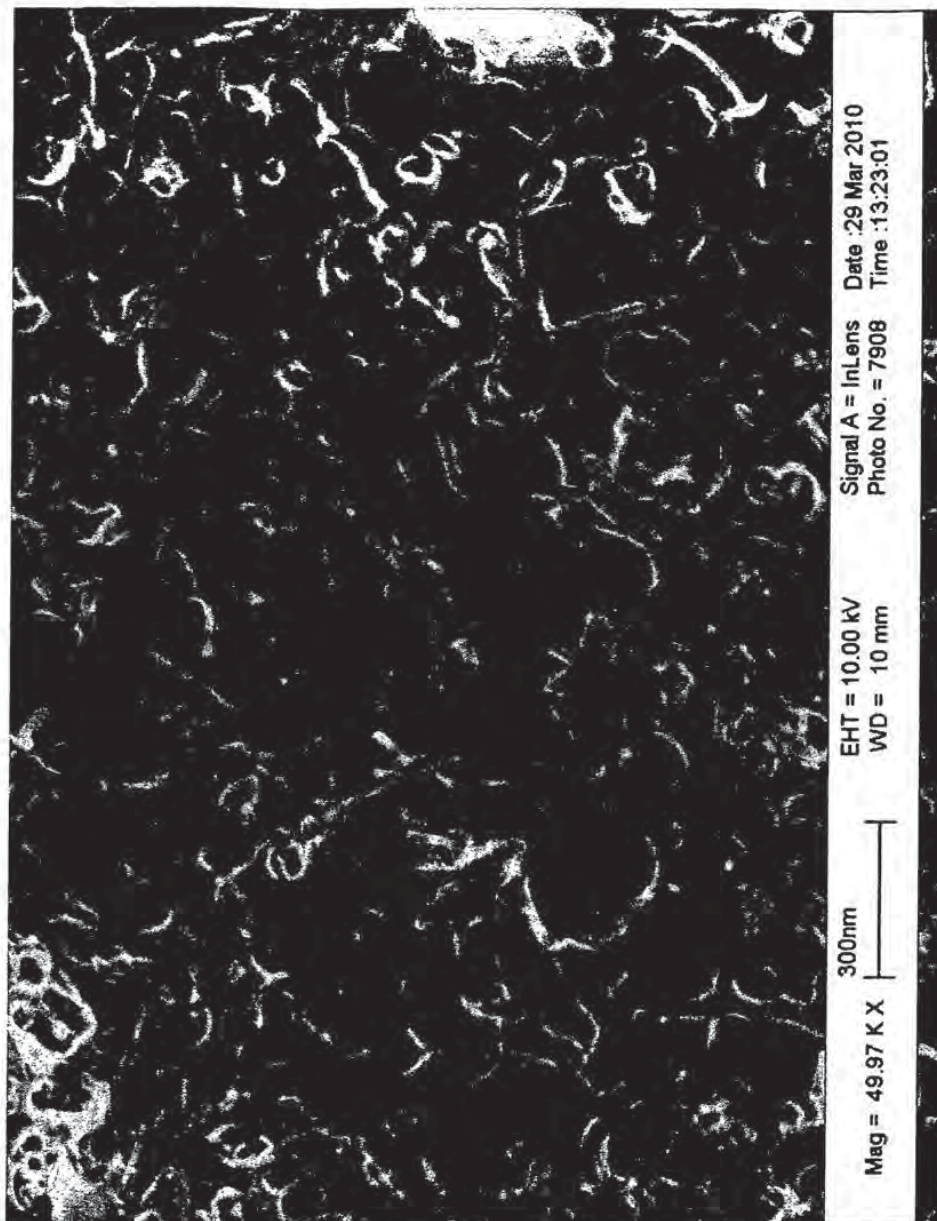


Figure 1

2/3

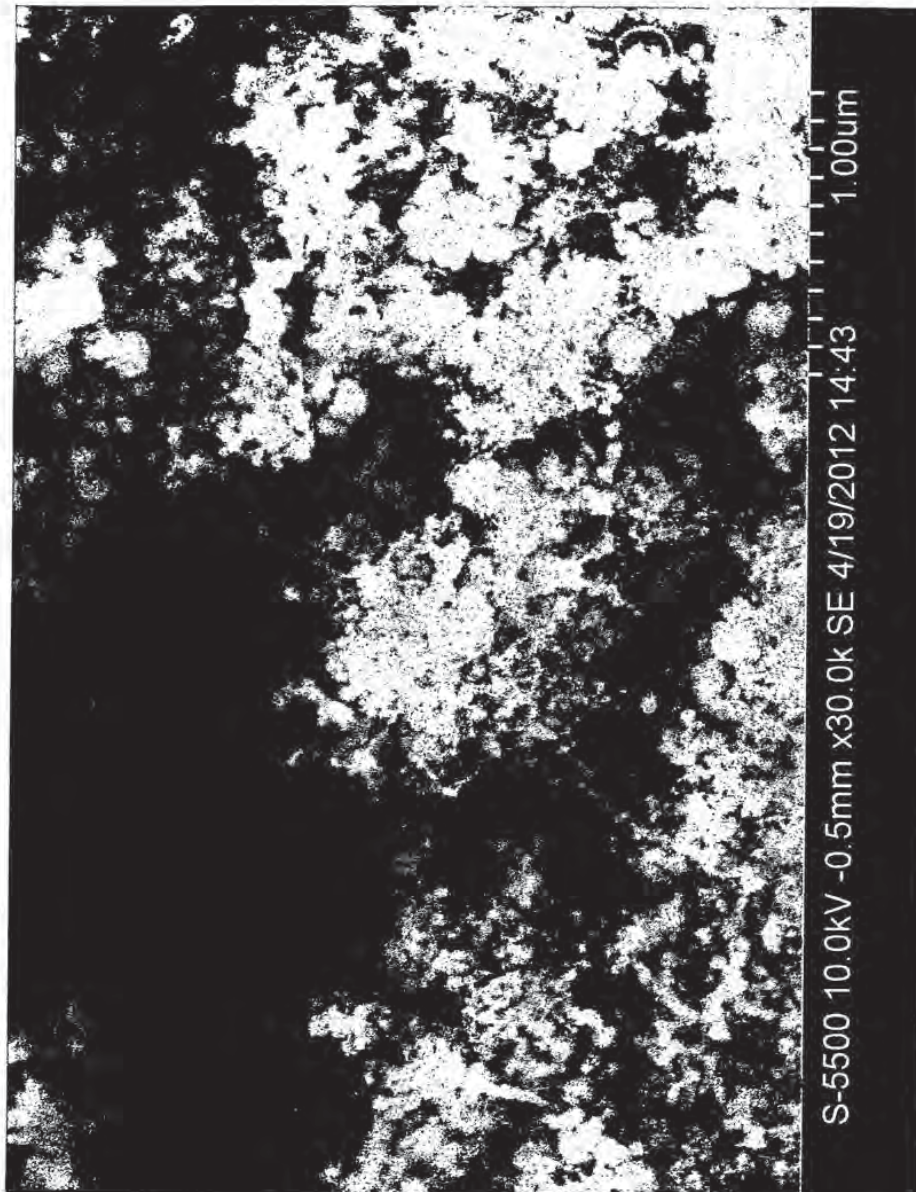


Figure 2

3/3

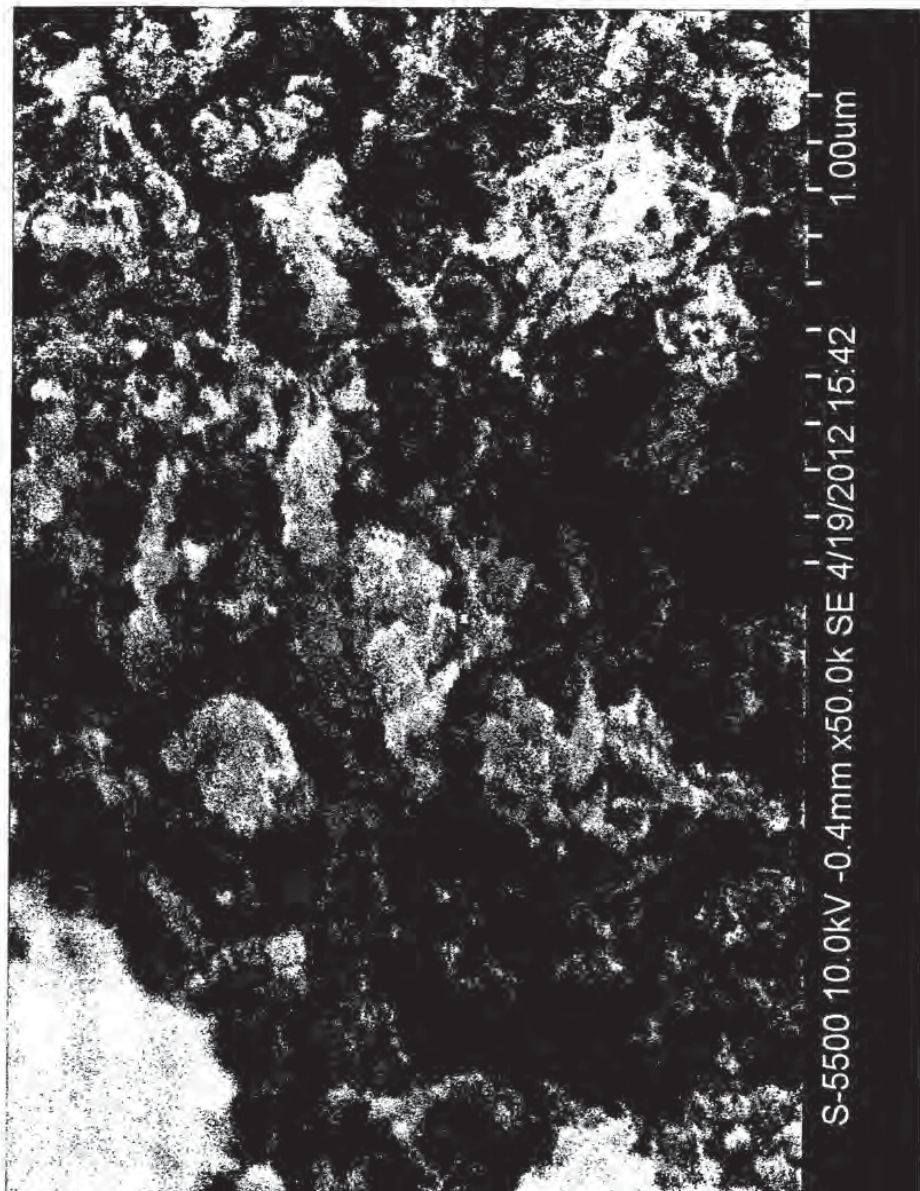


Figure 3



## Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

Submission number 3876474

Application number EP12731264.3

Date of receipt 30 October 2015

Receiving Office European Patent Office, The Hague

Your reference P100028EP00

Applicant All applicants as on file

Documents submitted  
package-data.xml  
epf1038.pdf (1 p.)  
CLMS-HWA-1.pdfP100028EP00  
Amended claims with revisions.pdf (4 p.)

ep-sfd-request.xml  
EPLETT-1.pdfP100028EP00 Letter to  
EPO.pdf (2 p.)  
CLMS-1.pdfP100028EP00 Amended  
claims - clean version.pdf (3 p.)

Submitted by CN=Hermanus Marsman 34472

Method of submission Online

Date and time receipt generated 30 October 2015, 11:06 (CET)

Message Digest 79:D3:78:B6:6E:18:FA:9C:53:E2:6A:39:B4:98:1C:EB:53:D0:8F:FA

### Correction by the EPO of errors in debit instructions filed by eOLF

Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

/European Patent Office/

## Claims

What is claimed is the following:

1. ~~A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:~~
- 5       ~~a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% by weight;~~
- ~~b) mixing the carbon nanotubes with a high boiling point liquid;~~
- ~~c) adding reagents in correct balance to synthesize a lithium salt;~~
- 10       ~~d) reacting the mixture at a temperature to form the lithium salt while sonicating the mixture;~~
- ~~e) separating the solid discrete carbon nanotube salts from the liquid; and~~
- ~~f) drying and annealing the solid discrete carbon nanotube salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.~~
2. ~~A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:~~
- 20       ~~a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level of 1% to 15% by weight;~~
- ~~b) mixing the carbon nanotubes and a lithium salt in a liquid with surfactant;~~
- 25       ~~c) sonicating the liquid carbon nanotube/lithium salt mixture;~~
- ~~d) separating the solid salts from the liquid; and~~

~~e) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.~~

5     ~~3.1.~~ A composition useful for lithium ion batteries comprising:  
       discrete carbon nanotubes, the discrete carbon nanotubes having crystals  
       or layers of lithium ion active material attached to their surface, wherein  
       the discrete carbon nanotubes have an aspect ratio of 10 to 500 and  
       oxidation levels from 1% to 15% by weight of the carbon nanotube.

10     ~~4.2.~~ The composition of claim ~~3~~ 1, wherein the crystals or layers of lithium ion  
       active material comprise a lithium metal salt and an element selected  
       from the group consisting of: iron, manganese, cobalt, copper, nickel,  
       vanadium, titanium, and mixtures thereof.

15     ~~5.3.~~ The composition of claim ~~4~~ 2, wherein the lithium metal salt has an  
       olivine crystal structure.

20     ~~6.4.~~ The composition of claim ~~3~~ 1, wherein the crystals or layers of lithium ion  
       active material comprise tin, silicon, copper, antimony, aluminum,  
       germanium, titanium, or mixtures thereof.

~~7.5.~~ The composition of any one of claims ~~3-6~~ 1-4, further comprising graphene  
       or oxygenated graphene.

25     ~~8.6.~~ The composition of claim ~~7~~ 5, wherein the weight ratio of graphene to  
       carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.

- 9.7. The composition of any one of claims ~~3-8~~ 1-6, wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.
- 5 | ~~10.8.~~ The composition of any one of claims ~~3-9~~ 1-7, comprising oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are uniformly dispersed without clustering on a dimension scale less than 1 micrometer.
- 10 | ~~11.9.~~ The composition of any one of claims ~~3-10~~ 1-8, comprising uniformly dispersible oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.
- 15 | ~~12.10.~~ The composition of claim ~~11~~ 9, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.
- 20 | 11. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface as defined in claim 3, comprising the steps of:
- a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% by weight;
- b) mixing the carbon nanotubes with a high boiling point liquid;
- c) adding reagents in correct balance to synthesize a lithium salt;
- 25 | d) reacting the mixture at a temperature to form the lithium salt while sonicating the mixture;
- e) separating the solid discrete carbon nanotubes with attached lithium salts from the liquid; and

f) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

- 5 12. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface as defined in claim 3, comprising the steps of:
- 10 a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level of 1% to 15% by weight;
- b) mixing the carbon nanotubes and a lithium salt in a liquid with surfactant;
- c) sonicating the liquid carbon nanotube/lithium salt mixture;
- d) separating the solid discrete carbon nanotubes with attached lithium salts from the liquid; and
- 15 e) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

## Claims

What is claimed is the following:

1. A composition useful for lithium ion batteries comprising:  
discrete carbon nanotubes, the discrete carbon nanotubes having crystals  
5 or layers of lithium ion active material attached to their surface, wherein  
the discrete carbon nanotubes have an aspect ratio of 10 to 500 and  
oxidation levels from 1% to 15% by weight of the carbon nanotube.
2. The composition of claim 1, wherein the crystals or layers of lithium ion  
10 active material comprise a lithium metal salt and an element selected  
from the group consisting of: iron, manganese, cobalt, copper, nickel,  
vanadium, titanium, and mixtures thereof.
3. The composition of claim 2, wherein the lithium metal salt has an olivine  
15 crystal structure.
4. The composition of claim 1, wherein the crystals or layers of lithium ion  
active material comprise tin, silicon, copper, antimony, aluminum,  
germanium, titanium, or mixtures thereof.
- 20 5. The composition of any one of claims 1-4, further comprising graphene or  
oxygenated graphene.
6. The composition of claim 5, wherein the weight ratio of graphene to  
25 carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.

7. The composition of any one of claims 1-6, wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.
8. The composition of any one of claims 1-7, comprising oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are uniformly dispersed without clustering on a dimension scale less than 1 micrometer.
9. The composition of any one of claims 1-8, comprising uniformly dispersible oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.
10. The composition of claim 9, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.
11. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface as defined in claim 3, comprising the steps of:
  - a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% by weight;
  - b) mixing the carbon nanotubes with a high boiling point liquid;
  - c) adding reagents in correct balance to synthesize a lithium salt;
  - d) reacting the mixture at a temperature to form the lithium salt while sonicating the mixture;
  - e) separating the solid discrete carbon nanotubes with attached lithium salts from the liquid; and
  - f) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

12. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface as defined in claim 3, comprising the steps of:
- a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level of 1% to 15% by weight;
  - b) mixing the carbon nanotubes and a lithium salt in a liquid with surfactant;
  - c) sonicating the liquid carbon nanotube/lithium salt mixture;
  - d) separating the solid discrete carbon nanotubes with attached lithium salts from the liquid; and
  - e) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.



## Letter accompanying subsequently filed items

Representative:

V.O.

106850

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Tel. +49(0)30 25901-0 | Fax -840

The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number

12731264.3

Applicant's or representative's reference

P100028EP00

|   | Description of document                                 | Original file name                             | Assigned file name |
|---|---------------------------------------------------------|------------------------------------------------|--------------------|
| 1 | Letter relating to the search and examination procedure | P100028EP00 Letter to EPO.pdf                  | EPLETT-1.pdf       |
| 2 | Amended claims with annotations                         | P100028EP00 Amended claims with revisions.pdf  | CLMS-HWA-1.pdf     |
| 3 | Amended claims (clean copy)                             | P100028EP00 Amended claims - clean version.pdf | CLMS-1.pdf         |

### Annotations

deposit-account(V.O.; 30.10.2015)

1. Remark(Annotate)

I herewith authorize the European Patent Office to deduct all necessary fees that are involved in this specific action from my deposit-account No. 2809.0002

### Signatures

Place:

Den Bosch

Date:

30 October 2015

Signed by:

/H.A.M. Marsman/

Association:

V.O.

Representative name:

H.A.M. Marsman

Capacity:

(Representative)

P100028EP00



**Patents & Trademarks**

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H.Marsman@vo.eu  
www.vo.eu

Your ref. 12731264.3/1360  
Our ref. MAS/P100028EP00

The Hague,  
October 30, 2015

Re: European patent application No. 12731264.3  
Molecular Rebar Design, LLC

With reference to your Communication of September 29, 2015, I enclose a set of amended claims both in a form showing revisions and in retyped form. In addition, the following is observed.

- 5 To meet the requirement under Art 84 EPC for the claims as a whole, independent claim 3 is now renumbered to new claim 1. The dependency of the claims dependent on claim 3 is adapted.

- 10 Further, to meet the requirement of R 43(4) EPC, previous claims 1 and 2 now refer to previous claim 5.

- 15 Finally, the terms "solid carbon nanotube salts" and "solid salts" as used in previous claims 1 and 2, respectively, are replaced by the terms "solid discrete carbon nanotubes with attached lithium salts" based on §§ [0010] and [0011] of the description as originally filed.

Page 2  
Your ref. 12731264.3/1360  
Our ref. MAS/P100028EP00  
Date October 30, 2015



In my view, these amendments are in line with your suggestions and I hence expect that all formalities are overcome. Should however some objection remain, it is requested that you contact me by phone or send another Communication.

The professional representative,

A handwritten signature in black ink, consisting of several overlapping, fluid strokes.

H.A.M. Marsman

Encl.: Amended claims (with revisions and clean version)

EK



European Patent Office  
80298 MUNICH  
GERMANY

Questions about this communication ?  
Contact Customer Services at [www.epo.org/contact](http://www.epo.org/contact)



V.O.  
P.O. Box 87930  
2508 DH Den Haag  
PAYS-BAS

Date  
08.10.15

|                                                     |                                                           |
|-----------------------------------------------------|-----------------------------------------------------------|
| Reference<br>P100028EP00                            | Application No./Patent No.<br>12731264.3 - 1360 / 2724403 |
| Applicant/Proprietor<br>Molecular Rebar Design, LLC |                                                           |

**Communication of amended entries concerning the representative (R. 143(1)(h) EPC)**

As requested, for the above-mentioned European patent application / European patent the entries concerning the representative have been amended as follows:

V.O.  
P.O. Box 87930  
2508 DH Den Haag  
NL

The amendment will be recorded in the Register of European Patents.

**For the Examining Division**



The examination is being carried out on the **following application documents**

#### Description, Pages

|      |                             |            |
|------|-----------------------------|------------|
| 1-11 | filed in electronic form on | 21-05-2015 |
|------|-----------------------------|------------|

#### Claims, Numbers

|      |                             |            |
|------|-----------------------------|------------|
| 1-12 | filed in electronic form on | 21-05-2015 |
|------|-----------------------------|------------|

#### Drawings, Sheets

|         |              |
|---------|--------------|
| 1/3-3/3 | as published |
|---------|--------------|

#### Clarity (Article 84 EPC)

The claims are not clear and concise as required by Article 84 EPC:

The feature "solid carbon nanotube salts" found in claim 1 in the final two steps (i.e., steps e) and f)), is not clear (Article 84 EPC). It is not clear what is defined by this term as it is considered vague and unclear and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claim unclear (Article 84 EPC).

Furthermore there is no support for this term in the description. In the description as originally filed on pages 4 and 5, paragraphs 0010 and 0011, the final two steps of the two processes are defined as such:

"separating the solid salts from the liquid and drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure".

The final two steps in claim 2 (steps d) and e)) also define:

"separating the solid salts from the liquid and drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure".

Datum  
Date 29.09.2015  
Date

Blatt  
Sheet 2  
Feuille

Anmelde-Nr:  
Application  
No: 12 731 264.3  
Demande n°:

It is clear from the description and the examples that solid discrete carbon nanotubes with attached lithium salts are separated from the liquid in the second last step.

The examining division suggest the use of the wording "solid discrete carbon nanotubes with attached lithium salts" to replace the terms "solid carbon nanotube salts" and "solid salts" in claims 1 and 2 and the description.

Article 84 EPC requires that the claims be clear not only individually but also as a whole. The broadest claim should be first in the sequence of claims. In this case the broadest claim is claim 3. If the broadest of a number of claims is not placed first, it could be overlooked; the applicant is therefore required either to re-arrange the claims in a more logical way (see the EPC Guidelines F-IV.4.24).

Rule 43(4) EPC requires that any claim which includes all the features of any other claim (dependent claim) shall contain, if possible at the beginning, a reference to the other claim and then state the additional features. In this respect claims 1 and 2 should be made dependent on claim 5 (in which the lithium metal salt with an olivine crystal structure is defined) and the claims renumbered.



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**Substantive Examiner**  
Name: Kelly, Michael  
Tel: +49 89 2399 - 8605

|                                          |                     |                    |
|------------------------------------------|---------------------|--------------------|
| Application No.<br>12 731 264.3 - 1360   | Ref.<br>P100028EP00 | Date<br>29.09.2015 |
| Applicant<br>Molecular Rebar Design, LLC |                     |                    |

#### Communication pursuant to Article 94(3) EPC

The examination of the above-identified application has revealed that it does not meet the requirements of the European Patent Convention for the reasons enclosed herewith. If the deficiencies indicated are not rectified the application may be refused pursuant to Article 97(2) EPC.

You are invited to file your observations and insofar as the deficiencies are such as to be rectifiable, to correct the indicated deficiencies within a period

**of 2 months**

from the notification of this communication, this period being computed in accordance with Rules 126(2) and 131(2) and (4) EPC. One set of amendments to the description, claims and drawings is to be filed within the said period on separate sheets (R. 50(1) EPC).

If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the Examining Division requesting that you correct this deficiency (R. 137(4) EPC).

**Failure to comply with this invitation in due time will result in the application being deemed to be withdrawn (Art. 94(4) EPC).**

Registered letter

EPO Form 2001 12.10CSX



Kelly, Michael  
Primary Examiner  
**For the Examining Division**

Enclosure(s): 2 page/s reasons (Form 2906)



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Attn. Mrs. Claudia Weber

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Your ref.  
Our ref. RvE/E100EPEP

The Hague,  
29 September 2015

Re.: Registration of the Association and change of address

Please exclusively use the registration of our Association V.O. No. 106850 solely for all our cases.

All correspondence is to be headed to :

V.O.  
P.O. Box 87930  
2508 DH Den Haag  
the Netherlands

The professional representative,

A handwritten signature in black ink, appearing to be "C.M. Jansen".

C.M. Jansen

Received at the EPO on Sep 29, 2015 10:59:41. Page 1 of 1



## Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

|                    |                                   |
|--------------------|-----------------------------------|
| Submission number  | 3512280                           |
| Application number | EP12731264.3                      |
| Date of receipt    | 21 May 2015                       |
| Receiving Office   | European Patent Office, The Hague |
| Your reference     | P100028EP00                       |
| Applicant          | All applicants as on file         |

|                     |                                                                                                                                                                                                                                     |                                                                                                                                                                                                                                                       |
|---------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Documents submitted | <div>package-data.xml</div> <div>epf1038.pdf (1 p.)</div> <div>CLMS-HWA-1.pdfP100028EP00<br/>Amended claims with revisions.pdf (3 p.)</div> <div>DESC-HWA-1.pdfP100028EP00<br/>Amended description with revisions.pdf (11 p.)</div> | <div>ep-sfd-request.xml</div> <div>EPLETT-1.pdfP100028EP00 Letter to EPO.pdf (4 p.)</div> <div>CLMS-1.pdfP100028EP00 Amended claims - clean version.pdf (3 p.)</div> <div>DESC-1.pdfP100028EP00 Amended description - clean version.pdf (11 p.)</div> |
|---------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

|                                 |                                                             |
|---------------------------------|-------------------------------------------------------------|
| Submitted by                    | CN=Hermanus Marsman 34472                                   |
| Method of submission            | Online                                                      |
| Date and time receipt generated | 21 May 2015, 12:34 (CEST)                                   |
| Message Digest                  | 24:F7:F1:D5:A7:9C:27:72:84:7D:0F:29:4E:66:83:F8:34:6A:A7:C6 |

### Correction by the EPO of errors in debit instructions filed by eOLF

Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82,

Acknowledgement of receipt - application number EP12731264.3

Page 1 of 2

OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

/European Patent Office/

Acknowledgement of receipt - application number EP12731264.3

Page 2 of 2

## Claims

What is claimed is the following:

1. A process for the production of discrete carbon nanotubes having crystals  
or layers of lithium ion active materials attached to their surface,  
5 comprising the steps of:
  - a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation  
level 1% to 15% ~~percent~~ by weight;
  - b) mixing the carbon nanotubes with a high boiling point liquid;
  - c) adding reagents in correct balance to synthesize a lithium salt;
  - 10 d) reacting the mixture at a temperature to form the lithium salt while  
sonicating the mixture;
  - e) separating the solid discrete carbon nanotube salts from the liquid;  
and
  - f) drying and annealing the solid discrete carbon nanotube salts under  
15 an inert atmosphere at sufficient temperature to obtain an olivine  
crystal structure.
2. A process for the production of discrete carbon nanotubes having crystals  
or layers of lithium ion active materials attached to their surface,  
20 comprising the steps of:
  - a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation  
level of 1% to 15% by weight;
  - b) mixing the carbon nanotubes and a lithium salt in a liquid with  
surfactant;
  - 25 c) sonicating the liquid carbon nanotube/lithium salt mixture;
  - d) separating the solid salts from the liquid; and

- e) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

- 5 3. A composition useful for lithium ion batteries comprising:  
discrete carbon nanotubes, the discrete carbon nanotubes having crystals  
or layers of lithium ion active material attached to their surface, wherein  
the discrete carbon nanotubes have an aspect ratio of 10 to 500 and  
oxidation levels from 1% to 15% by weight of the carbon nanotube.
- 10 4. The composition of claim 3, wherein the crystals or layers of lithium ion  
active material comprise a lithium metal salt and an element selected  
from the group consisting of: iron, manganese, cobalt, copper, nickel,  
vanadium, titanium, and mixtures thereof.
- 15 5. The composition of claim 4, wherein the lithium metal salt has an olivine  
crystal structure.
6. The composition of claim 3, wherein the crystals or layers of lithium ion  
20 active material comprise tin, silicon, copper, antimony, aluminum,  
germanium, titanium, or mixtures thereof.
7. The composition of any one of claims 3-6, further comprising graphene or  
oxygenated graphene.
- 25 8. The composition of claim 7, wherein the weight ratio of graphene to  
carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.
9. The composition of any one of claims 3-8, wherein the carbon nanotubes  
30 are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.

10. The composition of any one of claims 3-9, comprising oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are uniformly dispersed without clustering on a dimension scale less than 1 micrometer.
- 5
11. The composition of any one of claims 3-10, comprising uniformly dispersible oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.
- 10 12. The composition of claim 11, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.

Title: **LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM**

This application claims priority to U.S. Provisional Patent Application Serial No. 61/500,560, entitled "LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM," filed on June 23, 5 | 2011, the entire content of which is hereby incorporated by reference.

**FIELD OF THE INVENTION**

The present invention relates generally to the field of improved technologies for lithium batteries. In some embodiments, the invention relates to discrete carbon nanotubes having crystals or layers of lithium ion active 10 | materials attached to their surface.

**BACKGROUND**

Lithium batteries are used extensively for portable electronic equipment and are increasingly being used to provide electrical back-up for wind and solar energy. The commercially used lithium ion (Li-ion) rechargeable 15 | batteries based on cobalt, nickel or manganese oxides for the cathode materials are known for their poor electrical conductivity and poor electrochemical stability which results in poor cycling (charge/discharge) ability. Olivine structures such as lithium iron phosphate,  $\text{LiFePO}_4$  or lithium manganese phosphate,  $\text{LiMnPO}_4$ , operate at higher charge and discharge rates, but are 20 | still limited by low electrical conductivity and the kinetics of Li-ion diffusion.

Attempts to overcome the above deficiencies have included synthesis of nano-sized crystals, termed nanocrystals, of lithium salts as well as mixtures of lithium salts and carbon nanotubes. Even though the mixtures of carbon nanotubes and nanocrystals of lithium salts show improvements in

charge/discharge rates, the carbon nanotubes previously employed are not considered to be essentially discrete, i.e., individual uniformly dispersed tubes. Carbon nanotubes as conventionally made by gas phase reaction result in a tangled bundle of tubes with particle diameters ranging from 50 to 200

5 micrometers. Also, the lithium nanocrystals are not ionically or covalently attached to the surface of the discrete carbon nanotubes to provide for intimate electron transfer and enhanced mechanical strength of the active material. During charging and discharging of conventional lithium ion batteries, the nanocrystals expand and contract. Over a number of cycles, this leads to  
10 microcrack formation in the layer of active material and hence to higher internal resistance and decline of the battery performance. With crystals bound to and interconnected with discrete carbon nanotubes the microcrack formation due to severe mechanical vibration, bending, or expansion and contraction will be retarded.

15 In WO 2010/117392, exfoliated carbon nanotubes are described which may have an aspect ratio of at least 100. Further, it describes that for some embodiments the carbon nanotubes may be further associated or functionalized with an electroactive material, such as  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

20 US 2011/0104551 teaches a composite material suitable for use in an anode / or a lithium ion battery. Said composite material comprises a layer of a lithium-alloying material on the walls of an aligned nanotubular base material.

Lithium salts have also been carbon coated with very thin coatings on the nanometer scale to enhance inter-particle electrical conductivity, but the carbon coating can slow the lithium ion transport and may also react  
25 unfavorably with electrolytes over time. The carbon coating is considered to be amorphous in structure and is more likely to react with electrolyte than the crystalline carbon structure of the carbon nanotubes. Likewise, carbon particles have been added to the crystals of lithium salts to enhance inter-particle conductivity but these generally reduce the mechanical strength of dried pastes  
30 in the battery leading to cracking and reduced performance over time.

The present invention overcomes the difficulties of low electrical conduction, particularly due to expansion and contraction of the material during charging and discharging of the battery, improved lithium ion transport and mitigation of potentially damaging chemical side reactions by attaching  
5 nanosized crystals or nanosized layers of lithium ion active material to the surface of discrete, functionalized and well dispersed carbon nanotubes.

Likewise, for the lithium battery anode materials, active anode materials, such as carbon particles, tin oxide or silicon, can be attached to the discrete carbon nanotube surfaces to provide numerous benefits such as  
10 improved capacity, electron and ion conductivity and mechanical strength.

In addition to the discrete carbon nanotube network providing support and spatial stabilization of nanosized particles or layers for cathode or anode material of the lithium battery, other benefits include improved heat transfer media to avoid thermally-induced runaway, structural strength to the paste  
15 during manufacturing and high surface area per weight of lithium ion active material to provide good energy density. The uniform dispersion of discrete tubes will also provide a more uniform voltage gradient across the cathode or anode layer, therefore reducing the probability of locally high electrically resistive regions that can cause accelerated decay of performance in that local  
20 region.

### SUMMARY

One aspect of the invention is a composition useful for lithium ion batteries, comprising discrete carbon nanotubes having attached to their  
25 surface lithium ion active materials in the form of nanometer sized crystals or layers; the discrete carbon nanotubes having an aspect ratio of 10 to 500 and oxidation levels from 1% to 15% by weight of the carbon nanotube. For a cathode, the lithium ion active material comprises a lithium metal salt which may further comprise iron, manganese, cobalt, copper, nickel, vanadium,  
30 titanium, or mixtures thereof. The composition can further comprise the

lithium metal salt with an olivine crystal structure. For an anode, the lithium ion active material may comprise carbon, tin, silicon, copper, antimony, aluminum, germanium, titanium or mixtures thereof. The discrete carbon nanotubes of the composition preferably have an aspect ratio of 10 to 500 and oxidation levels from 1 to 15 weight percent of the carbon nanotube. The composition can further comprise graphene or oxygenated graphene. In one embodiment, the weight ratio of graphene to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.

Yet another aspect of this invention is a process for the production of discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers, comprising the steps of:

- a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1 to 15 weight percent,
- b) mixing the carbon nanotubes with a high boiling point liquid, optionally with a non-ionic surfactant,
- c) optionally sonicating the carbon nanotube liquid mixture,
- d) adding reagents in correct balance to synthesize the desired lithium salt,
- e) reacting the mixture at the desired temperature to form the lithium salt while sonicating the mixture,
- f) separating the solid salts from the liquid; and
- g) drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure.

A further aspect of the invention is a process for the production of the discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers, comprising the steps of:

- a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1 to 15 weight percent,
- b) mixing the carbon nanotubes and desired lithium salt in a liquid with surfactant,
- 5 c) sonicating the carbon nanotube/lithium salt liquid mixture,
- d) separating the solid salts from the liquid,
- e) drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure.

10 An additional aspect of this invention is a composition useful for lithium ion batteries comprising discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.

15 Yet another aspect of this invention useful for lithium ion batteries is a composition comprising oxidized carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers wherein the carbon nanotubes are uniformly dispersed without clustering on a dimension scale less than one micrometer.

20 A further aspect of this invention is a composition useful for lithium ion batteries comprising uniformly dispersible oxidized carbon nanotubes having lithium ion active materials attached to their surface, whether ionically or chemically.

## 25 **BRIEF DESCRIPTION OF THE FIGURES**

Figure 1 depicts lithium salt coated as a nanolayer on discrete carbon nanotubes.

Figure 2 shows  $\text{LiMnO}_4$  with 5% oxidized carbon nanotubes of this invention.

Figure 3 shows titanium dioxide crystals attached to discrete carbon nanotubes.

#### DETAILED DESCRIPTION

5       The term “carbon nanotubes” as used herein refers to allotropes of carbon with a cylindrical nanostructure. The nanotubes may be single, double or multiwall.

      The term “discrete carbon nanotubes” as used herein refers to carbon nanotubes capable of being separated to give individual tubes.

10       The term “graphene” as used herein refers to individual atomic thickness plates of carbon.

      The term “oxidized graphene” as used herein refers to the products of oxidizing graphene plates. The oxidized species are generally at the edges of the graphene plates.

15       The term “oxidized carbon nanotubes” as used herein refers to the products of oxidizing the carbon nanotubes. Generally the oxidized species are carboxylic, ketone or hydroxyl functionalities.

      The term “weight percent” or “percent weight” or “% by weight” as used herein is calculated by dividing the weight of a reagent by the total weight of a mixture to which it is added subsequent to the addition of the reagent. For  
20       example, adding 1 gram of a reagent A to 99 grams of a reagent B, thereby forming 100 grams of a mixture A+B would constitute adding 1 weight percent of the reagent A to the mixture.

      During the process of making discrete carbon nanotubes (which can be  
25       single, double and multiwall configurations), the nanotubes are cut into segments and residual catalyst particles that are interior to the carbon nanotubes as received from the manufacturer are dissolved. This cutting of the tubes helps with exfoliation. The cutting of the tubes reduces the length of the tubes into carbon nanotube segments that are defined here as Molecular Rebar.  
30       Proper selection of the carbon nanotube feed stock related to catalyst particle

type and distribution in the carbon nanotubes allows more control over the resulting individual tube lengths and overall tube length distribution. A preferred selection is where the internal catalyst sites are evenly spaced and where the catalyst is most efficient. The selection can be evaluated using  
 5 electron microscopy and determination of the exfoliated tube distribution. Molecular Rebar gives advantageous mechanical and transport properties when added to other materials compared to materials with no Molecular Rebar.

#### **Types of migratable ions and ion active materials**

The ion active material which can be attached to the discrete carbon  
 10 nanotubes is defined here as meaning an ion can migrate into or out of the ion active material thereby exchanging electrons. The migrating ion is preferably lithium ion, and is preferably 50 percent by mole of the available migratable ions, more preferably 75 mole percent or higher, most preferably 95 mole percent or higher and can be as high as 100 mole percent of the total  
 15 migratable ions. Other migratable ions can include magnesium, aluminium, iron, zinc, manganese, sodium, potassium, lead, mercury, silver, gold, nickel, cadmium and the like.

Examples of ion active materials are lithium iron phosphate, lithium  
 manganese phosphate, lithium cobalt oxide, silica, manganese dioxide,  
 20 cadmium, titanium dioxide and carbon.

The ion active materials can be the same or comprise different active materials. Further, ion species in these ion active materials can be the same, or they can be different. When using a mixture of migratable ions, it preferred that the lithium ions comprise the majority of the ions of the mixture.  
 25 Mixtures of migratable ions, when used, can be of 2 different ions, or can be three or more different ions in various proportions. In addition, the ion mixture can be varying valence (or oxidation) states of the same ion, such as  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ .

When mixing ion active materials for attachment to the carbon  
 30 nanotubes, the mixture may be merely accidental, such as that resulting from

either natural states of the ion active material compounds, or the mixture can be an intentional mixing of the different ion active materials, including those in differing chemical or physical state. In some cases comprising migratable ion mixture using lithium ion, the lithium ion may comprise the minority ionic component, of the mix, although this is not usually the preferred configuration. When more than one ion is used, then the ratio of Li ion to other total ions is preferably at least 2:1, or 3:1 or 10:1 and can be as high as 25:1 (mole ratios).

The ion active material attached to the discrete carbon nanotubes can also be useful for applications such as fuel cells, sensors, capacitors, photovoltaics and catalysts.

### Experimental Examples

The following experimental examples are included to demonstrate particular aspects of the present disclosure. It should be appreciated by those of ordinary skill in the art that the methods described in the examples that follow merely represent illustrative embodiments of the disclosure. ~~Those of ordinary skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present disclosure.~~

#### Example 1

##### Discrete carbon nanotubes with attached copper oxide nanoparticles suitable for a lithium ion battery anode material

102 mg of multi-wall carbon nanotubes (CNano, grade C9000) oxidized to about 8 weight percent and aspect ratio about 60 are added to 100 mg copper sulfate, 640 mg sodium EDTA, 15 mg of polyethylene glycol, 568 mg of sodium sulfate and 60 mL of deionized water. The mixture is sonicated for 10 minutes and then heated to 40°C. 3 mL of formaldehyde (37% solution) and 500 mg of sodium hydroxide is added to bring the pH to 12.2. The mixture is stirred for 30 minutes at 85°C and then filtered using a 5 micron PVDF filter and washed with 200 mL of deionized water. The resultant coated multiwall tubes show a

coppery hue color. An electron micrograph shows copper oxide particles of diameter about 50 to 150 nm interconnected by well-dispersed carbon nanotubes.

#### **Example 2**

##### **5        Discrete carbon nanotubes with lithium iron phosphate coated on the surface of the tubes. suitable for a lithium ion battery cathode material**

0.2 grams of multi-wall carbon nanotubes (CNano, grade C9000) oxidized to about 8 weight percent and aspect ratio about 60 are added to 23.5 grams of diethylene glycol and sonicated for 15 minutes. The solution is grey. 1.16 grams of iron acetate dissolved in 4 ml of deionized water is added and the mixture heated under nitrogen, stirring and sonication. After 1 hour at 140°C a solution of 0.65 grams of lithium acetate and 0.74 grams of ammonium phosphate in 4.2 ml of deionized water is added. The temperature is raised to about 185°C over 30 minutes, then held at 185°C for 4 hours. The mixture is cooled to 110°C and sonicated for 5 minutes followed by further cooling to ambient temperature while stirring. The solids are separated from the mixture by centrifugation followed by ethanol washing. The resultant powder is dried to constant weight *in vacuo*.

20        The resultant dried powder is determined to have a resistance of 2,000 ohm-cm compared to a commercially obtained sample determined as 19,000 ohm-cm.

#### **Example 3**

Lithium iron phosphate obtained commercially is ground with multiwall carbon nanotubes (CNano, grade C9000) oxidized to about 8 weight percent and of aspect ratio about 60, in a mortar and pestle at weight ratios of 5:1 and 1:1 lithium salt to carbon nanotube. Sodium dodecyl sulfate (SDS) is then added at a weight ratio of 0.7:1 compared to the carbon nanotube and deionized water added to resultant mixture to give a 0.5 weight percent solution of carbon nanotubes in the presence of lithium salt and surfactant.

The mixture is sonicated for 1 hour, then the solids filtered using a polyvinylidene fluoride filter (0.2 micron), washed with deionized water and dried. A micrograph of the discrete carbon nanotubes coated with lithium iron phosphate is shown in Figure 1. The results of the resistance of the powders are given in Table 1, units of resistance are ohm-cm.

Table 1

| Material               | 5:1 Weight ratio Lithium salt:carbon nanotube | 1:1 Weight ratio Lithium salt:carbon nanotube |
|------------------------|-----------------------------------------------|-----------------------------------------------|
| Dry mix                | 860                                           | 26                                            |
| Coated                 | 46.2                                          | 6.9                                           |
| Improvement of coating | 18.6 X                                        | 3.8X                                          |

#### Example 4

#### Preparation of lithium manganese phosphate in the presence of five percent by weight oxidized carbon nanotubes

37.439g manganese II acetate is dissolved in 5.0ml of water and added to 589mL of diethylene glycol (DEG) already in the reaction vessel. The mixture is then heated to a target temperature of 140°C, under stirring and gentle nitrogen flow to distill off the water. 1.119g of oxidized carbon nanotubes (originally CNano, grade C9000, average diameter 13 nm) nanotubes having an oxidation of 4% and average aspect ratio of 60 are dispersed in 222.2 mL diethylene glycol (0.5% w/v) using sonication while stirring for 30 minutes. Additionally, 14.4434g lithium acetate and 16.4497g ammonium dihydrogen phosphate are dissolved in 90 mL of water. The dispersion of oxidized carbon nanotubes, lithium acetate and ammonium dihydrogen phosphate are added to the reaction medium while stirring, and with sonication. Heating is increased to maintain a target temperature of 180 degrees centigrade for 3 hours, while maintaining constant nitrogen flow.

Following the end of the reaction, heating and sonication are turned off while stirring and nitrogen are maintained as the system cools to room temperature.

The product is a highly viscous, dark-grey colored fluid. The carbon nanotube coated with lithium manganese phosphate is centrifuged and the solids washed with anhydrous ethanol three times. An electron micrograph of the product is shown in Figure 2. In figure 2 the majority of tubes are shown to have coatings of lithium manganese phosphate about 20-40nm thick. The coatings are not smooth as seen in Example 1.

#### **Example 5**

**A composition useful as an anode active material in lithium batteries - *In situ* synthesis of TiO<sub>2</sub>-oxidized carbon nanotube composition from titanium isopropoxide as a precursor**

0.179g of carbon nanotubes (originally CNano, grade C-9000) oxidized to about 4 % by weight and aspect ratio about 60 is added to 27.3ml NMP and 2.7ml RO water and sonicated for 1 hour to obtain a fully exfoliated solution. A 19% v/v solution is prepared by adding 3.41ml of titanium isopropoxide (Sigma-Aldrich) to 18ml of isopropanol (Ultra Pure Solutions, Inc.) and is added dropwise with stirring to the exfoliated carbon nanotube dispersion while under sonication. The reaction vessel is then sealed and gently heated to slightly above room temperature for 1 hour. Sonication and a medium stirring speed are maintained over the entire duration of the reaction. The reaction products are obtained by filtering with a Buchner filter under vacuum, washing with ethanol to remove NMP and drying *in vacuo* to constant weight. An electron micrograph, Figure 3, shows crystals of titanium dioxide of scale 50-100nm bound to discrete well-dispersed carbon nanotubes.

## Claims

What is claimed is the following:

1. A process for the production of discrete carbon nanotubes having crystals  
or layers of lithium ion active materials attached to their surface,  
5 comprising the steps of:
  - a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation  
level 1% to 15% by weight;
  - b) mixing the carbon nanotubes with a high boiling point liquid;
  - c) adding reagents in correct balance to synthesize a lithium salt;
  - 10 d) reacting the mixture at a temperature to form the lithium salt while  
sonicating the mixture;
  - e) separating the solid discrete carbon nanotube salts from the liquid;  
and
  - f) drying and annealing the solid discrete carbon nanotube salts under  
15 an inert atmosphere at sufficient temperature to obtain an olivine  
crystal structure.
2. A process for the production of discrete carbon nanotubes having crystals  
or layers of lithium ion active materials attached to their surface,  
20 comprising the steps of:
  - a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation  
level of 1% to 15% by weight;
  - b) mixing the carbon nanotubes and a lithium salt in a liquid with  
surfactant;
  - 25 c) sonicating the liquid carbon nanotube/lithium salt mixture;
  - d) separating the solid salts from the liquid; and

- e) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

- 5 3. A composition useful for lithium ion batteries comprising:  
discrete carbon nanotubes, the discrete carbon nanotubes having crystals  
or layers of lithium ion active material attached to their surface, wherein  
the discrete carbon nanotubes have an aspect ratio of 10 to 500 and  
oxidation levels from 1% to 15% by weight of the carbon nanotube.
- 10 4. The composition of claim 3, wherein the crystals or layers of lithium ion  
active material comprise a lithium metal salt and an element selected  
from the group consisting of: iron, manganese, cobalt, copper, nickel,  
vanadium, titanium, and mixtures thereof.
- 15 5. The composition of claim 4, wherein the lithium metal salt has an olivine  
crystal structure.
- 20 6. The composition of claim 3, wherein the crystals or layers of lithium ion  
active material comprise tin, silicon, copper, antimony, aluminum,  
germanium, titanium, or mixtures thereof.
- 25 7. The composition of any one of claims 3-6, further comprising graphene or  
oxygenated graphene.
- 8. The composition of claim 7, wherein the weight ratio of graphene to  
carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.
- 30 9. The composition of any one of claims 3-8, wherein the carbon nanotubes  
are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.

10. The composition of any one of claims 3-9, comprising oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are uniformly dispersed without clustering on a dimension scale less than 1 micrometer.
- 5
11. The composition of any one of claims 3-10, comprising uniformly dispersible oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.
- 10 12. The composition of claim 11, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.

Title: **LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM**

This application claims priority to U.S. Provisional Patent Application Serial No. 61/500,560, entitled "LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM," filed on June 23, 5 2011.

**FIELD OF THE INVENTION**

The present invention relates generally to the field of improved technologies for lithium batteries. In some embodiments, the invention relates to discrete carbon nanotubes having crystals or layers of lithium ion active 10 materials attached to their surface.

**BACKGROUND**

Lithium batteries are used extensively for portable electronic equipment and are increasingly being used to provide electrical back-up for wind and solar energy. The commercially used lithium ion (Li-ion) rechargeable 15 batteries based on cobalt, nickel or manganese oxides for the cathode materials are known for their poor electrical conductivity and poor electrochemical stability which results in poor cycling (charge/discharge) ability. Olivine structures such as lithium iron phosphate,  $\text{LiFePO}_4$  or lithium manganese phosphate,  $\text{LiMnPO}_4$ , operate at higher charge and discharge rates, but are 20 still limited by low electrical conductivity and the kinetics of Li-ion diffusion.

Attempts to overcome the above deficiencies have included synthesis of nano-sized crystals, termed nanocrystals, of lithium salts as well as mixtures of lithium salts and carbon nanotubes. Even though the mixtures of carbon nanotubes and nanocrystals of lithium salts show improvements in

charge/discharge rates, the carbon nanotubes previously employed are not considered to be essentially discrete, i.e., individual uniformly dispersed tubes. Carbon nanotubes as conventionally made by gas phase reaction result in a tangled bundle of tubes with particle diameters ranging from 50 to 200

5 micrometers. Also, the lithium nanocrystals are not ionically or covalently attached to the surface of the discrete carbon nanotubes to provide for intimate electron transfer and enhanced mechanical strength of the active material. During charging and discharging of conventional lithium ion batteries, the nanocrystals expand and contract. Over a number of cycles, this leads to  
10 microcrack formation in the layer of active material and hence to higher internal resistance and decline of the battery performance. With crystals bound to and interconnected with discrete carbon nanotubes the microcrack formation due to severe mechanical vibration, bending, or expansion and contraction will be retarded.

15 In WO 2010/117392, exfoliated carbon nanotubes are described which may have an aspect ratio of at least 100. Further, it describes that for some embodiments the carbon nanotubes may be further associated or functionalized with an electroactive material, such as  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

US 2011/0104551 teaches a composite material suitable for use in an  
20 anode / or a lithium ion battery. Said composite material comprises a layer of a lithium-alloying material on the walls of an aligned nanotubular base material.

Lithium salts have also been carbon coated with very thin coatings on the nanometer scale to enhance inter-particle electrical conductivity, but the carbon coating can slow the lithium ion transport and may also react  
25 unfavorably with electrolytes over time. The carbon coating is considered to be amorphous in structure and is more likely to react with electrolyte than the crystalline carbon structure of the carbon nanotubes. Likewise, carbon particles have been added to the crystals of lithium salts to enhance inter-particle conductivity but these generally reduce the mechanical strength of dried pastes  
30 in the battery leading to cracking and reduced performance over time.

The present invention overcomes the difficulties of low electrical conduction, particularly due to expansion and contraction of the material during charging and discharging of the battery, improved lithium ion transport and mitigation of potentially damaging chemical side reactions by attaching  
5 nanosized crystals or nanosized layers of lithium ion active material to the surface of discrete, functionalized and well dispersed carbon nanotubes.

Likewise, for the lithium battery anode materials, active anode materials, such as carbon particles, tin oxide or silicon, can be attached to the discrete carbon nanotube surfaces to provide numerous benefits such as  
10 improved capacity, electron and ion conductivity and mechanical strength.

In addition to the discrete carbon nanotube network providing support and spatial stabilization of nanosized particles or layers for cathode or anode material of the lithium battery, other benefits include improved heat transfer media to avoid thermally-induced runaway, structural strength to the paste  
15 during manufacturing and high surface area per weight of lithium ion active material to provide good energy density. The uniform dispersion of discrete tubes will also provide a more uniform voltage gradient across the cathode or anode layer, therefore reducing the probability of locally high electrically resistive regions that can cause accelerated decay of performance in that local  
20 region.

### SUMMARY

One aspect of the invention is a composition useful for lithium ion batteries, comprising discrete carbon nanotubes having attached to their  
25 surface lithium ion active materials in the form of nanometer sized crystals or layers; the discrete carbon nanotubes having an aspect ratio of 10 to 500 and oxidation levels from 1% to 15% by weight of the carbon nanotube. For a cathode, the lithium ion active material comprises a lithium metal salt which may further comprise iron, manganese, cobalt, copper, nickel, vanadium,  
30 titanium, or mixtures thereof. The composition can further comprise the

lithium metal salt with an olivine crystal structure. For an anode, the lithium ion active material may comprise carbon, tin, silicon, copper, antimony, aluminum, germanium, titanium or mixtures thereof. The discrete carbon nanotubes of the composition have an aspect ratio of 10 to 500 and oxidation  
 5 levels from 1 to 15 weight percent of the carbon nanotube. The composition can further comprise graphene or oxygenated graphene. In one embodiment, the weight ratio of graphene to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.

Yet another aspect of this invention is a process for the production of  
 10 discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers, comprising the steps of:

- a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1 to 15 weight percent,
- 15 b) mixing the carbon nanotubes with a high boiling point liquid, optionally with a non-ionic surfactant,
- c) optionally sonicating the carbon nanotube liquid mixture,
- d) adding reagents in correct balance to synthesize the desired lithium salt,
- 20 e) reacting the mixture at the desired temperature to form the lithium salt while sonicating the mixture,
- f) separating the solid salts from the liquid; and
- g) drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient  
 25 temperature to obtain the olivine crystal structure.

A further aspect of the invention is a process for the production of the discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers, comprising the steps of:

- a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1 to 15 weight percent,
- b) mixing the carbon nanotubes and desired lithium salt in a liquid with surfactant,
- 5 c) sonicating the carbon nanotube/lithium salt liquid mixture,
- d) separating the solid salts from the liquid,
- e) drying and annealing under an inert atmosphere the solid discrete carbon nanotubes with attached lithium salts at sufficient temperature to obtain the olivine crystal structure.

10 An additional aspect of this invention is a composition useful for lithium ion batteries comprising discrete carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.

15 Yet another aspect of this invention useful for lithium ion batteries is a composition comprising oxidized carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers wherein the carbon nanotubes are uniformly dispersed without clustering on a dimension scale less than one micrometer.

20 A further aspect of this invention is a composition useful for lithium ion batteries comprising uniformly dispersible oxidized carbon nanotubes having lithium ion active materials attached to their surface, whether ionically or chemically.

## 25 **BRIEF DESCRIPTION OF THE FIGURES**

Figure 1 depicts lithium salt coated as a nanolayer on discrete carbon nanotubes.

Figure 2 shows  $\text{LiMnO}_4$  with 5% oxidized carbon nanotubes of this invention.

Figure 3 shows titanium dioxide crystals attached to discrete carbon nanotubes.

#### DETAILED DESCRIPTION

5       The term “carbon nanotubes” as used herein refers to allotropes of carbon with a cylindrical nanostructure. The nanotubes may be single, double or multiwall.

      The term “discrete carbon nanotubes” as used herein refers to carbon nanotubes capable of being separated to give individual tubes.

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      The term “weight percent” or “percent weight” or “% by weight” as used herein is calculated by dividing the weight of a reagent by the total weight of a mixture to which it is added subsequent to the addition of the reagent. For  
20       example, adding 1 gram of a reagent A to 99 grams of a reagent B, thereby forming 100 grams of a mixture A+B would constitute adding 1 weight percent of the reagent A to the mixture.

      During the process of making discrete carbon nanotubes (which can be  
25       single, double and multiwall configurations), the nanotubes are cut into segments and residual catalyst particles that are interior to the carbon nanotubes as received from the manufacturer are dissolved. This cutting of the tubes helps with exfoliation. The cutting of the tubes reduces the length of the tubes into carbon nanotube segments that are defined here as Molecular Rebar.  
30       Proper selection of the carbon nanotube feed stock related to catalyst particle

type and distribution in the carbon nanotubes allows more control over the resulting individual tube lengths and overall tube length distribution. A preferred selection is where the internal catalyst sites are evenly spaced and where the catalyst is most efficient. The selection can be evaluated using  
 5 electron microscopy and determination of the exfoliated tube distribution. Molecular Rebar gives advantageous mechanical and transport properties when added to other materials compared to materials with no Molecular Rebar.

#### **Types of migratable ions and ion active materials**

The ion active material which can be attached to the discrete carbon  
 10 nanotubes is defined here as meaning an ion can migrate into or out of the ion active material thereby exchanging electrons. The migrating ion is preferably lithium ion, and is preferably 50 percent by mole of the available migratable ions, more preferably 75 mole percent or higher, most preferably 95 mole percent or higher and can be as high as 100 mole percent of the total  
 15 migratable ions. Other migratable ions can include magnesium, aluminium, iron, zinc, manganese, sodium, potassium, lead, mercury, silver, gold, nickel, cadmium and the like.

Examples of ion active materials are lithium iron phosphate, lithium  
 manganese phosphate, lithium cobalt oxide, silica, manganese dioxide,  
 20 cadmium, titanium dioxide and carbon.

The ion active materials can be the same or comprise different active materials. Further, ion species in these ion active materials can be the same, or they can be different. When using a mixture of migratable ions, it preferred that the lithium ions comprise the majority of the ions of the mixture.  
 25 Mixtures of migratable ions, when used, can be of 2 different ions, or can be three or more different ions in various proportions. In addition, the ion mixture can be varying valence (or oxidation) states of the same ion, such as  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ .

When mixing ion active materials for attachment to the carbon  
 30 nanotubes, the mixture may be merely accidental, such as that resulting from

either natural states of the ion active material compounds, or the mixture can be an intentional mixing of the different ion active materials, including those in differing chemical or physical state. In some cases comprising migratable ion mixture using lithium ion, the lithium ion may comprise the minority ionic  
 5 component, of the mix, although this is not usually the preferred configuration. When more than one ion is used, then the ratio of Li ion to other total ions is preferably at least 2:1, or 3:1 or 10:1 and can be as high as 25:1 (mole ratios).

The ion active material attached to the discrete carbon nanotubes can also be useful for applications such as fuel cells, sensors, capacitors,  
 10 photovoltaics and catalysts.

### **Experimental Examples**

The following experimental examples are included to demonstrate particular aspects of the present disclosure. It should be appreciated by those of ordinary skill in the art that the methods described in the examples that follow  
 15 merely represent illustrative embodiments of the disclosure.

#### **Example 1**

##### **Discrete carbon nanotubes with attached copper oxide nanoparticles suitable for a lithium ion battery anode material**

102 mg of multi-wall carbon nanotubes (CNano, grade C9000) oxidized  
 20 to about 8 weight percent and aspect ratio about 60 are added to 100 mg copper sulfate, 640 mg sodium EDTA, 15 mg of polyethylene glycol, 568 mg of sodium sulfate and 60 mL of deionized water. The mixture is sonicated for 10 minutes and then heated to 40°C. 3 mL of formaldehyde (37% solution) and 500 mg of sodium hydroxide is added to bring the pH to 12.2. The mixture is stirred for  
 25 30 minutes at 85°C and then filtered using a 5 micron PVDF filter and washed with 200 mL of deionized water. The resultant coated multiwall tubes show a coppery hue color. An electron micrograph shows copper oxide particles of diameter about 50 to 150 nm interconnected by well-dispersed carbon nanotubes.

**Example 2**

**Discrete carbon nanotubes with lithium iron phosphate coated on the surface of the tubes, suitable for a lithium ion battery cathode material**

5           0.2 grams of multi-wall carbon nanotubes (CNano, grade C9000) oxidized to about 8 weight percent and aspect ratio about 60 are added to 23.5 grams of diethylene glycol and sonicated for 15 minutes. The solution is grey. 1.16 grams of iron acetate dissolved in 4 ml of deionized water is added and the mixture heated under nitrogen, stirring and sonication. After 1 hour at 140°C  
10 a solution of 0.65 grams of lithium acetate and 0.74 grams of ammonium phosphate in 4.2 ml of deionized water is added. The temperature is raised to about 185°C over 30 minutes, then held at 185°C for 4 hours. The mixture is cooled to 110°C and sonicated for 5 minutes followed by further cooling to ambient temperature while stirring. The solids are separated from the mixture  
15 by centrifugation followed by ethanol washing. The resultant powder is dried to constant weight *in vacuo*.

The resultant dried powder is determined to have a resistance of 2,000 ohm-cm compared to a commercially obtained sample determined as 19,000 ohm-cm.

20           **Example 3**

Lithium iron phosphate obtained commercially is ground with multiwall carbon nanotubes (CNano, grade C9000) oxidized to about 8 weight percent and of aspect ratio about 60, in a mortar and pestle at weight ratios of 5:1 and 1:1 lithium salt to carbon nanotube. Sodium dodecyl sulfate (SDS) is  
25 then added at a weight ratio of 0.7:1 compared to the carbon nanotube and deionized water added to resultant mixture to give a 0.5 weight percent solution of carbon nanotubes in the presence of lithium salt and surfactant. The mixture is sonicated for 1 hour, then the solids filtered using a polyvinylidene fluoride filter (0.2 micron), washed with deionized water and  
30 dried. A micrograph of the discrete carbon nanotubes coated with lithium iron

phosphate is shown in Figure 1. The results of the resistance of the powders are given in Table 1, units of resistance are ohm-cm.

Table 1

| Material               | 5:1 Weight ratio Lithium salt:carbon nanotube | 1:1 Weight ratio Lithium salt:carbon nanotube |
|------------------------|-----------------------------------------------|-----------------------------------------------|
| Dry mix                | 860                                           | 26                                            |
| Coated                 | 46.2                                          | 6.9                                           |
| Improvement of coating | 18.6 X                                        | 3.8X                                          |

5

#### Example 4

##### **Preparation of lithium manganese phosphate in the presence of five percent by weight oxidized carbon nanotubes**

37.439g manganese II acetate is dissolved in 5.0ml of water and added to 589mL of diethylene glycol (DEG) already in the reaction vessel. The mixture is then heated to a target temperature of 140°C, under stirring and gentle nitrogen flow to distill off the water. 1.119g of oxidized carbon nanotubes (originally CNano, grade C9000, average diameter 13 nm) nanotubes having an oxidation of 4% and average aspect ratio of 60 are dispersed in 222.2 mL diethylene glycol (0.5% w/v) using sonication while stirring for 30 minutes. Additionally, 14.4434g lithium acetate and 16.4497g and ammonium dihydrogen phosphate are dissolved in 90 mL of water. The dispersion of oxidized carbon nanotubes, lithium acetate and ammonium dihydrogen phosphate are added to the reaction medium while stirring, and with sonication. Heating is increased to maintain a target temperature of 180 degrees centigrade for 3 hours, while maintaining constant nitrogen flow. Following the end of the reaction, heating and sonication are turned off while stirring and nitrogen are maintained as the system cools to room temperature.

10

15

20

The product is a highly viscous, dark-grey colored fluid. The carbon nanotube coated with lithium manganese phosphate is centrifuged and the solids washed with anhydrous ethanol three times. An electron micrograph of the product is shown in Figure 2. In figure 2 the majority of tubes are shown to have coatings of lithium manganese phosphate about 20-40nm thick. The coatings are not smooth as seen in Example 1.

#### **Example 5**

**A composition useful as an anode active material in lithium batteries - *In situ* synthesis of TiO<sub>2</sub>-oxidized carbon nanotube composition from titanium isopropoxide as a precursor**

0.179g of carbon nanotubes (originally CNano, grade C-9000) oxidized to about 4 % by weight and aspect ratio about 60 is added to 27.3ml NMP and 2.7ml RO water and sonicated for 1 hour to obtain a fully exfoliated solution. A 19% v/v solution is prepared by adding 3.41ml of titanium isopropoxide (Sigma-Aldrich) to 18ml of isopropanol (Ultra Pure Solutions, Inc.) and is added dropwise with stirring to the exfoliated carbon nanotube dispersion while under sonication. The reaction vessel is then sealed and gently heated to slightly above room temperature for 1 hour. Sonication and a medium stirring speed are maintained over the entire duration of the reaction. The reaction products are obtained by filtering with a Buchner filter under vacuum, washing with ethanol to remove NMP and drying *in vacuo* to constant weight. An electron micrograph, Figure 3, shows crystals of titanium dioxide of scale 50-100nm bound to discrete well-dispersed carbon nanotubes.



## Letter accompanying subsequently filed items

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The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number

12731264.3

Applicant's or representative's reference

P100028EP00

|   | Description of document                                 | Original file name                                  | Assigned file name |
|---|---------------------------------------------------------|-----------------------------------------------------|--------------------|
| 1 | Letter relating to the search and examination procedure | P100028EP00 Letter to EPO.pdf                       | EPLETT-1.pdf       |
| 2 | Amended claims with annotations                         | P100028EP00 Amended claims with revisions.pdf       | CLMS-HWA-1.pdf     |
| 3 | Amended claims (clean copy)                             | P100028EP00 Amended claims - clean version.pdf      | CLMS-1.pdf         |
| 4 | Amended description with annotations                    | P100028EP00 Amended description with revisions.pdf  | DESC-HWA-1.pdf     |
| 5 | Amended description (clean copy)                        | P100028EP00 Amended description - clean version.pdf | DESC-1.pdf         |

### Annotations

deposit-account(V.O.; 21.05.2015)

1. Remark(Annotate)

I herewith authorize the European Patent Office to deduct all necessary fees that are involved in this specific action from my deposit-account No. 2809.0002

### Signatures

Place: Den Haag  
Date: 21 May 2015  
Signed by: /H.A.M. Marsman/  
Representative name: C.M. JANSEN  
Capacity: (Representative)

P100028EP00

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Your ref. 12731264.3/1360  
Our ref. MAS/P100028EP00

The Hague,  
May 21, 2015

Re: European patent application No. 12731264.3  
Molecular Rebar Design, LLC

In response to your Communication dated January 19, 2015, I observe as follows.

Unity of invention

The objection of lack of unity is not justified. Claims 1-3 have the following features in  
5 common (wording included in each of claims 1-3):

- discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface
- carbon nanotubes having an aspect ratio of 10 to 500 and oxidation levels from 1% to 15% by weight.

10 This combination of features is neither taught nor suggested in the prior art, as was established during the international phase of the PCT application.

Present claims 1 and 2 have basis in claims 8 and 9 of the application as filed and  
15 include the feature of “an olivine crystal structure”. This cannot be prejudicial to unity of invention. This merely relates to specific embodiments that also for another reason

than for the features common in claims 3 and 1 and 2 meet the requirements of novelty and inventive step.

Clarity

- 5 Claim 3 specifies that “the discrete carbon nanotubes have [...] oxidation levels from 1% to 15% by weight of the carbon nanotube”.

This feature has support in §[0003] of the application as filed, which contains exactly this wording.

10

The feature is clear as such. Oxidizing carbon nanotubes to a desired level is something within the scope of the skilled person.

- 15 Claim 3 specifies a lower limit of the oxidation level of 1%. This addresses any concern based on our letter dated September 10, 2013.

Claim 3 further specifies “the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface”.

- 20 You seem to consider that some allegedly essential features are omitted from claim 3. This seems to be based on a misunderstanding.

Claim 3 includes all features which are stated in the description to be essential.

- 25 Based on your reference to “educt”, it seems that you expect that after the discrete carbon nanotubes are oxidized (to a particular level), this degree of oxidation of the tubes will be disturbed or changed by the attachment of crystals or layers of lithium ion active material.

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Date May 21, 2015



This is not the case.

The number of oxygen atoms directly coupled to the carbon nanotube via a covalent bond will not be changed by association with lithium compounds. Perhaps carboxylic acids could be converted to lithium carboxylate but that does not affect the degree of oxidation of the tubes nor the covalent attachment of oxygen.

#### Claim amendments

I attach a set of amended claims (in a version showing revisions and in retyped form) wherein the superfluous term "percent" is deleted from claim 1, and a typographical error is corrected in claim 8. Your guidance in this respect is appreciated.

Moreover, I enclose a description (in a form showing revisions and in retyped form) which is brought into conformity with the claims, wherein the requested changes have been made; and which is brought in accordance with European patent practice.

#### Conclusion

Based on the above, I believe that the enclosed set of amended claims and the amended description meet the formal and material requirements of the EPC. Your communication under R (71(3) EPC is hence awaited.

Should however some objections remain, it is requested that you issue another communication or contact me by phone at +31 73 548 20 70.

Page 4  
Your ref. 12731264.3/1360  
Our ref. MAS/P100028EP00  
Date May 21, 2015



In the (unexpected) case the Examining Division would intend to refuse the present application, Oral Proceedings in accordance with Article 116 EPC are requested.

The professional representative,

A handwritten signature in black ink, consisting of several overlapping, fluid strokes.

H.A.M. Marsman

Encl.: - amended claims (with revisions and clean version)  
- amended description (with revisions and clean version)

EK

Datum  
Date 19.01.2015  
Date

Blatt  
Sheet 1  
Feuille

Anmelde-Nr:  
Application  
No: 12 731 264.3  
Demande n°:

The examination is being carried out on the **following application documents**

**Description, Pages**

1-12 as published

**Claims, Numbers**

1-12 as annexed to the Int. Prel. Examination Report

**Drawings, Sheets**

1/3-3/3 as published

Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure.

D1 WO 2010/117392 A1 (BOSNYAK CLIVE P [US]; SWOGGER KURT W [US]) 14 October 2010 (2010-10-14)

D2 US 2011/104551 A1 (YANG JUNBING [US] ET AL) 5 May 2011 (2011-05-05)

**Non unity (Article 83 EPC)**

The application lacks unity within the meaning of Article 82 EPC as the following inventions are not so linked as to form a single general inventive concept:

Invention 1 (Claims 1 and 2): A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:  
selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% percent by weight; mixing the carbon nanotubes with a lithium salt or with reagents to synthesize a lithium salt; sonicating the liquid carbon nanotube/lithium salt mixture; separating the solid discrete carbon nanotube salts from the liquid; and drying and annealing the solid discrete carbon nanotube salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

Datum  
Date 19.01.2015  
Date

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Sheet 2  
Feuille

Anmelde-Nr:  
Application  
No: 12 731 264.3  
Demande n°:

Invention 2 (Claims 3-12): A composition comprising discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface, wherein the discrete carbon nanotubes have an aspect ratio of 10 to 500 and oxidation levels from 1% to 15% by weight of the carbon nanotube.

The inventions are not linked through the same or corresponding special technical feature (Rule 44 EPC) and define 2 different inventions not linked as to form a single general inventive concept (Article 82 EPC):

Independent claims 1-2 (Invention 1) are defined by the special technical feature of obtaining of a lithium ion salt with an olivine crystal structure. This feature is not present in claim 3.

Based on the description the problem to be solved by the subject matter of claims 1 and 2 is to provide an improved lithium ion battery cathode material (see paragraphs 0005-0006 and 0009).

Independent claim 3 (Invention 2) is defined by the special technical feature of crystals or layers of lithium ion active material attached to the surface of the nanotubes. There is no restriction of the lithium ion active material or structure (i.e. no restriction to lithium salt or olivine).

Based on the description the problem to be solved by the subject matter of claims 1 and 2 is to provide an improved electrode (cathode or anode) material (see paragraphs 0005-0007 and 0009). Note that "lithium ion active material" in claim 3 does not limit the material to lithium ion batteries, it is merely suitable for such.

The independent claims are therefore not linked by a single general inventive concept and the application therefore does not fulfill the requirements of unity of invention as prescribed in Article 82 EPC.

#### **Clarity (Article 84 EPC)**

Claim 3 refers to a product (composition useful for lithium ion batteries) which is characterised by the a feature of the educt (discrete carbon nanotubes with oxidation levels of 1% to 15% percent by weight). There is no support in the description to

Datum  
Date 19.01.2015  
Date

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Sheet 3  
Feuille

Anmelde-Nr:  
Application  
No: 12 731 264.3  
Demande n°:

indicate that the product comprises discrete carbon nanotubes with oxidation levels of 1% to 15% percent by weight, in fact the skilled person would expect these to change during the production process. The subject matter of claim 3, and claims dependent on it, is therefore not clear (Article 84 EPC).

Furthermore, as pointed out in additionally filed evidence filed with the applicants letter dated 10.09.2013, "the level of oxidation allows control of the degree of binding of the crystals" and "at oxidation levels below 1%, the degree of attachment of nanocrystals is very low".

This shows that the the attachment of nanocrystals of lithium ion active material to the surface of the discrete carbon nanotubes is an essential feature to the invention.

Since independent claim 3 does not contain this feature it does not meet the requirement following from Article 84 EPC, taken in combination with Rule 43(1) and (3) EPC, that any independent claim must contain all the technical features essential to the definition of the invention.

The expression "hereby incorporated by reference" on page 1 should be deleted (see the Guidelines F.III, 8).

The vague and imprecise statement in the description on page 9 implies that the subject-matter for which protection is sought may be different to that defined by the claims, thereby resulting in a lack of clarity of the claims (Article 84 EPC) when the description is used to interpret the claims (see Guidelines F-IV, 4.4). This statement should therefore be amended to remove this inconsistency.

The word "grapheme" on page 4 and in claim 8 should be corrected to "graphene".

The word "percent" in claim 1 is superfluous and should be deleted.

**Furthermore:**

To meet the requirements of Rule 42(1)(b) EPC, D1 and D2 should be identified in the description and the relevant background art disclosed therein should be briefly discussed.



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|                                          |                     |                    |
|------------------------------------------|---------------------|--------------------|
| Application No.<br>12 731 264.3 - 1360   | Ref.<br>P100028EP00 | Date<br>19.01.2015 |
| Applicant<br>Molecular Rebar Design, LLC |                     |                    |

#### Communication pursuant to Article 94(3) EPC

The examination of the above-identified application has revealed that it does not meet the requirements of the European Patent Convention for the reasons enclosed herewith. If the deficiencies indicated are not rectified the application may be refused pursuant to Article 97(2) EPC.

You are invited to file your observations and insofar as the deficiencies are such as to be rectifiable, to correct the indicated deficiencies within a period

**of 4 months**

from the notification of this communication, this period being computed in accordance with Rules 126(2) and 131(2) and (4) EPC. One set of amendments to the description, claims and drawings is to be filed within the said period on separate sheets (R. 50(1) EPC).

If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the Examining Division requesting that you correct this deficiency (R. 137(4) EPC).

**Failure to comply with this invitation in due time will result in the application being deemed to be withdrawn (Art. 94(4) EPC).**

Registered letter

EPO Form 2001 12.10CSX



Kelly, Michael  
Primary Examiner  
**For the Examining Division**

Enclosure(s): 3 page/s reasons (Form 2906)



Application No.: 12731264.3

Substantive examination has started on 17.10.14 (see Notice from the European Patent Office dated 29.01.2013, OJ EPO 2013, 153).

**For the Examining Division**



## Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

|                                 |                                                             |                                                                                      |
|---------------------------------|-------------------------------------------------------------|--------------------------------------------------------------------------------------|
| Submission number               | 3042817                                                     |                                                                                      |
| Application number              | EP12731264.3                                                |                                                                                      |
| Date of receipt                 | 06 October 2014                                             |                                                                                      |
| Receiving Office                | European Patent Office, The Hague                           |                                                                                      |
| Your reference                  | P100028EP00                                                 |                                                                                      |
| Applicant                       | All applicants as on file                                   |                                                                                      |
| Documents submitted             | package-data.xml<br><br>epf1038.pdf (1 p.)                  | ep-sfd-request.xml<br><br>EPLETT-1.pdf\P100028EP00 L to epo<br>06-10-2014.pdf (1 p.) |
| Submitted by                    | CN=Cornelis Box 34457                                       |                                                                                      |
| Method of submission            | Online                                                      |                                                                                      |
| Date and time receipt generated | 06 October 2014, 16:14 (CEST)                               |                                                                                      |
| Message Digest                  | 1D:FA:88:E2:E3:29:DF:30:B2:B0:65:B4:DD:D9:26:43:C8:18:72:BD |                                                                                      |

### Correction by the EPO of errors in debit instructions filed by eOLF

Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

/European Patent Office/



## Letter accompanying subsequently filed items

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The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number

12731264.3

Applicant's or representative's reference

P100028EP00

|   | Description of document                                 | Original file name                  | Assigned file name |
|---|---------------------------------------------------------|-------------------------------------|--------------------|
| 1 | Letter relating to the search and examination procedure | P100028EP00 L to epo 06-10-2014.pdf | EPLETT-1.pdf       |

### Annotations

deposit-account(V.O.; 06.10.2014)

1. Remark(Annotate)

I herewith authorize the European Patent Office to deduct all necessary fees that are involved in this specific action from my deposit-account  
No. 2809.0002

### Signatures

Place: Den Bosch  
Date: 06 October 2014  
Signed by: /H.A.M. Marsman/  
Capacity: (Representative)

P100028EP00



## Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

|                                 |                                                             |                                                                            |
|---------------------------------|-------------------------------------------------------------|----------------------------------------------------------------------------|
| Submission number               | 2834869                                                     |                                                                            |
| Application number              | EP12731264.3                                                |                                                                            |
| Date of receipt                 | 20 June 2014                                                |                                                                            |
| Receiving Office                | European Patent Office, The Hague                           |                                                                            |
| Your reference                  | P100028EP00                                                 |                                                                            |
| Applicant                       | All applicants as on file                                   |                                                                            |
| Documents submitted             | package-data.xml<br><br>epf1038.pdf (1 p.)                  | ep-sfd-request.xml<br><br>EPLETT-1.pdfP100028EP00 Letter to EPO.pdf (1 p.) |
| Submitted by                    | CN=Hermanus Marsman 34472                                   |                                                                            |
| Method of submission            | Online                                                      |                                                                            |
| Date and time receipt generated | 20 June 2014, 10:46 (CEST)                                  |                                                                            |
| Message Digest                  | F6:27:81:B7:3F:E5:82:FC:69:72:DD:D5:A8:3B:2E:8B:1B:C7:19:B8 |                                                                            |

### Correction by the EPO of errors in debit instructions filed by eOLF

Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

/European Patent Office/



## Letter accompanying subsequently filed items

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The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number

12731264.3

Applicant's or representative's reference

P100028EP00

|   | Description of document                                 | Original file name            | Assigned file name |
|---|---------------------------------------------------------|-------------------------------|--------------------|
| 1 | Letter relating to the search and examination procedure | P100028EP00 Letter to EPO.pdf | EPLETT-1.pdf       |

### Annotations

deposit-account(V.O.; 19.06.2014)

1. Remark(Annotate)

I herewith authorize the European Patent Office to deduct all necessary fees that are involved in this specific action from my deposit-account  
No. 2809.0002

### Signatures

Place: Den Bosch  
Date: 20 June 2014  
Signed by: /H.A.M. Marsman/  
Capacity: (Representative)

P100028EP00

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Your ref. 12731264.3/1359  
Our ref. MAS/P100028EP00

The Hague,  
June 20, 2014

Re: European patent application No. 12731264.3  
Molecular Rebar Design, LLC

---

In response to your Communication dated January 31, 2014, I request that the  
substantive examination is based on the pending claims.

The professional representative,



H.A.M. Marsman

EK



European Patent Office  
80298 MUNICH  
GERMANY

Questions about this communication ?  
Contact Customer Services at [www.epo.org/contact](http://www.epo.org/contact)



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V.O.  
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Date  
02.04.14

|                                                     |                                                           |
|-----------------------------------------------------|-----------------------------------------------------------|
| Reference<br>P100028EP00                            | Application No./Patent No.<br>12731264.3 - 1359 / 2724403 |
| Applicant/Proprietor<br>Molecular Rebar Design, LLC |                                                           |

**Communication of European publication number and information on the application of Article 67(3) EPC**

The provisional protection under Article 67(1) and (2) EPC in the individual Contracting States becomes effective only when the conditions referred to in Article 67(3) EPC have been fulfilled (for further details, see information brochure of the European Patent Office "National Law relating to the EPC" and additional information in the Official Journal of the European Patent Office).

Pursuant to Article 153(3) EPC the publication under Article 21 PCT of an international application for which the European Patent Office is a designated or elected Office takes the place of the publication of a European patent application.

The bibliographic data of the above-mentioned Euro-PCT application will be published on 30.04.14 in Section I.1 of the European Patent Bulletin. The European publication number is 2724403.

In all future communications to the European Patent Office, please quote the application number plus Directorate number.

**For the Examining Division**





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For any questions about  
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Date  
31.01.14

|                                                     |                                                 |
|-----------------------------------------------------|-------------------------------------------------|
| Reference<br>P100028EP00                            | Application No./Patent No.<br>12731264.3 - 1359 |
| Applicant/Proprietor<br>Molecular Rebar Design, LLC |                                                 |

## Communication pursuant to Rules 161(1) and 162 EPC

### 1. Comments on the written opinion and amendment of the application (R. 161(1) EPC)

The above-mentioned international (Euro-PCT) application has entered the European phase.

The EPO as International Searching Authority and, where a demand under Article 31 PCT was filed, also as International Preliminary Examining Authority has drawn up a written opinion on this application or the EPO as Supplementary International Searching Authority has issued explanations pursuant to Rule 45bis.7(e) PCT to the supplementary international search report.

In accordance with Rule 161(1) EPC, you may comment on the written opinion or on the explanations to the supplementary international search report within a **non-extendable period of six months** after notification of the present communication.

Under Articles 28, 41 PCT and Rules 52, 78 PCT the application may be amended before a designated or elected Office, and in accordance with Rule 137(2) EPC the applicant may amend the description, claims and drawings of his own volition together with any comments, corrections or amendments made in response to the communication under Rule 161(1) EPC.

Whether or not you have already done so, you now have a further opportunity to file amended claims or other application documents within the above-mentioned period.

**Please note that under Rule 137(2) and (3) EPC as in force from 1 April 2010, you may amend the description, claims and drawings of your own volition in response to this communication, if the international search report has been drawn up on or after 1 April 2010 or the EPO has issued a supplementary international search report. In these cases no further amendments may be made without the consent of the Examining Division. This may be in particular relevant if you have already filed comments/amendments with respect to a written opinion of the International Searching Authority or an international preliminary examination report, or to any explanations pursuant to Rule 45bis.7(e) PCT to the supplementary international search report, which however do not address the deficiencies noted therein and you choose not to react to the present communication.**

If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the Examining Division requesting that you correct this deficiency (R. 137(4) EPC).

The claims applicable on expiry of this period, i.e. those filed on entry into the European phase or in response to the present communication, will form the basis for the calculation of any claims fee to be paid (see p. 2).

## 2. Claims fees under Rule 162 EPC

If the application documents on which the European grant procedure is to be based comprise more than fifteen claims, a claims fee shall be payable for the sixteenth and each subsequent claim within the period provided for in Rule 159(1) EPC.

- ☒ Based on the application documents currently on file, all necessary claims fees have already been paid (or the documents do not comprise more than 15 claims).
- ☐ All necessary fees will be/have been debited automatically according to the automatic debit order.
- ☐ The claims fees due for the claims ..... to ..... were not paid within the above-mentioned period.

Any outstanding claims fee, either based on the current set of claims or on any amended claims to be filed pursuant to Rule 161 EPC (see page 1), may still be validly paid within a **non-extendable period of six months** after notification of this communication (R. 162(2) EPC).

If a payment is made for only some of the claims, you must indicate for which claims it is intended. If a claims fee is not paid in due time, the claim concerned is deemed to be abandoned (R. 162(4) EPC).

If claims fees have already been paid, but on expiry of the above-mentioned period there is a new set of claims containing fewer fee-incurring claims than before, the claims fees in excess of those due under Rule 162(2), second sentence EPC will be refunded (R. 162(3) EPC).

The claims fee is currently

**EUR 225 for the 16th and each subsequent claim up to the limit of 50**  
**EUR 555 for the 51st and each subsequent claim**

### Note to users of the automatic debiting procedure

Unless the EPO receives prior instructions to the contrary, the fees for all claims incurring fees will be debited on the last day of the period for payment. For further details see the Arrangements for the automatic debiting procedure, Supplement to OJ EPO 3/2009.

### Important information concerning fee amounts

Following any amendment to the Rules relating to Fees, the amount(s) mentioned in this communication may be different from the amount(s) **actually due on the date of payment**. The latest version of the Schedule of fees and expenses, published as a Supplement to the Official Journal of the EPO, is also available on the EPO website ([www.epo.org](http://www.epo.org)) and can be found under [www.epo.org/schedule-of-fees](http://www.epo.org/schedule-of-fees), which allows the viewing, downloading and searching for individual fee amounts, both current and previous.

Please note that procedural fees are usually adjusted every two years, on even years, with effect from 1 April.

Payments by cheque delivered or sent direct to the EPO are no longer accepted as from 1 April 2008 (see OJ EPO 2007, 626).

For the Examining Division





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For any questions about  
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Date  
29.01.14

|                                                     |                                                 |
|-----------------------------------------------------|-------------------------------------------------|
| Reference                                           | Application No./Patent No.<br>12731264.3 - 1359 |
| Applicant/Proprietor<br>Molecular Rebar Design, LLC |                                                 |

#### Notification of the data mentioned in Rule 19(3) EPC

In the above-identified patent application you are designated as inventor/co-inventor.  
Pursuant to Rule 19(3) EPC the following data are notified herewith:

DATE OF FILING : 21.06.12  
PRIORITY : US/23.06.11/ USP201161500560  
TITLE : LITHIUM ION BATTERIES USING DISCRETE CARBON  
NANOTUBES, METHODS FOR PRODUCTION THEREOF AND  
PRODUCTS OBTAINED THEREFROM  
DESIGNATED STATES : AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE  
IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM  
TR

#### Receiving Section





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this communication:  
Tel. +31 (0)70 340 45 00

Date  
29.01.14

|                                                     |                                                 |
|-----------------------------------------------------|-------------------------------------------------|
| Reference                                           | Application No./Patent No.<br>12731264.3 - 1359 |
| Applicant/Proprietor<br>Molecular Rebar Design, LLC |                                                 |

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In the above-identified patent application you are designated as inventor/co-inventor.  
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DATE OF FILING : 21.06.12  
PRIORITY : US/23.06.11/ USP201161500560  
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NANOTUBES, METHODS FOR PRODUCTION THEREOF AND  
PRODUCTS OBTAINED THEREFROM  
DESIGNATED STATES : AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE  
IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM  
TR

#### Receiving Section



## CLAIMS

What is claimed is the following:

1. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:
  - a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% percent by weight;
  - b) mixing the carbon nanotubes with a high boiling point liquid;
  - c) adding reagents in correct balance to synthesize a lithium salt;
  - d) reacting the mixture at a temperature to form the lithium salt while sonicating the mixture;
  - e) separating the solid discrete carbon nanotube salts from the liquid; and
  - f) drying and annealing the solid discrete carbon nanotube salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.
2. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:
  - a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level of 1% to 15% by weight;
  - b) mixing the carbon nanotubes and a lithium salt in a liquid with surfactant;
  - c) sonicating the liquid carbon nanotube/lithium salt mixture;
  - d) separating the solid salts from the liquid; and
  - e) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

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8239309v.1

Duration: 23.04.2013 11:54:45 - 23.04.2013 11:56:21. This page 6 of 12; AMENDED SHEET 2013 11:55:31  
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3. A composition useful for lithium ion batteries comprising:  
discrete carbon nanotubes, the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface, wherein the discrete carbon nanotubes have an aspect ratio of 10 to 500 and oxidation levels from 1% to 15% by weight of the carbon nanotube.
4. The composition of claim 3, wherein the crystals or layers of lithium ion active material comprise a lithium metal salt and an element selected from the group consisting of: iron, manganese, cobalt, copper, nickel, vanadium, titanium, and mixtures thereof.
5. The composition of claim 4, wherein the lithium metal salt has an olivine crystal structure.
6. The composition of claim 3, wherein the crystals or layers of lithium ion active material comprise tin, silicon, copper, antimony, aluminum, germanium, titanium, or mixtures thereof.
7. The composition of any one of claims 3-6, further comprising graphene or oxygenated graphene.
8. The composition of claim 7, wherein the weight ratio of graphene to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.
9. The composition of any one of claims 3-8, wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.
10. The composition of any one of claims 3-9, comprising oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are uniformly dispersed

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Duration: 23.04.2013 11:54:45 - 23.04.2013 11:56:21. This page 7 of 12. AMENDED SHEET 213 11:55:39  
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without clustering on a dimension scale less than 1 micrometer.

11. The composition of any one of claims 3-10, comprising uniformly dispersible oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.
12. The composition of claim 11, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.

**PATENT COOPERATION TREATY**  
**PCT**  
**INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY**  
(Chapter II of the Patent Cooperation Treaty)  
(PCT Article 36 and Rule 70)

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                   |                                                                                |                      |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|--------------------------------------------------------------------------------|----------------------|
| Applicant's or agent's file reference<br>P100028PC00                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | <b>FOR FURTHER ACTION</b>                                         |                                                                                | See Form PCT/PEA/416 |
| International application No.<br>PCT/US2012/043534                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | International filing date ( <i>day/month/year</i> )<br>21.06.2012 | Priority date ( <i>day/month/year</i> )<br>23.06.2011                          |                      |
| International Patent Classification (IPC) or national classification and IPC<br>INV. H01M4/62                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                   |                                                                                |                      |
| Applicant<br>Molecular Rebar Design, LLC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                   |                                                                                |                      |
| <p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>6</u> sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p style="margin-left: 20px;">a. <input checked="" type="checkbox"/> <i>sent to the applicant and to the International Bureau</i> a total of <u>6</u> sheets, as follows:</p> <p style="margin-left: 40px;"><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p style="margin-left: 40px;"><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> (<i>sent to the International Bureau only</i>) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see paragraph 3bis of Annex C of the Administrative Instructions).</p> |                                                                   |                                                                                |                      |
| <p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I      Basis of the report</p> <p><input type="checkbox"/> Box No. II      Priority</p> <p><input type="checkbox"/> Box No. III      Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV      Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V      Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI      Certain documents cited</p> <p><input type="checkbox"/> Box No. VII      Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII      Certain observations on the international application</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                   |                                                                                |                      |
| Date of submission of the demand<br><br>23.04.2013                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                   | Date of completion of this report<br><br>24.09.2013                            |                      |
| Name and mailing address of the international preliminary examining authority:<br> European Patent Office P.B. 5818 Patentlaan 2<br>NL-2280 HV Rijswijk - Pays Bas<br>Tel. +31 70 340 - 2040<br>Fax: +31 70 340 - 3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                   | Authorized officer:<br><br>Kelly, Michael<br><br>Telephone No. +31 70 340-8973 |                      |



**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/US2012/043534

**Box No. I Basis of the report**

1. With regard to the **language**, this report is based on
  - ☒ the international application in the language in which it was filed
  - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
    - ☐ international search (under Rules 12.3(a) and 23.1(b))
    - ☐ publication of the international application (under Rule 12.4(a))
    - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a))
2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

**Description, Pages**

1-12 as originally filed

**Claims, Numbers**

1-12 filed with telefax on 23-04-2013

**Drawings, Sheets**

1/3-3/3 as originally filed

- ☐ a sequence listing - see Supplemental Box Relating to Sequence Listing.

3. ☒ The amendments have resulted in the cancellation of:
  - ☐ the description, pages
  - ☒ the claims, Nos. 13
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-bis)):
  - ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
5. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 70.2 (e)).
6. ☐ Supplementary international search report(s) from Authority(ies) have been received and taken into account in drawing up this report (Rule 45bis.8(b) and (c)).

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/US2012/043534

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

---

1. Statement

|                               |             |             |
|-------------------------------|-------------|-------------|
| Novelty (N)                   | Yes: Claims | <u>1-12</u> |
|                               | No: Claims  |             |
| Inventive step (IS)           | Yes: Claims | <u>1-12</u> |
|                               | No: Claims  |             |
| Industrial applicability (IA) | Yes: Claims | <u>1-12</u> |
|                               | No: Claims  |             |

2. Citations and explanations (Rule 70.7):

see separate sheet

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

D1 WO 2010/117392 A1 (BOSNYAK CLIVE P [US]; SWOGGER KURT W [US])  
14 October 2010 (2010-10-14)

D2 US 2011/104551 A1 (YANG JUNBING [US] ET AL) 5 May 2011 (2011-05-05)

**Novelty**

A composition useful for lithium ion batteries comprising: discrete carbon nanotubes, the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface wherein the discrete carbon nanotubes have an aspect ratio of 10 to 500 and oxidation levels from 1 % to 15% by weight of the carbon nanotube is not disclosed in the cited prior art.

The subject matter of independent product claim 3 and independent method claims 1 and 2 are therefore new.

Claims 4-12 are dependent on claim 3. The present application therefore meets the criteria of Article 33(2) PCT, because the subject-matter of claims 1-12 is new.

**Inventive step**

The present application meets the criteria of Article 33(3) PCT, because the subject-matter of claims 1-12 involves an inventive step.

D1 is regarded as being the prior art closest to the subject-matter of independent product claim 3 and discloses: a composition useful for lithium ion batteries comprising: discrete carbon nanotubes (D1: page 15, paragraph 0061), the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface (D1: page 21, paragraph 0082 to page 22, paragraph 0083), wherein the discrete carbon nanotubes have an aspect ratio of 100 to 1000 (D1: page 10, paragraph 0042) and the carbon nanotubes are oxidised (D1: page 6, paragraph 0032).

The document D1 does not disclose carbon nanotubes with oxidation levels of 1% to 15% percent by weight.

The problem to be solved by the subject matter of claim 3 is to provide intimate electron transfer and enhanced mechanical strength of the active material.

Taking into account later-filed evidence provided by the applicant and supporting an inventive step, it is considered not obvious to the skilled person to select carbon nanotubes with oxidation levels of 1% to 15% percent by weight in order to provide intimate electron transfer and enhanced mechanical strength of the active material as it is not disclosed nor suggested in the cited prior art nor is it common knowledge in the technical field to do so.

Therefore the subject matter of claim 3 meets the requirements of the PCT in respect of inventive step.

Dependent claims 4-12 are dependent on claim 3 and as such also meet the requirements of the PCT in respect of inventive step.

D1 is regarded as being the prior art closest to the subject-matter of independent method claims 1 and 2, and discloses a process for the production of the discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the discrete carbon nanotubes have an aspect ratio of 100 to 1000 (D1: page 10, paragraph 0042) and the carbon nanotubes are oxidised (D1: page 6, paragraph 0032), comprising the steps of: mixing the carbon nanotubes with a liquid, reagents to synthesize a lithium salt and a surfactant, reacting the mixture at a temperature to form the lithium salt while sonicating the mixture, separating the solid discrete carbon nanotube salts from the liquid; and drying solid discrete carbon nanotube salts (D1: page 11, paragraph 0049 to page 12, paragraph 0052, page 21, paragraph 0082 to page 22, paragraph 0083 and page 28-29, example 9)

The subject-matter of claims 1 and 2 therefore differ from this known method in that the carbon nanotubes have oxidation levels of 1% to 15% percent by weight and the solid discrete carbon nanotube salts are annealed under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

The problem to be solved by the present invention may therefore be regarded as providing a method to produce improved electrode material for lithium ion batteries.

The solution proposed in claims 1 and 2 of the present application can be considered as involving an inventive step (Article 33(3) PCT) for the following reasons: It is not obvious to the skilled person starting out from D1 to provide a method to produce improved electrode material for lithium ion batteries by selecting carbon nanotubes with oxidation levels of 1% to 15% percent by weight and producing discrete carbon nanotubes having crystals or layers of olivine lithium ion active material attached to

their surface, by annealing under an inert atmosphere at sufficient temperature to obtain the olivine crystal structure, as it is not disclosed nor suggested in the cited prior art nor is it common knowledge to do so.

**Industrial applicability**

The subject matter described in claims 1-12 can find use in industry and is therefore industrially applicable(Article 33(4) PCT).

The Hague • Groningen • Arnhem • 's-Hertogenbosch  
Amersfoort • Eindhoven • Munich • Regensburg • Louvain



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Your ref. PCT/US2012/043534  
Our ref. MAS/P100028PC00

The Hague,  
April 23, 2013  
*by facsimile*

Re: International Patent Application No. PCT/US2012/043534  
Designed NanoTubes, LLC

I refer to the sub-authorization filed with the WIPO on April 19, 2013, and request international preliminary examination (IPE) of the above-identified international application. The Demand, please find attached.

- 5 In addition, I enclose a set of claims in hand-written and retyped form as basis for the IPE. In this set of claims, claims 8 and 9 as originally filed are renumbered to claims 1 and 2. New claim 3 is a combination of original claims 1 and 5 and is additionally supported by § [0009] of the application.
- 10 New claim 4 is based on original claim 2 and § [0009]; new claim 5 is based on original claim 3; new claim 6 is based on original claim 4; claim 7 is based on original claim 6 and § [0009]; claim 8 is based on original claim 7; new claim 9 is based on original claim 10 and § [0012]; new claim 10 is based on claim 11 and § [0013]; and new claim 12 is based on original claim 13.

15

Page 2  
Your ref. PCT/US2012/043534  
Our ref. MAS/P100028PC00  
Date April 23, 2013



In the Written Opinion of the International Searching Authority, original claims 8 and 9 were held to meet the requirements of novelty and inventive step, and were – like the other claims – also held to be industrially applicable.

- 5 Also claim 5 as originally filed was considered novel and hence presently proposed claim 3 is novel as well.

In the written opinion of the ISA, under Re Item V, Inventive step, the ISA observed “(t)hat the discrete carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% by weight is not considered to involve an inventive step, as there is no surprising technical effect attributed to this feature. Therefore the subject matter of claim 5 is not inventive”.

- 15 I disagree with this position taken in respect of claim 5 as filed and hence claim 3 as presently proposed.

Not only do the discrete, well-dispersed carbon nanotubes bearing nanosized crystals or layers of lithium ion active material to their surface, overcome the sketched problems with the low electrical conduction; can anode materials be obtained to provide benefits like improved capacity, electron and ion conductivity and mechanical strength; and can other benefits including improved heat transfer media to avoid thermally-induced runaway, structural strength to the paste during manufacture and high surface area per weight of lithium ion active material to provide good energy density be obtained, while the uniform dispersion of discrete tubes will also provide a more uniform voltage gradient across the cathode or anode layer, therefore reducing the probability of locally high electrically resistive regions that can cause accelerated decay of performance in that local region (see especially §§ [0006]-[0008] of the present application).

Page 3  
Your ref. PCT/US2012/043534  
Our ref. MAS/P100028PC00  
Date April 23, 2013



In addition, the claimed material of new claim 3 having a specific aspect ratio of 10 to 500 and oxidation levels from 1-15% by weight of the carbon nanotubes is also an intermediate product to be used in the novel and inventive processes of claims 1 and 2. That is, these products can, for instance through step f of new claim 1 and step e of new  
5 claim 2, be converted to the end result of these two process claims.

This aspect *per se* is already sufficient to have an inventive step.

Finally, in accordance with Art 34(2)(a) PCT, I request you to contact me by phone in  
10 order to arrange for a telephonic interview with one of the experts of Applicant and myself before you finalize the International Preliminary Examination Report.

The Agent,

A handwritten signature in black ink, appearing to be 'H.A.M. Marsman', written over a horizontal line.

H.A.M. Marsman

Encl.: - amended claims (handwritten and retyped form)  
- PCT Demand Chapter II

EK



## Acknowledgement of receipt

We hereby acknowledge receipt of the form for entry into the European phase (EPO as designated or elected Office) as follows:

|                                 |                                                                                                          |                                       |
|---------------------------------|----------------------------------------------------------------------------------------------------------|---------------------------------------|
| Submission number               | 2500245                                                                                                  |                                       |
| PCT application number          | PCT/US2012/043534                                                                                        |                                       |
| EP application number           | 12731264.3                                                                                               |                                       |
| Date of receipt                 | 30 December 2013                                                                                         |                                       |
| Receiving Office                | European Patent Office, The Hague                                                                        |                                       |
| Your reference                  | P100028EP00                                                                                              |                                       |
| Applicant                       |                                                                                                          |                                       |
| Country                         |                                                                                                          |                                       |
| Documents submitted             | package-data.xml<br>application-body.xml<br>AMSPECEPO-1.pdf\P100028EP00<br>Claims to be filed.pdf (3 p.) | ep-euro-pct.xml<br>epf1200.pdf (5 p.) |
| Submitted by                    | CN=A. Dalmulder 14413,O=Vereenigde,C=NL                                                                  |                                       |
| Method of submission            | Online                                                                                                   |                                       |
| Date and time receipt generated | 30 December 2013, 15:24 (CET)                                                                            |                                       |
| Message Digest                  | 11:2E:24:1B:D3:13:D5:37:1F:5C:8A:E5:82:B9:52:A5:72:3C:C9:2F                                              |                                       |

**Correction by the EPO of errors in debit instructions filed by eOLF**

Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

/European Patent Office/

## CLAIMS

What is claimed is the following:

1. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:
  - a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% percent by weight;
  - b) mixing the carbon nanotubes with a high boiling point liquid;
  - c) adding reagents in correct balance to synthesize a lithium salt;
  - d) reacting the mixture at a temperature to form the lithium salt while sonicating the mixture;
  - e) separating the solid discrete carbon nanotube salts from the liquid; and
  - f) drying and annealing the solid discrete carbon nanotube salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.
2. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:
  - a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level of 1% to 15% by weight;
  - b) mixing the carbon nanotubes and a lithium salt in a liquid with surfactant;
  - c) sonicating the liquid carbon nanotube/lithium salt mixture;
  - d) separating the solid salts from the liquid; and
  - e) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

3. A composition useful for lithium ion batteries comprising:  
discrete carbon nanotubes, the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface, wherein the discrete carbon nanotubes have an aspect ratio of 10 to 500 and oxidation levels from 1% to 15% by weight of the carbon nanotube.
4. The composition of claim 3, wherein the crystals or layers of lithium ion active material comprise a lithium metal salt and an element selected from the group consisting of: iron, manganese, cobalt, copper, nickel, vanadium, titanium, and mixtures thereof.
5. The composition of claim 4, wherein the lithium metal salt has an olivine crystal structure.
6. The composition of claim 3, wherein the crystals or layers of lithium ion active material comprise tin, silicon, copper, antimony, aluminum, germanium, titanium, or mixtures thereof.
7. The composition of any one of claims 3-6, further comprising graphene or oxygenated graphene.
8. The composition of claim 7, wherein the weight ratio of grapheme to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.
9. The composition of any one of claims 3-8, wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.
10. The composition of any one of claims 3-9, comprising oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are uniformly dispersed

without clustering on a dimension scale less than 1 micrometer.

11. The composition of any one of claims 3-10, comprising uniformly dispersible oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.
12. The composition of claim 11, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.



**Entry into the European phase  
(EPO as designated or elected Office)**  
To the European Patent Office

|                                                                                                                                                                          |                                                         |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------|
| European application number                                                                                                                                              | EP12731264.3                                            |
| PCT application number                                                                                                                                                   | PCT/US2012/043534                                       |
| PCT publication number                                                                                                                                                   | WO2012177865                                            |
| Applicant's or representative's reference                                                                                                                                | P100028EP00                                             |
| International Filing Date                                                                                                                                                | 21.06.2012                                              |
| International Searching Authority (ISA)                                                                                                                                  | EP                                                      |
| International Preliminary Examining Authority (IPEA)                                                                                                                     | EP                                                      |
| <b>1. Applicant</b>                                                                                                                                                      |                                                         |
| Indications concerning the applicant(s) are contained in the international publication or were recorded by the International Bureau after the international publication. | <input checked="" type="checkbox"/>                     |
| Changes which have not yet been recorded by the International Bureau are set out here:                                                                                   | <input type="checkbox"/>                                |
| <b>2. Representative</b>                                                                                                                                                 |                                                         |
| This is the representative who will be listed in the Register of European Patents and to whom notifications will be made                                                 |                                                         |
| <b>Representative 1</b>                                                                                                                                                  |                                                         |
| Name:                                                                                                                                                                    | JANSEN, Ir. C.M.                                        |
| Company:                                                                                                                                                                 | V.O.                                                    |
| Address of place of business:                                                                                                                                            | Johan de Wittlaan 7<br>2517 JR Den Haag,<br>Netherlands |
| Telephone:                                                                                                                                                               | +31 70 4166711                                          |
| Fax:                                                                                                                                                                     | +31 70 4166799                                          |
| e-mail:                                                                                                                                                                  | patent@vo.eu                                            |
| <b>3. Authorisation</b>                                                                                                                                                  |                                                         |
| An individual authorisation is attached.                                                                                                                                 | <input type="checkbox"/>                                |
| A general authorisation has been registered under No:                                                                                                                    | <input type="checkbox"/>                                |
| A general authorisation has been filed, but not yet registered.                                                                                                          | <input type="checkbox"/>                                |
| The authorisation filed with the EPO as PCT receiving Office expressly includes the European phase.                                                                      | <input type="checkbox"/>                                |
| <b>4. Request for examination</b>                                                                                                                                        |                                                         |
| Examination of the application under Art. 94 EPC is hereby requested. The examination fee is being (has been, will be) paid.                                             | <input checked="" type="checkbox"/>                     |
| Request for examination in an admissible non-EPO language:                                                                                                               | <input type="checkbox"/>                                |
| The applicant waives his right to be asked under Rule 70(2) EPC whether he wishes to proceed further with the application.                                               | <input type="checkbox"/>                                |
| <b>5. Copies</b>                                                                                                                                                         |                                                         |
| Additional copies of the documents cited in the supplementary European search report are requested.                                                                      | <input type="checkbox"/>                                |
| Number of additional sets of copies                                                                                                                                      |                                                         |
| <b>6. Documents intended for proceedings before the EPO</b>                                                                                                              |                                                         |
| Number of claims on entry into the European phase:                                                                                                                       | 12                                                      |
| 6.1 Proceedings before the EPO as designated Office (PCT I) are to be based on the following documents:                                                                  |                                                         |
| the application documents published by the International Bureau (with all claims, description and drawings), where applicable with amended claims under Art. 19 PCT      | <input type="checkbox"/>                                |
| unless replaced by the amendments attached.                                                                                                                              | <input type="checkbox"/>                                |

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|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|
| <i>Where necessary, clarifications should be attached as 'Other documents'</i>                                                                                                                                                                                            |                                     |
| 6.2 Proceedings before the EPO as elected Office (PCT II) are to be based on the following documents:                                                                                                                                                                     | <input type="checkbox"/>            |
| the documents on which the international preliminary examination report is based, including any annexes                                                                                                                                                                   | <input checked="" type="checkbox"/> |
| unless replaced by the amendments attached.                                                                                                                                                                                                                               | <input checked="" type="checkbox"/> |
| <i>Where necessary, clarifications should be attached as 'Other documents'</i>                                                                                                                                                                                            |                                     |
| If the EPO as International Preliminary Examining Authority has been supplied with test reports, these may be used as the basis of proceedings before the EPO.                                                                                                            | <input checked="" type="checkbox"/> |
| 6.3 A copy of the results of the search carried out by the authority with which the previous application(s) whose priority is claimed was (were) filed is attached (R. 141(1) EPC).                                                                                       | <input type="checkbox"/>            |
| 6.4 The applicant waives his right to the communication under Rules 161(1) or (2) and 162 EPC.                                                                                                                                                                            | <input type="checkbox"/>            |
| <b>7. Translations</b>                                                                                                                                                                                                                                                    |                                     |
| Translations in one of the official languages of the EPO (English, French, German) are attached as crossed below:                                                                                                                                                         | <input type="checkbox"/>            |
| <i>* In proceedings before the EPO as designated or elected Office (PCT I + II):</i>                                                                                                                                                                                      |                                     |
| Translation of the international application (description, claims, any text in the drawings) as originally filed, of the abstract as published and of any indication under Rule 13bis.3 and 13bis.4 PCT regarding biological material                                     | <input type="checkbox"/>            |
| Translation of the priority application(s) (to be filed only at the EPO's request, Rule 53(3) EPC)                                                                                                                                                                        | <input type="checkbox"/>            |
| It is hereby declared that the international application as originally filed is a complete translation of the previous application (Rule 53(3) EPC)                                                                                                                       | <input type="checkbox"/>            |
| <i>* In addition, in proceedings before the EPO as designated Office (PCT I):</i>                                                                                                                                                                                         |                                     |
| Translation of amended claims and any statement under Art. 19 PCT, if the claims as amended are to form the basis for the proceedings before the EPO (see Section 6).                                                                                                     | <input type="checkbox"/>            |
| <i>* In addition, in proceedings before the EPO as elected Office (PCT II):</i>                                                                                                                                                                                           |                                     |
| Translation of annexes to the international preliminary examination report                                                                                                                                                                                                | <input type="checkbox"/>            |
| <b>8. Biological material</b>                                                                                                                                                                                                                                             |                                     |
| The invention uses and/or relates to biological material deposited under Rule 31 EPC.                                                                                                                                                                                     | <input type="checkbox"/>            |
| The particulars referred to in Rule 31(1)(c) EPC (if not yet known, the depositary institution and the identification reference(s)) [number, symbols, etc.] of the depositor) are given in the international publication or in the translation submitted in Section 7 on: | <input type="checkbox"/>            |
| page(s) / line(s)                                                                                                                                                                                                                                                         |                                     |
| The receipt(s) of deposit issued by the depositary institution                                                                                                                                                                                                            | <input type="checkbox"/>            |
| is (are) enclosed.                                                                                                                                                                                                                                                        | <input type="checkbox"/>            |
| will be filed later.                                                                                                                                                                                                                                                      | <input type="checkbox"/>            |
| Waiver of the right to an undertaking from the requester pursuant to Rule 33(2) EPC attached.                                                                                                                                                                             | <input type="checkbox"/>            |
| <b>9. Nucleotide and amino acid sequences</b>                                                                                                                                                                                                                             |                                     |
| The international application discloses nucleotide and/or amino acid sequences.                                                                                                                                                                                           | <input type="checkbox"/>            |
| 9.1 The sequence listing was filed under Rule 5.2(a) PCT, or furnished to the EPO as ISA under Rule 13ter.1(a) PCT, or is otherwise available to the EPO, in computer-readable format in accordance with WIPO ST.25.                                                      | <input type="checkbox"/>            |
| 9.2                                                                                                                                                                                                                                                                       |                                     |
| The sequence listing is attached in computer-readable format in accordance with WIPO Standard ST.25                                                                                                                                                                       | <input type="checkbox"/>            |
| The sequence listing is attached in PDF format.                                                                                                                                                                                                                           | <input type="checkbox"/>            |
| The sequence listing does not include matter which goes beyond the content of the application as filed.                                                                                                                                                                   | <input type="checkbox"/>            |
| <b>10. Designation fees</b>                                                                                                                                                                                                                                               |                                     |
| All the contracting states party to the EPC at the time of filing of the international patent application and designated in the international application are deemed to                                                                                                   | <input checked="" type="checkbox"/> |

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| <p>be designated (see Article 79(1) EPC).</p> <p>The following states, which were contracting states to the EPC at the time of filing of the international application, are designated:</p> <p>AL AT BE BG CH&amp;LI CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                                                                                                                                                                |                                    |                         |                          |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
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| <p><b>11. Extension of the European patent</b></p> <p>This application is deemed to be a request to extend the European patent application and the European patent granted in respect of it to all the non-contracting states to the EPC designated in the international application and with which extension agreements are in force on the date on which the international application is filed. However, the extension only takes effect if the prescribed extension fee is paid.</p> <p>It is currently intended to pay the extension fee for the following states:</p> <p>Note: Under the automatic debiting procedure, extension fees will only be debited for states indicated here, unless the EPO is instructed otherwise before expiry of the period for payment.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | <input type="checkbox"/>                                                                                                                                                                                                                                                       |                                    |                         |                          |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| <p><b>12. List of enclosed documents</b></p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 5%;">No.</th> <th style="width: 40%;">Description of document</th> <th style="width: 30%;">Original file name</th> <th style="width: 25%;">Assigned file name</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">1</td> <td>Combined Amendments</td> <td>P100028EP00 Claims to be filed.pdf</td> <td>AMSPECEPO-1.pdf</td> </tr> </tbody> </table>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                                                                                                                                                                | No.                                | Description of document | Original file name       | Assigned file name | 1                 | Combined Amendments | P100028EP00 Claims to be filed.pdf                                     | AMSPECEPO-1.pdf |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| No.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | Description of document                                                                                                                                                                                                                                                        | Original file name                 | Assigned file name      |                          |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | Combined Amendments                                                                                                                                                                                                                                                            | P100028EP00 Claims to be filed.pdf | AMSPECEPO-1.pdf         |                          |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| <p><b>13. Mode of payment: Debit from deposit account</b></p> <p>Currency</p> <p>The European Patent Office is hereby authorised, to debit from the deposit account with the EPO any fees and costs indicated on the fees page.</p> <p>Deposit account number</p> <p>Account holder</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | <p style="text-align: center;"><input checked="" type="checkbox"/></p> <p>EUR</p> <p>28090002</p> <p>V.O.</p>                                                                                                                                                                  |                                    |                         |                          |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| <p><b>14. Any refunds should be made to the following EPO deposit account:</b></p> <p>Number and account holder</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | <p style="text-align: center;"><input checked="" type="checkbox"/></p> <p>V.O., 28090002</p>                                                                                                                                                                                   |                                    |                         |                          |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| <p><b>15. Fees</b></p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">No.</th> <th style="width: 45%;">Description</th> <th style="width: 10%;">Factor/reduction applied</th> <th style="width: 15%;">Fee schedule</th> <th style="width: 20%;">Amount to be paid</th> </tr> </thead> <tbody> <tr> <td>15-1</td> <td>002 Fee for a European search - Applications filed on/after 01.07.2005</td> <td style="text-align: center;">-1165</td> <td style="text-align: right;">1 165.00</td> <td style="text-align: right;">0.00</td> </tr> <tr> <td>15-2</td> <td>005 Designation fee - For each State designated (max. 7x) for applications filed before 01.04.2009<br/>Designated states: AL, AT, BE, BG, CH&amp;LI, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR</td> <td style="text-align: center;">0</td> <td style="text-align: right;">95.00</td> <td style="text-align: right;">0.00</td> </tr> <tr> <td>15-3</td> <td>005e Designation fee - For all contracting States designated for applications filed on/after 01.04.2009</td> <td style="text-align: center;">1</td> <td style="text-align: right;">555.00</td> <td style="text-align: right;">555.00</td> </tr> <tr> <td>15-4</td> <td>006e Examination fee - For applications filed before 01.07.2005 and for international applications filed on/after 01.07.2005 without supplementary European search report</td> <td style="text-align: center;">0.5</td> <td style="text-align: right;">1 730.00</td> <td style="text-align: right;">865.00</td> </tr> <tr> <td>15-5</td> <td>015 Claims fee - For the 16th to the 50th claim</td> <td style="text-align: center;">0</td> <td style="text-align: right;">225.00</td> <td style="text-align: right;">0.00</td> </tr> <tr> <td>15-6</td> <td>15e Claims fee - For the 51st and each subsequent claim</td> <td style="text-align: center;">0</td> <td style="text-align: right;">555.00</td> <td style="text-align: right;">0.00</td> </tr> <tr> <td>15-7</td> <td>020 Filing fee - entry EP phase - online</td> <td style="text-align: center;">1</td> <td style="text-align: right;">115.00</td> <td style="text-align: right;">115.00</td> </tr> <tr> <td>15-8</td> <td>520 Additional filing fee for the 36th and each subsequent page - entry into EP phase</td> <td style="text-align: center;">0</td> <td style="text-align: right;">14.00</td> <td style="text-align: right;">0.00</td> </tr> <tr> <td colspan="2" style="text-align: right;"><b>Total:</b></td> <td></td> <td style="text-align: right;"><b>EUR</b></td> <td style="text-align: right;"><b>1 535.00</b></td> </tr> </tbody> </table> |                                                                                                                                                                                                                                                                                | No.                                | Description             | Factor/reduction applied | Fee schedule       | Amount to be paid | 15-1                | 002 Fee for a European search - Applications filed on/after 01.07.2005 | -1165           | 1 165.00 | 0.00 | 15-2 | 005 Designation fee - For each State designated (max. 7x) for applications filed before 01.04.2009<br>Designated states: AL, AT, BE, BG, CH&LI, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR | 0 | 95.00 | 0.00 | 15-3 | 005e Designation fee - For all contracting States designated for applications filed on/after 01.04.2009 | 1 | 555.00 | 555.00 | 15-4 | 006e Examination fee - For applications filed before 01.07.2005 and for international applications filed on/after 01.07.2005 without supplementary European search report | 0.5 | 1 730.00 | 865.00 | 15-5 | 015 Claims fee - For the 16th to the 50th claim | 0 | 225.00 | 0.00 | 15-6 | 15e Claims fee - For the 51st and each subsequent claim | 0 | 555.00 | 0.00 | 15-7 | 020 Filing fee - entry EP phase - online | 1 | 115.00 | 115.00 | 15-8 | 520 Additional filing fee for the 36th and each subsequent page - entry into EP phase | 0 | 14.00 | 0.00 | <b>Total:</b> |  |  | <b>EUR</b> | <b>1 535.00</b> |
| No.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | Description                                                                                                                                                                                                                                                                    | Factor/reduction applied           | Fee schedule            | Amount to be paid        |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| 15-1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 002 Fee for a European search - Applications filed on/after 01.07.2005                                                                                                                                                                                                         | -1165                              | 1 165.00                | 0.00                     |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| 15-2                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 005 Designation fee - For each State designated (max. 7x) for applications filed before 01.04.2009<br>Designated states: AL, AT, BE, BG, CH&LI, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR | 0                                  | 95.00                   | 0.00                     |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| 15-3                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 005e Designation fee - For all contracting States designated for applications filed on/after 01.04.2009                                                                                                                                                                        | 1                                  | 555.00                  | 555.00                   |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| 15-4                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 006e Examination fee - For applications filed before 01.07.2005 and for international applications filed on/after 01.07.2005 without supplementary European search report                                                                                                      | 0.5                                | 1 730.00                | 865.00                   |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| 15-5                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 015 Claims fee - For the 16th to the 50th claim                                                                                                                                                                                                                                | 0                                  | 225.00                  | 0.00                     |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| 15-6                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 15e Claims fee - For the 51st and each subsequent claim                                                                                                                                                                                                                        | 0                                  | 555.00                  | 0.00                     |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| 15-7                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 020 Filing fee - entry EP phase - online                                                                                                                                                                                                                                       | 1                                  | 115.00                  | 115.00                   |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| 15-8                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 520 Additional filing fee for the 36th and each subsequent page - entry into EP phase                                                                                                                                                                                          | 0                                  | 14.00                   | 0.00                     |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| <b>Total:</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                |                                    | <b>EUR</b>              | <b>1 535.00</b>          |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |
| <p><b>16. Annotations</b></p> <p><b>16-1. Note (for EPO) (EP Phase)</b></p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | <p>Weiterer Vertreter – Additional representatives – Autres mandataires (V.O.)</p> <p><b>SUPPLEMENTARY SHEET</b></p>                                                                                                                                                           |                                    |                         |                          |                    |                   |                     |                                                                        |                 |          |      |      |                                                                                                                                                                                                                                                                                |   |       |      |      |                                                                                                         |   |        |        |      |                                                                                                                                                                           |     |          |        |      |                                                 |   |        |      |      |                                                         |   |        |      |      |                                          |   |        |        |      |                                                                                       |   |       |      |               |  |  |            |                 |

P100028EP00

Weiterer Vertreter - Additional  
representatives - Autres  
mandataires

Ir A.H.K. Tan  
Ir H.A. Witmans  
Drs H.A.M. Marsman  
Ir L.J.J. Jessen  
Drs K.M.L. Bijvank  
Ir B.Ch. Ledeboer  
Dr Ir O.L. Oudshoorn  
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Mr Drs L.A.C.M. van  
Wezenbeek  
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Dr A.D. Tepper  
Ing D.A. Ploeg  
Ir D.J. de Jong  
Dr Ir K. de Jong  
Ir A.P.M. Duijker  
Dr Ir H.P.A. Maas  
Dr G.A.M. Michiels  
Drs Ir A. Jaeken  
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M. Blood, BSc  
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M.D. Dokter, MSc  
Dr N.G. Panina  
Dr T.J. Elmore  
Dr M.J. Luys  
Ir J.W. ten Dam  
Dr M.M. Westra  
==

17. Signature(s) of applicant(s) or representative

Place: Den Haag  
Date: 30 December 2013  
Signed by: /C.M.Jansen/  
Capacity: (Representative)

P100028EP00

### Table for section 6 of Form 1200.3

In accordance with the Notice from the European Patent Office dated 26 January 2009 concerning the 2009 fee structure (OJ EPO 2009, 118, and Guidelines for Examination in the EPO, April 2009, A-III, 13.2), the amount of the additional fee (Art. 2, item 1a, Rules relating to Fees) for the pages of this European patent application is calculated as follows:

Documents intended for proceedings before the EPO (R. 159 (1) (b) EPC) and for calculating the additional fee (Art. 2, item 1a, RFees):

|                                           |                                               | Page(s) from ... to ... | Number of pages     |
|-------------------------------------------|-----------------------------------------------|-------------------------|---------------------|
| Description:                              | International application as published        | 1 to 12                 | 12                  |
| Claims:                                   | Amendments filed on entry into European phase | 1 to 3                  | 3                   |
| Drawings:                                 | International application as published        | 1 to 3                  | 3                   |
| Abstract:                                 | Default count: one page                       |                         | 1                   |
| Total number of pages                     |                                               |                         | 19                  |
| Fee-exempt pages (Art. 2, item 1a, RFees) |                                               |                         | -35                 |
| Number of pages to be paid for            |                                               |                         | 0                   |
|                                           |                                               |                         | (x 14 EUR per page) |
| Total amount payable                      | EUR                                           |                         | 0                   |

P100028EP00



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Molecular Rebar Design, LLC  
13477 Fitzhugh Road  
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ETATS-UNIS D'AMERIQUE

For any questions about  
this communication:

Tel. +31 (0)70 340 45 00

Date  
04.11.13

|                                                     |                                                                  |
|-----------------------------------------------------|------------------------------------------------------------------|
| Reference                                           | Application No./Patent No.<br>12731264.3 - 1359 PCT/US2012043534 |
| Applicant/Proprietor<br>Molecular Rebar Design, LLC |                                                                  |

#### Entry into the European phase before the European Patent Office

The following information describes the procedural steps required for entry into the European phase before the European Patent Office (EPO). You are advised to read it carefully because failure to take the necessary action in due time can lead to a loss of rights.

1. The above mentioned international patent application has been given the **European application No. 12731264.3**.
2. Applicants **without a residence or their principal place of business** in an EPC Contracting State may themselves initiate European processing of their international applications, provided they do so before expiry of the 31st month from the priority date.

During the European phase before the EPO as designated or elected Office, however, such applicants **must** be represented by a professional representative (Art. 133(2) and Art. 134(1) and (8) EPC).

Where, at the expiry of the time period laid down in Rule 163(5) EPC, the requirements of Article 133(2) EPC have not been complied with, the European patent application will be **refused**, pursuant to Rule 163(6) EPC.

Please note that a professional representative authorised to act before the EPO and who acted for the applicant during the international phase does not automatically become the representative for the European phase. Applicants are therefore strongly advised to appoint in good time any representative they wish to initiate the European phase for them; otherwise the EPO has to send all communications directly to the applicant.

3. Applicants **with a residence or their principal place of business** in an EPC Contracting State are not obliged to appoint for the European phase a professional representative authorised to act before the EPO. However, in view of the complexity of the procedure it is recommended that they do so.
4. Applicants and professional representatives are also strongly advised to initiate the European phase using **EPO Form 1200**. It is available free of charge from the EPO or via the EPO website at **www.epo.org**. Similarly, it can be or generated with the Online Filing software, obtainable free of charge from the EPO (**www.epoline.org**) The use of the form is not compulsory.

5. Where the EPO acts as designated or elected Office (Art. 22(1) and (3) and 39(1) PCT), to enter the European phase before the EPO, the **following acts** must be performed by the applicant within **31 months** from the date of filing of the international application or (where applicable) the earliest priority date:

- a) Supply a translation of the international application into an EPO official language, if the International Bureau did not publish the application in such language (Art. 22(1) PCT and R. 159(1)(a) EPC);
- b) Specify the application documents, as originally filed or as amended, on which the European grant procedure is to be based (R. 159(1)(b) EPC);
- c) Pay the filing fee and, where applicable, the additional fee for a European patent application comprising more than 35 pages (R. 159(1)(c) EPC, Art. 2, items 1, 1a Rules relating to Fees);
- d) Pay the search fee where a supplementary European search report has to be drawn up (R. 159(1)(e) EPC);
- e) Pay the designation fee if the time limit laid down in Rule 39(1) EPC (i.e. six months after publication of the international search report) has expired before the 31-month period pursuant to Rule 159(1) EPC (R. 159(1)(d) EPC);
- f) File the written request for examination and pay the examination fee if the time limit laid down in Rule 70(1) EPC has expired before the 31-month period pursuant to Rule 159(1) EPC (R. 159(1)(f) EPC);
- g) Pay the renewal fee in respect of the third year, if the fee has fallen due (see Rule 51(1) EPC) before expiry of the 31-month period pursuant to Rule 159(1) EPC (R. 159(1)(g) EPC);
- h) File, where applicable, the certificate of exhibition referred to in Article 55(2) and Rule 25 EPC (R. 159(1)(h) EPC);
- i) Pay the claims fees for the sixteenth and each subsequent claim when the application documents on which the European grant procedure is to be based comprise more than fifteen claims (R. 162(1) EPC). For applications entering the European phase on or after 1 April 2009, a higher amount is payable for the 51st and each subsequent claim (Decision of the Administrative Council of 14 December 2007 amending the Rules relating to Fees, OJ EPO 2008, 10).

If either the translation of the international application or the request for examination is not filed in time, or if the filing fee, the additional fee, the search fee, the designation fee or the examination fee is not paid in due time, the application shall be deemed to be withdrawn (R. 160(1) EPC).

#### 6. Payment of fees

An up-to-date guidance for the payment of fees, expenses and prices and a list of the euro accounts of the European Patent Organisation are published in each issue of the Official Journal of the EPO. The guidance includes inter alia a reference to the latest version of the Schedule of fees and expenses where the amounts of fees are set out.

The Schedule of fees and expenses, published as a Supplement to the Official Journal of the EPO, is also available on the EPO website ([www.epo.org](http://www.epo.org)) and can be found under [www.epo.org/schedule-of-fees](http://www.epo.org/schedule-of-fees), which allows the viewing, downloading and searching for individual fee amounts, both current and previous.

Applicants should always check the fee amounts applying at the time of payment.

Payments can be validly made by any person. Permissible methods of payment are laid down in Article 5 Rules relating to Fees. Please note that payment cannot be made by cheque sent to the EPO.

For information on the calculation of the additional fee for applications comprising more than 35 pages, see Notice from the European Patent Office dated 26 January 2009 concerning the 2009 fee structure (OJ EPO 2009, 118), Notice supplementing the notice from the European Patent Office dated 26 January 2009 concerning the 2009 fee structure (OJ EPO 2009, 338) and Guidelines for Examination in the EPO, April 2010, A-III, 13.2.

For an overview of search and examination fees, see Notice from the European Patent Office dated 6 February 2012 (OJ EPO 2012, 212). Fee information is also published on the EPO website under [www.epo.org/fees](http://www.epo.org/fees).

#### 7. Restoration of priority right

Where the international application contains a priority claim to an earlier application and it has been filed within two months from the expiration of the 12-month priority period, a request for restoration before the EPO as designated Office (R. 49ter.2 PCT) applies under the following circumstances:

- a) No request for restoration filed before the receiving Office (RO) during the international phase (R. 26bis.3 PCT)
- b) Negative decision by the RO irrespective of the criterion applied (due care/ unintentionality)
- c) Positive decision by the RO based on the unintentionality criterion.

For a request to be admissible, it must be filed and the requisite fee must be paid (R. 49ter.2(b)(iii) and R. 49ter.2(d) PCT) within one month from the applicable time limit under Article 22 PCT for entering the regional phase (R. 49ter.2(b)(i) PCT). The request for restoration also needs to state the reasons for the failure to file the international application within the priority period (Rule 49ter.2(b)(ii) PCT).

- 8. If the applicant had appointed a representative during the application's international phase, the present Form will be sent to the representative, asking him to inform the applicant accordingly. All subsequent communications will be sent to the applicant, or - if the EPO is informed of his appointment in time - to the applicant's European representative.
- 9. For more details about time limits and procedural acts before the EPO as designated or elected Office, see the EPO brochure "How to get an European patent", Guide for applicants - Part 2, PCT procedure before the EPO - "Euro-PCT" (EPO PCT Guide). This brochure, the list of professional representatives before the EPO, Form 1200 and details of the latest fees are available on the Internet under <http://www.epo.org>.

#### 10. Programme for accelerated prosecution of European patent applications - "PACE"

Applicants wishing to accelerate proceedings before the EPO as designated or elected Office may request accelerated search and/or examination under the PACE programme (Notice from the European Patent Office dated 4 May 2010 concerning the programme for accelerated prosecution of European patent applications - "PACE", OJ EPO 2010, 352). To be as effective as possible, this should preferably be requested immediately on entry into the European phase.

#### Receiving Section



EPO Form 1201 04.13 NFS

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Your ref. PCT/US2012/043534  
Our ref. MAS/P100028PC00

The Hague,  
April 23, 2013  
*by facsimile*

Re: International Patent Application No. PCT/US2012/043534  
Designed NanoTubes, LLC

I refer to the sub-authorization filed with the WIPO on April 19, 2013, and request international preliminary examination (IPE) of the above-identified international application. The Demand, please find attached.

- 5 In addition, I enclose a set of claims in hand-written and retyped form as basis for the IPE. In this set of claims, claims 8 and 9 as originally filed are renumbered to claims 1 and 2. New claim 3 is a combination of original claims 1 and 5 and is additionally supported by § [0009] of the application.
- 10 New claim 4 is based on original claim 2 and § [0009]; new claim 5 is based on original claim 3; new claim 6 is based on original claim 4; claim 7 is based on original claim 6 and § [0009]; claim 8 is based on original claim 7; new claim 9 is based on original claim 10 and § [0012]; new claim 10 is based on claim 11 and § [0013]; and new claim 12 is based on original claim 13.

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Date April 23, 2013



In the Written Opinion of the International Searching Authority, original claims 8 and 9 were held to meet the requirements of novelty and inventive step, and were – like the other claims – also held to be industrially applicable.

- 5 Also claim 5 as originally filed was considered novel and hence presently proposed claim 3 is novel as well.

- In the written opinion of the ISA, under Re Item V, Inventive step, the ISA observed “(t)hat the discrete carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% by weight is not considered to involve an inventive step, as there is no surprising technical effect attributed to this feature. Therefore the subject matter of claim 5 is not inventive”.

- I disagree with this position taken in respect of claim 5 as filed and hence claim 3 as presently proposed.

- Not only do the discrete, well-dispersed carbon nanotubes bearing nanosized crystals or layers of lithium ion active material to their surface, overcome the sketched problems with the low electrical conduction; can anode materials be obtained to provide benefits like improved capacity, electron and ion conductivity and mechanical strength; and can other benefits including improved heat transfer media to avoid thermally-induced runaway, structural strength to the paste during manufacture and high surface area per weight of lithium ion active material to provide good energy density be obtained, while the uniform dispersion of discrete tubes will also provide a more uniform voltage gradient across the cathode or anode layer, therefore reducing the probability of locally high electrically resistive regions that can cause accelerated decay of performance in that local region (see especially §§ [0006]-[0008] of the present application).

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V.O.

PAG. 03/12

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Date April 23, 2013



In addition, the claimed material of new claim 3 having a specific aspect ratio of 10 to 500 and oxidation levels from 1-15% by weight of the carbon nanotubes is also an intermediate product to be used in the novel and inventive processes of claims 1 and 2. That is, these products can, for instance through step f of new claim 1 and step e of new claim 2, be converted to the end result of these two process claims.

This aspect *per se* is already sufficient to have an inventive step.

Finally, in accordance with Art 34(2)(a) PCT, I request you to contact me by phone in order to arrange for a telephonic interview with one of the experts of Applicant and myself before you finalize the International Preliminary Examination Report.

The Agent,

A handwritten signature in black ink, appearing to be 'H.A.M. Marsman'. The signature is written in a cursive, somewhat stylized manner with a long horizontal stroke extending to the right.

H.A.M. Marsman

Encl.: - amended claims (handwritten and retyped form)  
- PCT Demand Chapter II

EK

## CLAIMS

What is claimed is the following:

1. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:
  - a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level 1% to 15% percent by weight;
  - b) mixing the carbon nanotubes with a high boiling point liquid;
  - c) adding reagents in correct balance to synthesize a lithium salt;
  - d) reacting the mixture at a temperature to form the lithium salt while sonicating the mixture;
  - e) separating the solid discrete carbon nanotube salts from the liquid; and
  - f) drying and annealing the solid discrete carbon nanotube salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.
2. A process for the production of discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, comprising the steps of:
  - a) selecting carbon nanotubes of aspect ratio 10 to 500 and oxidation level of 1% to 15% by weight;
  - b) mixing the carbon nanotubes and a lithium salt in a liquid with surfactant;
  - c) sonicating the liquid carbon nanotube/lithium salt mixture;
  - d) separating the solid salts from the liquid; and
  - e) drying and annealing the solid discrete carbon nanotubes with attached lithium salts under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

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3. A composition useful for lithium ion batteries comprising:  
discrete carbon nanotubes, the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface, wherein the discrete carbon nanotubes have an aspect ratio of 10 to 500 and oxidation levels from 1% to 15% by weight of the carbon nanotube.
4. The composition of claim 3, wherein the crystals or layers of lithium ion active material comprise a lithium metal salt and an element selected from the group consisting of: iron, manganese, cobalt, copper, nickel, vanadium, titanium, and mixtures thereof.
5. The composition of claim 4, wherein the lithium metal salt has an olivine crystal structure.
6. The composition of claim 3, wherein the crystals or layers of lithium ion active material comprise tin, silicon, copper, antimony, aluminum, germanium, titanium, or mixtures thereof.
7. The composition of any one of claims 3-6, further comprising graphene or oxygenated graphene.
8. The composition of claim 7, wherein the weight ratio of graphene to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.
9. The composition of any one of claims 3-8, wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.
10. The composition of any one of claims 3-9, comprising oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are uniformly dispersed

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without clustering on a dimension scale less than 1 micrometer.

11. The composition of any one of claims 3-10, comprising uniformly dispersible oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.
12. The composition of claim 11, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.

15/15

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AMENDED SHEET  
Received at the EPO on Apr 23, 2013 11:56:21. Page 8 of 12

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23/04/2013

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

## PCT

NOTIFICATION CONCERNING INFORMAL  
COMMUNICATIONS WITH THE APPLICANT

(PCT Rule 66.6)

|                                                                                                                                                                                                                                                                                                                      |  |                                                                                                                                                                       |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>To:</b><br><br>Vereenigde<br>Johan De Wittlaan 7<br>2517 JR Den Haag<br>PAYS-BAS                                                                                                                                                                                                                                  |  | <b>Date of mailing</b><br><i>(day/month/year)</i> 24.09.2013                                                                                                          |
| <b>Applicant's or agent's file reference</b><br>P100028PC00                                                                                                                                                                                                                                                          |  | <b>TRANSMITTAL FOR INFORMATION</b>                                                                                                                                    |
| <b>International application No.</b><br>PCT/US2012/043534                                                                                                                                                                                                                                                            |  | <b>International filing date</b> <i>(day/month/year)</i><br>21.06.2012                                                                                                |
| <b>Applicant</b><br>Molecular Rebar Design, LLC                                                                                                                                                                                                                                                                      |  |                                                                                                                                                                       |
| <p>An informal communication took place on <u>13.09.2013</u>, between the International Preliminary Examining Authority and the applicant / the agent.</p> <p>A copy of the note on that communication (Form PCT/IPEA/428) is herewith transmitted for your information.</p>                                         |  |                                                                                                                                                                       |
| <b>Name and mailing address of the international preliminary examining authority:</b><br><br> European Patent Office P.B. 5818 Patentlaan 2<br>NL-2280 HV Rijswijk - Pays Bas<br>Tel. +31 70 340 - 2040<br>Fax: +31 70 340 - 3016 |  | <b>Authorized Officer</b><br><br>Giel-Barragán Ramos<br>Tel. +31 70 340-3046<br> |

Form PCT/IPEA/429 (January 2004)

**PATENT COOPERATION TREATY**  
**PCT**  
**INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY**  
(Chapter II of the Patent Cooperation Treaty)  
(PCT Article 36 and Rule 70)

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                   |                                                                                |                      |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|--------------------------------------------------------------------------------|----------------------|
| Applicant's or agent's file reference<br>P100028PC00                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | <b>FOR FURTHER ACTION</b>                                         |                                                                                | See Form PCT/PEA/416 |
| International application No.<br>PCT/US2012/043534                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | International filing date ( <i>day/month/year</i> )<br>21.06.2012 | Priority date ( <i>day/month/year</i> )<br>23.06.2011                          |                      |
| International Patent Classification (IPC) or national classification and IPC<br>INV. H01M4/62                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                   |                                                                                |                      |
| Applicant<br>Molecular Rebar Design, LLC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                   |                                                                                |                      |
| <p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>6</u> sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p style="margin-left: 20px;">a. <input checked="" type="checkbox"/> <i>sent to the applicant and to the International Bureau</i> a total of <u>6</u> sheets, as follows:</p> <p style="margin-left: 40px;"><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p style="margin-left: 40px;"><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> (<i>sent to the International Bureau only</i>) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see paragraph 3bis of Annex C of the Administrative Instructions).</p> |                                                                   |                                                                                |                      |
| <p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I      Basis of the report</p> <p><input type="checkbox"/> Box No. II      Priority</p> <p><input type="checkbox"/> Box No. III      Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV      Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V      Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI      Certain documents cited</p> <p><input type="checkbox"/> Box No. VII      Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII      Certain observations on the international application</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                   |                                                                                |                      |
| Date of submission of the demand<br><br>23.04.2013                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                   | Date of completion of this report<br><br>24.09.2013                            |                      |
| Name and mailing address of the international preliminary examining authority:<br> European Patent Office P.B. 5818 Patentlaan 2<br>NL-2280 HV Rijswijk - Pays Bas<br>Tel. +31 70 340 - 2040<br>Fax: +31 70 340 - 3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                   | Authorized officer:<br><br>Kelly, Michael<br><br>Telephone No. +31 70 340-8973 |                      |



**PATENT COOPERATION TREATY**  
**PCT**  
**INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY**  
(Chapter II of the Patent Cooperation Treaty)  
(PCT Article 36 and Rule 70)

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                          |                                                                                |                      |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------|--------------------------------------------------------------------------------|----------------------|
| Applicant's or agent's file reference<br>P100028PC00                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | <b>FOR FURTHER ACTION</b>                                |                                                                                | See Form PCT/PEA/416 |
| International application No.<br>PCT/US2012/043534                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | International filing date (day/month/year)<br>21.06.2012 | Priority date (day/month/year)<br>23.06.2011                                   |                      |
| International Patent Classification (IPC) or national classification and IPC<br>INV. H01M4/62                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                          |                                                                                |                      |
| Applicant<br>Molecular Rebar Design, LLC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                          |                                                                                |                      |
| <p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>6</u> sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p style="margin-left: 20px;">a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of <u>6</u> sheets, as follows:</p> <p style="margin-left: 40px;"><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p style="margin-left: 40px;"><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see paragraph 3bis of Annex C of the Administrative Instructions).</p> |                                                          |                                                                                |                      |
| <p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the report</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                          |                                                                                |                      |
| Date of submission of the demand<br><br>23.04.2013                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                          | Date of completion of this report<br><br>24.09.2013                            |                      |
| Name and mailing address of the international preliminary examining authority:<br> European Patent Office P.B. 5818 Patentlaan 2<br>NL-2280 HV Rijswijk - Pays Bas<br>Tel. +31 70 340 - 2040<br>Fax: +31 70 340 - 3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                          | Authorized officer:<br><br>Kelly, Michael<br><br>Telephone No. +31 70 340-8973 |                      |



**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

D1 WO 2010/117392 A1 (BOSNYAK CLIVE P [US]; SWOGGER KURT W [US])  
14 October 2010 (2010-10-14)

D2 US 2011/104551 A1 (YANG JUNBING [US] ET AL) 5 May 2011 (2011-05-05)

**Novelty**

A composition useful for lithium ion batteries comprising: discrete carbon nanotubes, the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface wherein the discrete carbon nanotubes have an aspect ratio of 10 to 500 and oxidation levels from 1 % to 15% by weight of the carbon nanotube is not disclosed in the cited prior art.

The subject matter of independent product claim 3 and independent method claims 1 and 2 are therefore new.

Claims 4-12 are dependent on claim 3. The present application therefore meets the criteria of Article 33(2) PCT, because the subject-matter of claims 1-12 is new.

**Inventive step**

The present application meets the criteria of Article 33(3) PCT, because the subject-matter of claims 1-12 involves an inventive step.

D1 is regarded as being the prior art closest to the subject-matter of independent product claim 3 and discloses: a composition useful for lithium ion batteries comprising: discrete carbon nanotubes (D1: page 15, paragraph 0061), the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface (D1: page 21, paragraph 0082 to page 22, paragraph 0083), wherein the discrete carbon nanotubes have an aspect ratio of 100 to 1000 (D1: page 10, paragraph 0042) and the carbon nanotubes are oxidised (D1: page 6, paragraph 0032).

The document D1 does not disclose carbon nanotubes with oxidation levels of 1% to 15% percent by weight.

The problem to be solved by the subject matter of claim 3 is to provide intimate electron transfer and enhanced mechanical strength of the active material.

Taking into account later-filed evidence provided by the applicant and supporting an inventive step, it is considered not obvious to the skilled person to select carbon nanotubes with oxidation levels of 1% to 15% percent by weight in order to provide intimate electron transfer and enhanced mechanical strength of the active material as it is not disclosed nor suggested in the cited prior art nor is it common knowledge in the technical field to do so.

Therefore the subject matter of claim 3 meets the requirements of the PCT in respect of inventive step.

Dependent claims 4-12 are dependent on claim 3 and as such also meet the requirements of the PCT in respect of inventive step.

D1 is regarded as being the prior art closest to the subject-matter of independent method claims 1 and 2, and discloses a process for the production of the discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the discrete carbon nanotubes have an aspect ratio of 100 to 1000 (D1: page 10, paragraph 0042) and the carbon nanotubes are oxidised (D1: page 6, paragraph 0032), comprising the steps of: mixing the carbon nanotubes with a liquid, reagents to synthesize a lithium salt and a surfactant, reacting the mixture at a temperature to form the lithium salt while sonicating the mixture, separating the solid discrete carbon nanotube salts from the liquid; and drying solid discrete carbon nanotube salts (D1: page 11, paragraph 0049 to page 12, paragraph 0052, page 21, paragraph 0082 to page 22, paragraph 0083 and page 28-29, example 9)

The subject-matter of claims 1 and 2 therefore differ from this known method in that the carbon nanotubes have oxidation levels of 1% to 15% percent by weight and the solid discrete carbon nanotube salts are annealed under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

The problem to be solved by the present invention may therefore be regarded as providing a method to produce improved electrode material for lithium ion batteries.

The solution proposed in claims 1 and 2 of the present application can be considered as involving an inventive step (Article 33(3) PCT) for the following reasons: It is not obvious to the skilled person starting out from D1 to provide a method to produce improved electrode material for lithium ion batteries by selecting carbon nanotubes with oxidation levels of 1% to 15% percent by weight and producing discrete carbon nanotubes having crystals or layers of olivine lithium ion active material attached to

their surface, by annealing under an inert atmosphere at sufficient temperature to obtain the olivine crystal structure, as it is not disclosed nor suggested in the cited prior art nor is it common knowledge to do so.

**Industrial applicability**

The subject matter described in claims 1-12 can find use in industry and is therefore industrially applicable(Article 33(4) PCT).

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

D1 WO 2010/117392 A1 (BOSNYAK CLIVE P [US]; SWOGGER KURT W [US])  
14 October 2010 (2010-10-14)

D2 US 2011/104551 A1 (YANG JUNBING [US] ET AL) 5 May 2011 (2011-05-05)

**Novelty**

A composition useful for lithium ion batteries comprising: discrete carbon nanotubes, the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface wherein the discrete carbon nanotubes have an aspect ratio of 10 to 500 and oxidation levels from 1 % to 15% by weight of the carbon nanotube is not disclosed in the cited prior art.

The subject matter of independent product claim 3 and independent method claims 1 and 2 are therefore new.

Claims 4-12 are dependent on claim 3. The present application therefore meets the criteria of Article 33(2) PCT, because the subject-matter of claims 1-12 is new.

**Inventive step**

The present application meets the criteria of Article 33(3) PCT, because the subject-matter of claims 1-12 involves an inventive step.

D1 is regarded as being the prior art closest to the subject-matter of independent product claim 3 and discloses: a composition useful for lithium ion batteries comprising: discrete carbon nanotubes (D1: page 15, paragraph 0061), the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface (D1: page 21, paragraph 0082 to page 22, paragraph 0083), wherein the discrete carbon nanotubes have an aspect ratio of 100 to 1000 (D1: page 10, paragraph 0042) and the carbon nanotubes are oxidised (D1: page 6, paragraph 0032).

The document D1 does not disclose carbon nanotubes with oxidation levels of 1% to 15% percent by weight.

The problem to be solved by the subject matter of claim 3 is to provide intimate electron transfer and enhanced mechanical strength of the active material.

Taking into account later-filed evidence provided by the applicant and supporting an inventive step, it is considered not obvious to the skilled person to select carbon nanotubes with oxidation levels of 1% to 15% percent by weight in order to provide intimate electron transfer and enhanced mechanical strength of the active material as it is not disclosed nor suggested in the cited prior art nor is it common knowledge in the technical field to do so.

Therefore the subject matter of claim 3 meets the requirements of the PCT in respect of inventive step.

Dependent claims 4-12 are dependent on claim 3 and as such also meet the requirements of the PCT in respect of inventive step.

D1 is regarded as being the prior art closest to the subject-matter of independent method claims 1 and 2, and discloses a process for the production of the discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the discrete carbon nanotubes have an aspect ratio of 100 to 1000 (D1: page 10, paragraph 0042) and the carbon nanotubes are oxidised (D1: page 6, paragraph 0032), comprising the steps of: mixing the carbon nanotubes with a liquid, reagents to synthesize a lithium salt and a surfactant, reacting the mixture at a temperature to form the lithium salt while sonicating the mixture, separating the solid discrete carbon nanotube salts from the liquid; and drying solid discrete carbon nanotube salts (D1: page 11, paragraph 0049 to page 12, paragraph 0052, page 21, paragraph 0082 to page 22, paragraph 0083 and page 28-29, example 9)

The subject-matter of claims 1 and 2 therefore differ from this known method in that the carbon nanotubes have oxidation levels of 1% to 15% percent by weight and the solid discrete carbon nanotube salts are annealed under an inert atmosphere at sufficient temperature to obtain an olivine crystal structure.

The problem to be solved by the present invention may therefore be regarded as providing a method to produce improved electrode material for lithium ion batteries.

The solution proposed in claims 1 and 2 of the present application can be considered as involving an inventive step (Article 33(3) PCT) for the following reasons: It is not obvious to the skilled person starting out from D1 to provide a method to produce improved electrode material for lithium ion batteries by selecting carbon nanotubes with oxidation levels of 1% to 15% percent by weight and producing discrete carbon nanotubes having crystals or layers of olivine lithium ion active material attached to

their surface, by annealing under an inert atmosphere at sufficient temperature to obtain the olivine crystal structure, as it is not disclosed nor suggested in the cited prior art nor is it common knowledge to do so.

**Industrial applicability**

The subject matter described in claims 1-12 can find use in industry and is therefore industrially applicable(Article 33(4) PCT).

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/US2012/043534

**Box No. I Basis of the report**

1. With regard to the **language**, this report is based on
  - ☒ the international application in the language in which it was filed
  - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
    - ☐ international search (under Rules 12.3(a) and 23.1(b))
    - ☐ publication of the international application (under Rule 12.4(a))
    - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a))
2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

**Description, Pages**

1-12 as originally filed

**Claims, Numbers**

1-12 filed with telefax on 23-04-2013

**Drawings, Sheets**

1/3-3/3 as originally filed

- ☐ a sequence listing - see Supplemental Box Relating to Sequence Listing.

3. ☒ The amendments have resulted in the cancellation of:
  - ☐ the description, pages
  - ☒ the claims, Nos. 13
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-bis)):
  - ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
5. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 70.2 (e)).
6. ☐ Supplementary international search report(s) from Authority(ies) have been received and taken into account in drawing up this report (Rule 45bis.8(b) and (c)).

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/US2012/043534

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

---

1. Statement

|                               |             |             |
|-------------------------------|-------------|-------------|
| Novelty (N)                   | Yes: Claims | <u>1-12</u> |
|                               | No: Claims  |             |
| Inventive step (IS)           | Yes: Claims | <u>1-12</u> |
|                               | No: Claims  |             |
| Industrial applicability (IA) | Yes: Claims | <u>1-12</u> |
|                               | No: Claims  |             |

2. Citations and explanations (Rule 70.7):

see separate sheet

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/US2012/043534

**Box No. I Basis of the report**

1. With regard to the **language**, this report is based on
  - ☒ the international application in the language in which it was filed
  - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
    - ☐ international search (under Rules 12.3(a) and 23.1(b))
    - ☐ publication of the international application (under Rule 12.4(a))
    - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a))
2. With regard to the **elements\*** of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):

**Description, Pages**

1-12 as originally filed

**Claims, Numbers**

1-12 filed with telefax on 23-04-2013

**Drawings, Sheets**

1/3-3/3 as originally filed

- ☐ a sequence listing - see Supplemental Box Relating to Sequence Listing.

3. ☒ The amendments have resulted in the cancellation of:
  - ☐ the description, pages
  - ☒ the claims, Nos. 13
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-bis)):
  - ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
5. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 70.2 (e)).
6. ☐ Supplementary international search report(s) from Authority(ies) have been received and taken into account in drawing up this report (Rule 45bis.8(b) and (c)).

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/US2012/043534

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

---

1. Statement

|                               |             |             |
|-------------------------------|-------------|-------------|
| Novelty (N)                   | Yes: Claims | <u>1-12</u> |
|                               | No: Claims  |             |
| Inventive step (IS)           | Yes: Claims | <u>1-12</u> |
|                               | No: Claims  |             |
| Industrial applicability (IA) | Yes: Claims | <u>1-12</u> |
|                               | No: Claims  |             |

2. Citations and explanations (Rule 70.7):

see separate sheet

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

## PCT

NOTIFICATION CONCERNING  
DOCUMENTS TRANSMITTED

To:

**The International Bureau of WIPO**  
34, chemin des Colombettes  
CH - 1211 Geneva 20  
Switzerland

Date of mailing  
(day/month/year)

24.09.2013

International application No: PCT/US2012/043534

This International Preliminary Examining Authority transmits herewith the following documents:

1. ☐ demand (Rule 61.1(a)).
2. ☒ copy of the international preliminary examination report and its annexes (Rule 71.1).
3. ☐ \_\_\_\_\_ other documents (*specify*):

Name and mailing address of the international  
preliminary examining authority:



European Patent Office P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk - Pays Bas  
Tel. +31 70 340 - 2040  
Fax: +31 70 340 - 3016

Authorized Officer

Giel-Barragán Ramos

Tel. +31 70 340-3046



Form PCT/IPEA/415 (January 2004)

Vertrag über die internationale Zusammenarbeit auf dem Gebiet des Patentwesens  
Patent Cooperation Treaty  
Traité de coopération en matière de brevets

**PCT**

Application No.:

PCT/US2012/043534

**Note on an informal communication by telephone with the Applicant**

A copy of this note is being sent to the Applicant for information

**Participants**

Applicant: Molecular Rebar Design, LLC

Representative: Harrie Marsman

Examiner(s): Kelly, Michael

**Summary of the communication**

See Separate Sheet



13.09.2013

.....  
Date

Kelly, Michael

.....  
Authorized officer of IPEA

Enclosure(s):

**Vertrag über die Internationale Zusammenarbeit auf dem Gebiet des Patentwesens  
Patent Cooperation Treaty  
Traité de coopération en matière de brevets**

**PCT**

Application number:

US2012/043534

The telephone consultation was attended by Michael Kelly (examiner), Harrie Marsman (agent) and Dr. Stephen Krupp (chief patent counsel of applicant).

Mr. Marsman spoke on behalf of the applicant. Dr. Krupp listened to the telephone consultation.

The discussion concerned inventive step with regard to claim 3.

The agent, referring to later filed evidence from his communication of 10.09.2013, discussed why D1 was the closest prior art and why D2 was further away from the claimed subject matter. With continued reference to the later filed evidence, the agent provided his reasoning for an inventive step with regard to claim 3.

The examiner, taking D1 as the closest prior art, and in light of the later filed evidence concluded that the subject matter of claim 3 involves an inventive step.

The examiner will dispatch a positive International Preliminary Examination Report.

# PATENT COOPERATION TREATY

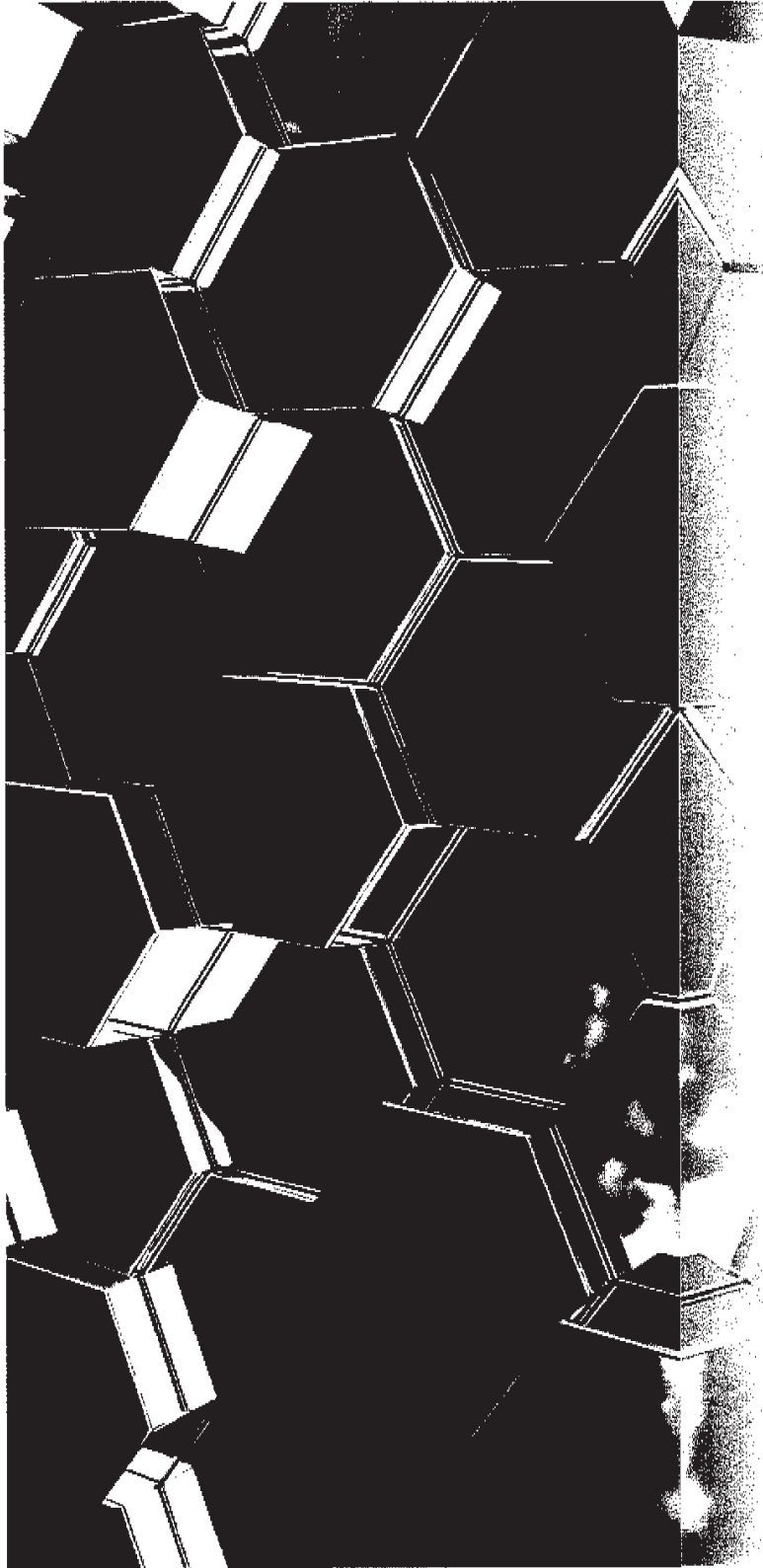
From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

## PCT

### NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (PCT Rule 71.1)

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                 |                                                                                                                                                                               |  |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|
| <b>To:</b><br><br>Vereenigde<br>Johan De Wittlaan 7<br>2517 JR Den Haag<br>PAYS-BAS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                 | <b>Date of mailing</b><br>(day/month/year) 24.09.2013                                                                                                                         |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                 | <b>Applicant's or agent's file reference</b><br>P100028PC00                                                                                                                   |  |
| <b>Applicant's or agent's file reference</b><br>P100028PC00                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                 | <b>IMPORTANT NOTIFICATION</b>                                                                                                                                                 |  |
| <b>International application No.</b><br>PCT/US2012/043534                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | <b>International filing date (day/month/year)</b><br>21.06.2012 | <b>Priority date (day/month/year)</b><br>23.06.2011                                                                                                                           |  |
| <b>Applicant</b><br>Molecular Rebar Design, LLC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                 |                                                                                                                                                                               |  |
| <p>1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.</p> <p>2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.</p> <p>3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.</p> <p>4. <b>REMINDER</b></p> <p>The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).</p> <p>Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.</p> <p>For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.</p> <p>The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.</p> |                                                                 |                                                                                                                                                                               |  |
| <b>Name and mailing address of the international preliminary examining authority:</b><br><br> European Patent Office P.B. 5818 Patentlaan 2<br>NL-2280 HV Rijswijk - Pays Bas<br>Tel. +31 70 340 - 2040<br>Fax: +31 70 340 - 3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                 | <b>Authorized Officer</b><br><br>Giel-Barragán Ramos<br><br>Tel. +31 70 340-3046<br><br> |  |

Form PCT/PEA/416 (January 2004)



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**European Patent Office**

**Sept 13, 2013**

Duration: 10.09.2013 16:41:42 - 10.09.2013 16:42:53. This page 4 of 9 was completed at 10.09.2013 16:42:10  
Received at the EPO on Sep 10, 2013 16:42:53. Page 4 of 9

**Ref D1. WO 2010/117392****EXFOLIATED CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM**

- ◆ *Claim 1. A composition comprising exfoliated carbon nanotubes, wherein the exfoliated carbon nanotubes are not dispersed in a continuous matrix that maintains the carbon nanotubes in an exfoliated state.*
- ◆ *Claim 2. The composition of claim 1, wherein the composition comprises a mat of exfoliated carbon nanotubes.*
- ◆ *Relates to a mat of unentangled tubes of a range of aspect ratios*
- ◆ *Nanocrystals added to get the cluster of tubes unentangled (they act as amplifiers for sonication vibration), then the nanocrystals are separated from tubes*
- ◆ *Level of Oxidation not recognized as being important to control amount of attachment of crystals to the tube surface*

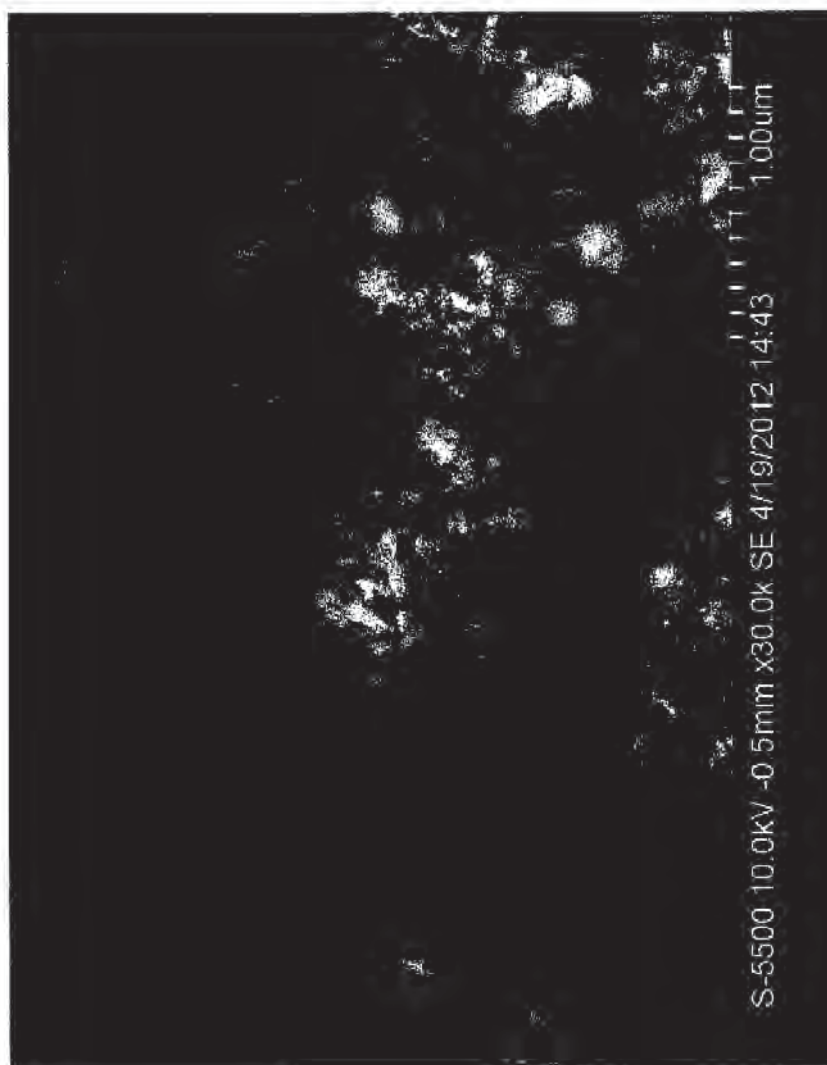
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9/10/2013

2

## Example of $\text{LiMnPO}_4$ nanocrystals attached to carbon nanotubes described in PCT/US2012/043534



The tubes are discrete, well separated, and not as a mat. They are not aligned

The tubes have about 4% oxidation

9/10/2013

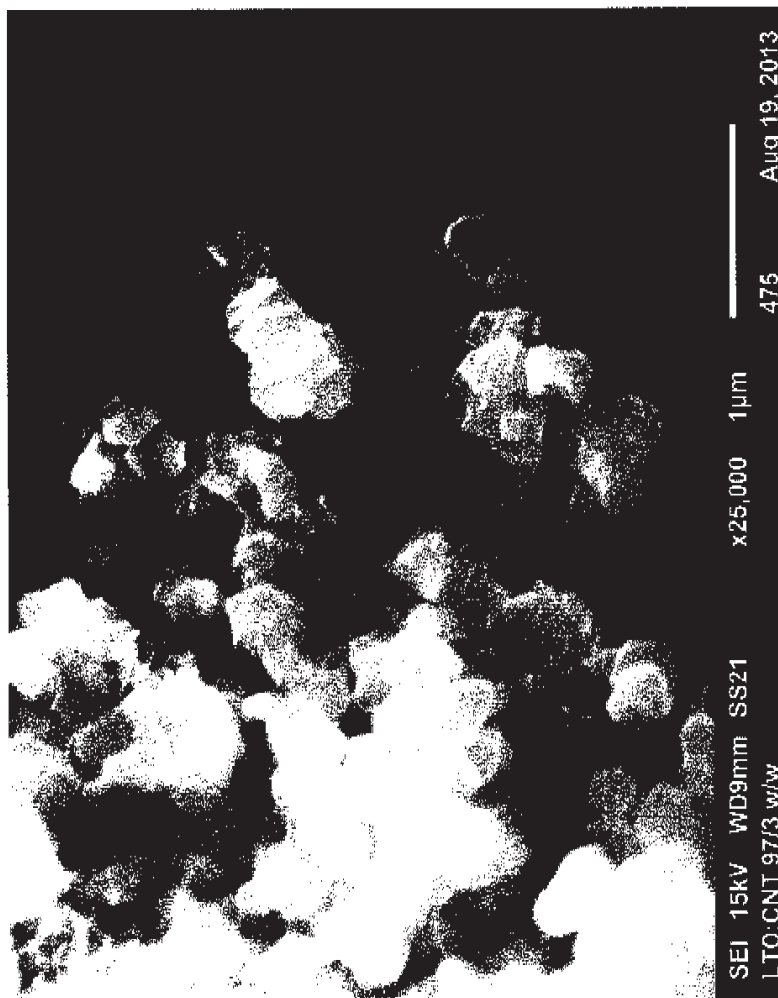
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## Lithium titanate + discrete tubes of invention described in PCT/US2012/043534

Example of a Lithium titanate,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  crystals with attached discrete tubes having about 2% wt oxidation



Clearly there are segments of tubes with attachment to the crystals and other segments that simply bridge the crystals with no crystal attachments. The level of oxidation allows control of the degree of binding of the crystals

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# Claims for range of oxidation

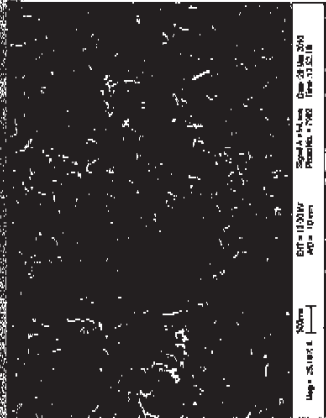
- ◆ The degree of oxidation was discovered to control the amount of tethered nanocrystals and uniformity of their coverage.
- ◆ Above 15% wt oxidation the tube walls become severely damaged and much impair strength & conductivity
- ◆ Below 1% oxidation the degree of attachment of nanocrystals is very low
- ◆ The ability to use levels of oxidation to control the morphology was not recognized in WO 2010/117392

Increasing oxidation level on tubes

8% wt

4% wt

2% wt



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5

# International Patent Application No. PCT/US2011/104551 Yan Yunbing et al.

*"The aligned nanotubular base material preferably comprises a material selected from the group consisting of a conductive organic polymer, a conductive or semiconductive inorganic material, or a combination thereof"*

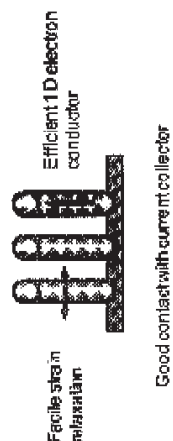


FIG. 1

- Tubes are not dispersible since it is taught they are grown from and attached to the base silicon or copper which is commonly known to grow an array of tubes
- The invention is for use as an anode only.
- The invention is for a layer of a lithium ion alloying (i.e. new chemical structure) like silicon, not lithium salts which reversibly incorporate Lithium ions without forming an alloy or new chemical structure.

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European Patent Office  
P.O. Box 5818  
Patentlaan 2  
2280 HV Rijswijk (ZH)

**PER TELEFAX**  
**070-3403016**

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Johan de Wittlaan 7  
P.O. Box 87930  
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Telefax +31 70 416 67 99

H.Marsman@vo.eu  
www.vo.eu

Your ref. PCT/US2012/043534/  
Our ref. MAS/P100028PC00

The Hague,  
10 September 2013

Re: International Patent Application No. PCT/US2012/043534  
Designed NanoTubes, LLC

**URGENT - IN THE HANDS OF MR KELLY**  
**TELEPHONIC INTERVIEW ON FRIDAY 13. 2013**

5

With reference to the Notification dated September 9, 2013, and with thanks for  
allowing a telephonic interview coming Friday, September 13, 2013, I enclose a short  
10 power point presentation, wherein the differences between the subject-matter of  
presently pending claim 3 and D1 and D2 are illustrated.

For the question of inventive step, I believe that D1 forms the closest prior art. It  
teaches carbon nanotubes of the same origin as used as starting compound in the  
15 present application.

On slide 2 of the power point presentation, Inventor Bosnyak observes what a skilled  
person understands from D1. After copying the words of claims 1 and 2 of D1, he notes  
that in fact D1 teaches mats of unentangled tubes of a range of aspect ratios.

Page 2  
Your ref. PCT/US2012/043534/  
Our ref. MAS/P100028PC00  
Date 10 September 2013



In the preparation of the unentangled tubes use is made of nanocrystals and the role of these crystals is as amplifiers for sonication vibration.

- 5 D1 does not put any emphasis on specific degrees of oxidation and is very general to any aspect ratios. That is, D1 does not teach nor suggest nanotubes having the oxidation levels required by claim 3. No technical effects are associated with these concepts in D1, and there are no pointers to the subject-matter of present claim 3.
- 10 You refer to paragraph [0082] of D1 and state that "the discrete carbon nanotubes having crystals or layers of lithium ion active material attached to their surface" and that "D1 discloses that the lithium ion active material can be "for example SnO<sub>2</sub>, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, silicon nanotubes, silicon nanoparticles and various combinations thereof".
- 15 Said paragraph does not explicitly make these statements. It seems that you have read this paragraph with the present invention in your mind. Especially, said paragraph does not teach that crystals or layers of lithium active material are present; it does not state that such crystals or layers are present on the surface; and it does not use the phrase "lithium ion active material". In D1, the only reference to a lithium compound is
- 20 Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>.

The invention is illustrated in slides 3-5, focusing especially on the oxidation levels.

- D2 is discussed at slide 6. It is considerably further away from the claimed subject-
- 25 matter than D1.

The telephonic interview will be attended by the undersigned (speaking), Dr Stephen P. Krupp, chief patent counsel of Molecular Rebar Design LLC (listening), Dr Amy Dunstan, U.S. patent attorney of Jackson Walker L.L.P. (listening), and possibly Dr

Page 3  
Your ref. PCT/US2012/043534/  
Our ref. MAS/P100028PC00  
Date 10 September 2013



Clive Bosnyak, inventor. I will inform you of the telephone details in a separate message.

The Agent,

A handwritten signature in black ink, appearing to read 'H.A.M. Marsman'. The signature is written over the printed name 'H.A.M. Marsman'.

H.A.M. Marsman

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

## PCT

NOTIFICATION CONCERNING INFORMAL  
COMMUNICATIONS WITH THE APPLICANT

(PCT Rule 66.6)

|                                                                                                                                                                                                                                                                                                                      |  |                                                                                                                                                                             |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>To:</b><br><br>Vereenigde<br>Johan De Wittlaan 7<br>2517 JR Den Haag<br>PAYS-BAS                                                                                                                                                                                                                                  |  | <b>Date of mailing</b><br><i>(day/month/year)</i> 09.09.2013                                                                                                                |
| <b>Applicant's or agent's file reference</b><br>P100028PC00                                                                                                                                                                                                                                                          |  | <b>TRANSMITTAL FOR INFORMATION</b>                                                                                                                                          |
| <b>International application No.</b><br>PCT/US2012/043534                                                                                                                                                                                                                                                            |  | <b>International filing date</b> <i>(day/month/year)</i><br>21.06.2012                                                                                                      |
| <b>Applicant</b><br>Molecular Rebar Design, LLC                                                                                                                                                                                                                                                                      |  |                                                                                                                                                                             |
| <p>An informal communication took place on <u>03.09.2013</u>, between the International Preliminary Examining Authority and the applicant / the agent.</p> <p>A copy of the note on that communication (Form PCT/IPEA/428) is herewith transmitted for your information.</p>                                         |  |                                                                                                                                                                             |
| <b>Name and mailing address of the international preliminary examining authority:</b><br><br> European Patent Office P.B. 5818 Patentlaan 2<br>NL-2280 HV Rijswijk - Pays Bas<br>Tel. +31 70 340 - 2040<br>Fax: +31 70 340 - 3016 |  | <b>Authorized Officer</b><br><br>Smits, Anne-Marie<br><br>Tel. +31 70 340-3596<br><br> |

Form PCT/IPEA/429 (January 2004)

Vertrag über die internationale Zusammenarbeit auf dem Gebiet des Patentwesens  
Patent Cooperation Treaty  
Traité de coopération en matière de brevets

**PCT**

Application No.:

PCT/US2012/043534

**Note on an informal communication by telephone with the Applicant**

No extension of time limit is granted and the time limit remains as previously set

**Participants**

Applicant: Molecular Rebar Design, LLC

Representative: Harrie Marsman

Examiner(s): Kelly, Michael

**Summary of the communication**

See Separate Sheet



03.09.2013

.....  
Date

Kelly, Michael

.....  
Authorized officer of IPEA

Enclosure(s):

**Vertrag über die Internationale Zusammenarbeit auf dem Gebiet des Patentwesens  
Patent Cooperation Treaty  
Traité de coopération en matière de brevets**

**PCT**

Application number:

US2012/043534

A telephone consultation has been arranged to take place on the 13.09.2013 at 15:00.

The applicant will send in advance of the telephone consultation additional documentation and amended claims if applicable to the examiner.

The following item will be discussed:

Inventive step.

Copy for (IPEA-EP) 34  
PATENT COOPERATION TREATY

PCT/US2012/043534

From the INTERNATIONAL BUREAU

**PCT**

NOTIFICATION OF THE RECORDING  
OF A CHANGE

(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

|                                                                                                                           |
|---------------------------------------------------------------------------------------------------------------------------|
| To:                                                                                                                       |
| DUNSTAN, Amy, Ulfers<br>Jackson Walker L.L.P.<br>901 Main Street, Suite 6000<br>Dallas, TX 75202<br>ETATS-UNIS D'AMERIQUE |

|                                                                 |                                                                         |
|-----------------------------------------------------------------|-------------------------------------------------------------------------|
| Date of mailing (day/month/year)<br>16 August 2013 (16.08.2013) |                                                                         |
| Applicant's or agent's file reference<br>DENA-0008WO            | IMPORTANT NOTIFICATION                                                  |
| International application No.<br>PCT/US2012/043534              | International filing date (day/month/year)<br>21 June 2012 (21.06.2012) |

|                                                                                                                        |                                                                                       |                                                                               |                                                                                 |
|------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| 1. The following indications appeared on record concerning:                                                            |                                                                                       |                                                                               |                                                                                 |
| <input checked="" type="checkbox"/> the applicant                                                                      | <input type="checkbox"/> the inventor                                                 | <input type="checkbox"/> the agent                                            | <input type="checkbox"/> the common representative                              |
| Name and Address<br>DESIGNED NANOTUBES, LLC<br>4211 Waters Edge Cove<br>Austin, TX 78731<br>United States of America   |                                                                                       | State of Nationality<br>US                                                    | State of Residence<br>US                                                        |
|                                                                                                                        |                                                                                       | Telephone No.<br>512-394-0922                                                 |                                                                                 |
|                                                                                                                        |                                                                                       | Facsimile No.                                                                 |                                                                                 |
|                                                                                                                        |                                                                                       | E-mail address                                                                |                                                                                 |
| 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:      |                                                                                       |                                                                               |                                                                                 |
| <input type="checkbox"/> the person                                                                                    | <input checked="" type="checkbox"/> the name                                          | <input checked="" type="checkbox"/> the address                               | <input type="checkbox"/> the nationality <input type="checkbox"/> the residence |
| Name and Address<br>MOLECULAR REBAR DESIGN, LLC<br>13477 Fitzhugh Road<br>Austin, TX 78736<br>United States of America |                                                                                       | State of Nationality<br>US                                                    | State of Residence<br>US                                                        |
|                                                                                                                        |                                                                                       | Telephone No.<br>512-394-0922                                                 |                                                                                 |
|                                                                                                                        |                                                                                       | Facsimile No.                                                                 |                                                                                 |
|                                                                                                                        |                                                                                       | E-mail address<br><input type="checkbox"/> Notifications by e-mail authorized |                                                                                 |
| 3. Further observations, if necessary:                                                                                 |                                                                                       |                                                                               |                                                                                 |
| 4. A copy of this notification has been sent to:                                                                       |                                                                                       |                                                                               |                                                                                 |
| <input checked="" type="checkbox"/> the receiving Office                                                               | <input checked="" type="checkbox"/> the International Preliminary Examining Authority |                                                                               |                                                                                 |
| <input type="checkbox"/> the International Searching Authority                                                         | <input type="checkbox"/> the designated Offices concerned                             |                                                                               |                                                                                 |
| <input type="checkbox"/> the Authority(ies) specified for supplementary search                                         | <input checked="" type="checkbox"/> the elected Offices concerned                     |                                                                               |                                                                                 |
|                                                                                                                        | <input type="checkbox"/> other:                                                       |                                                                               |                                                                                 |

|                                                                                               |                                      |
|-----------------------------------------------------------------------------------------------|--------------------------------------|
| The International Bureau of WIPO<br>34, chemin des Colombettes<br>1211 Geneva 20, Switzerland | Authorized officer<br>Beard Nathalie |
| Facsimile No. +41 22 338 89 70                                                                | e-mail pt06.pct@wipo.int             |
|                                                                                               | Telephone No. +41 22 338 74 06       |

Form PCT/IB/306 (January 2009)

1/FA3LS9JA99AHC0

## PCT

(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

DUNSTAN, Amy, Ulfers  
Jackson Walker L.L.P.  
901 Main Street, Suite 6000  
Dallas, TX 75202  
ETATS-UNIS D'AMERIQUE

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------|--|---------------|--|-------------------------------------------------------------------------------|--|
| Date of mailing (day/month/year)<br><b>16 August 2013 (16.08.2013)</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| Applicant's or agent's file reference<br><b>DENA-0008WO</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                            | <b>IMPORTANT NOTIFICATION</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| International application No.<br><b>PCT/US2012/043534</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                                                                                                                                            | International filing date (day/month/year)<br><b>21 June 2012 (21.06.2012)</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| 1. The following indications appeared on record concerning:<br><input checked="" type="checkbox"/> the applicant <input type="checkbox"/> the inventor <input type="checkbox"/> the agent <input type="checkbox"/> the common representative                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| Name and Address<br><b>DESIGNED NANOTUBES, LLC</b><br><b>4211 Waters Edge Cove</b><br><b>Austin, TX 78731</b><br><b>United States of America</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            | <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;">           State of Nationality<br/> <div style="text-align: center;"><b>US</b></div> </td> <td style="width: 50%; padding: 5px;">           State of Residence<br/> <div style="text-align: center;"><b>US</b></div> </td> </tr> <tr> <td colspan="2" style="padding: 5px;">           Telephone No.<br/> <b>512-394-0922</b> </td> </tr> <tr> <td colspan="2" style="padding: 5px;">           Facsimile No.         </td> </tr> <tr> <td colspan="2" style="padding: 5px;">           E-mail address         </td> </tr> </table>                                                                  |  | State of Nationality<br><div style="text-align: center;"><b>US</b></div>                                                                                                                                     | State of Residence<br><div style="text-align: center;"><b>US</b></div>                                                                                                                                                                                     | Telephone No.<br><b>512-394-0922</b> |  | Facsimile No. |  | E-mail address                                                                |  |
| State of Nationality<br><div style="text-align: center;"><b>US</b></div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | State of Residence<br><div style="text-align: center;"><b>US</b></div>                                                                                                                                                                                     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| Telephone No.<br><b>512-394-0922</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| Facsimile No.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| E-mail address                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:<br><input type="checkbox"/> the person <input checked="" type="checkbox"/> the name <input checked="" type="checkbox"/> the address <input type="checkbox"/> the nationality <input type="checkbox"/> the residence                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| Name and Address<br><b>MOLECULAR REBAR DESIGN, LLC</b><br><b>13477 Fitzhugh Road</b><br><b>Austin, TX 78736</b><br><b>United States of America</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                            | <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;">           State of Nationality<br/> <div style="text-align: center;"><b>US</b></div> </td> <td style="width: 50%; padding: 5px;">           State of Residence<br/> <div style="text-align: center;"><b>US</b></div> </td> </tr> <tr> <td colspan="2" style="padding: 5px;">           Telephone No.<br/> <b>512-394-0922</b> </td> </tr> <tr> <td colspan="2" style="padding: 5px;">           Facsimile No.         </td> </tr> <tr> <td colspan="2" style="padding: 5px;">           E-mail address<br/> <input type="checkbox"/> Notifications by e-mail authorized         </td> </tr> </table> |  | State of Nationality<br><div style="text-align: center;"><b>US</b></div>                                                                                                                                     | State of Residence<br><div style="text-align: center;"><b>US</b></div>                                                                                                                                                                                     | Telephone No.<br><b>512-394-0922</b> |  | Facsimile No. |  | E-mail address<br><input type="checkbox"/> Notifications by e-mail authorized |  |
| State of Nationality<br><div style="text-align: center;"><b>US</b></div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | State of Residence<br><div style="text-align: center;"><b>US</b></div>                                                                                                                                                                                     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| Telephone No.<br><b>512-394-0922</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| Facsimile No.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| E-mail address<br><input type="checkbox"/> Notifications by e-mail authorized                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| 3. Further observations, if necessary:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| 4. A copy of this notification has been sent to: <table style="width: 100%; margin-top: 10px;"> <tr> <td style="width: 50%; vertical-align: top;"> <input checked="" type="checkbox"/> the receiving Office<br/> <input type="checkbox"/> the International Searching Authority<br/> <input type="checkbox"/> the Authority(ies) specified for supplementary search         </td> <td style="width: 50%; vertical-align: top;"> <input checked="" type="checkbox"/> the International Preliminary Examining Authority<br/> <input type="checkbox"/> the designated Offices concerned<br/> <input checked="" type="checkbox"/> the elected Offices concerned<br/> <input type="checkbox"/> other:         </td> </tr> </table> |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  | <input checked="" type="checkbox"/> the receiving Office<br><input type="checkbox"/> the International Searching Authority<br><input type="checkbox"/> the Authority(ies) specified for supplementary search | <input checked="" type="checkbox"/> the International Preliminary Examining Authority<br><input type="checkbox"/> the designated Offices concerned<br><input checked="" type="checkbox"/> the elected Offices concerned<br><input type="checkbox"/> other: |                                      |  |               |  |                                                                               |  |
| <input checked="" type="checkbox"/> the receiving Office<br><input type="checkbox"/> the International Searching Authority<br><input type="checkbox"/> the Authority(ies) specified for supplementary search                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | <input checked="" type="checkbox"/> the International Preliminary Examining Authority<br><input type="checkbox"/> the designated Offices concerned<br><input checked="" type="checkbox"/> the elected Offices concerned<br><input type="checkbox"/> other: |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| The International Bureau of WIPO<br>34, chemin des Colombettes<br>1211 Geneva 20, Switzerland                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                                                                                                                                            | Authorized officer<br><div style="text-align: right; font-weight: bold; font-size: 1.2em;">Beard Nathalie</div> e-mail pt06.pct@wipo.int<br>Telephone No. +41 22 338 74 06                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |
| Facsimile No. +41 22 338 89 70                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                                                                                                                                                              |                                                                                                                                                                                                                                                            |                                      |  |               |  |                                                                               |  |

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

# PCT

To:  
JANSEN, C.M.  
Vereenigde  
Johan De Wittlaan 7  
2517 JR Den Haag  
PAYS-BAS

## COMMUNICATION REGARDING EXTENSION OF TIME LIMIT

(PCT Rules 60.1(a) and 66.2(d))

Date of mailing  
(day/month/year) 01-08-2013

Applicant's or agent's file reference  
P100028PC00

### IMPORTANT COMMUNICATION

International application No.  
PCT/US2012/043534

International filing date (day/month/year)  
21 June 2012 (21-06-2012)

Applicant  
Designed Nanotubes, LLC et al.

1. In response of the applicant's request of 29.07.13, by phone, the time limit for replying to:

☒ the second written opinion

☐ (other) \_\_\_\_\_

has been extended as follows:

☒ extension of 1 months/days from 19.08.13

☒ extension until 19 September 2013 (19-09-2013)

2. ☐ No extension of the time limit is granted and the time limit remains as previously set.

Name and mailing address of the IPEA



European Patent Office  
D-80298 Munich  
Tel: (+49-89) 2399-0  
Fax: (+49-89) 2399-4465

Authorized officer

Smits, Anne-Marie  
Tel: (+31-70)340-3596



Form PCT/IPEA/427 (July 1992); reprint January 2004)

From the INTERNATIONAL BUREAU

**PCT**

## NOTIFICATION OF ELECTION

(PCT Article 31(7) and Rule 61.2)

To:

European Patent Office  
Postbus 5818  
Patentlaan 2  
NL-2280 HV RIJSWIJK  
PAYS-BAS  
in its capacity as elected Office

|                                                                                  |                                                                      |
|----------------------------------------------------------------------------------|----------------------------------------------------------------------|
| Date of mailing ( <i>day/month/year</i> )<br>27 June 2013 (27.06.2013)           |                                                                      |
| International application No.<br>PCT/US2012/043534                               | Applicant's or agent's file reference<br>DENA-0008WO                 |
| International filing date ( <i>day/month/year</i> )<br>21 June 2012 (21.06.2012) | Priority date ( <i>day/month/year</i> )<br>23 June 2011 (23.06.2011) |
| Applicant<br>DESIGNED NANOTUBES, LLC et al                                       |                                                                      |

1. The designated Office is hereby notified of its election made in the demand filed with the International Preliminary Examining Authority on:

23 April 2013 (23.04.2013)

2. The election ☒ was  
☐ was not

made before the expiration of 19 months from the priority date (PCT Article 39(1)(a)).

|                                                                                               |                                            |
|-----------------------------------------------------------------------------------------------|--------------------------------------------|
| The International Bureau of WIPO<br>34, chemin des Colombettes<br>1211 Geneva 20, Switzerland | Authorized officer<br>Agnès Wittmann-Regis |
| Facsimile No. +41 22 338 82 70                                                                | e-mail: pt06.pct@wipo.int                  |

Form PCT/TB/331 (January 2004)

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

Vereenigde  
Johan De Wittlaan 7  
2517 JR Den Haag  
PAYS-BAS

## PCT

WRITTEN OPINION OF THE  
INTERNATIONAL PRELIMINARY  
EXAMINING AUTHORITY  
(PCT Rule 66)

|                                     |            |
|-------------------------------------|------------|
| Date of mailing<br>(day/month/year) | 19.06.2013 |
|-------------------------------------|------------|

Applicant's or agent's file reference  
P100028PC00

**REPLY DUE** within 2 month(s)  
from the above date of mailing

International application No.  
PCT/US2012/043534

International filing date (day/month/year)  
21.06.2012

Priority date (day/month/year)  
23.06.2011

International Patent Classification (IPC) or both national classification and IPC  
INV. H01M4/62

Applicant  
Designed Nanotubes, LLC

1. ☒ The written opinion established by the International Searching Authority:  

☒ is ☐ is not  
 considered to be a written opinion of the International Preliminary Examining Authority.
2. This second opinion contains indications relating to the following items:
 

☒ Box No. I Basis of the opinion  
☐ Box No. II Priority  
☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability  
☐ Box No. IV Lack of unity of invention  
☒ Box No. V Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement  
☐ Box No. VI Certain documents cited  
☐ Box No. VII Certain defects in the international application  
☐ Box No. VIII Certain observations on the international application
3. The applicant is hereby **invited to reply** to this opinion.  
  

**When?** See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(e).

**How?** By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 55.3 and 66.8.

**Also:** For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4bis. For an informal communication with the examiner, see Rule 66.6. For an additional opportunity to submit amendments, see Rule 66.4.

**If no reply is filed,** the international preliminary examination report will be established on the basis of this opinion.
4. The final date by which the international preliminary report on patentability (Chapter II of the PCT) must be established according to Rule 69.2 is: 23.10.2013

Name and mailing address of the international preliminary examining authority:

European Patent Office P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk - Pays Bas  
Tel. +31 70 340 - 2040  
Fax: +31 70 340 - 3016

Authorized Officer

Kelly, Michael

Telephone No. +31 70 340-8973

