

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

[0001] 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, 2011, the entire content of which is hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] 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 materials attached to their surface.

BACKGROUND

[0003] 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 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, LiFePO_4 or lithium manganese phosphate, LiMnPO_4 , operate at higher charge and discharge rates, but are still limited by low electrical conductivity and the kinetics of Li-ion diffusion.

[0004] 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

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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.

[0005] 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.

[0006] 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 nanosized crystals or nanosized layers of lithium ion active material to the surface of discrete, functionalized and well dispersed carbon nanotubes.

[0007] 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 improved capacity, electron and ion conductivity and mechanical strength.

[0008] 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 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 region.

SUMMARY

[0009] One aspect of the 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. For a cathode, the lithium ion active material comprises a lithium metal salt which may further comprise iron, manganese, cobalt, copper, nickel, vanadium, 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 grapheme to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.

[0010] 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.

[0011] 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,
- 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.

[0012] 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%.

[0013] 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.

[0014] 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.

BRIEF DESCRIPTION OF THE FIGURES

[0015] Figure 1 depicts lithium salt coated as a nanolayer on discrete carbon nanotubes.

[0016] Figure 2 shows LiMnO_4 with 5% oxidized carbon nanotubes of this invention.

[0017] Figure 3 shows titanium dioxide crystals attached to discrete carbon nanotubes.

DETAILED DESCRIPTION

[0018] The term “carbon nanotubes” as used herein refers to allotropes of carbon with a cylindrical nanostructure. The nanotubes may be single, double or multiwall.

[0019] The term “discrete carbon nanotubes” as used herein refers to carbon nanotubes capable of being separated to give individual tubes.

[0020] The term “graphene” as used herein refers to individual atomic thickness plates of carbon.

[0021] 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.

[0022] 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.

[0023] 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 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.

[0024] During the process of making discrete carbon nanotubes (which can be 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. 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 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

[0025] The ion active material which can be attached to the discrete carbon 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 migratable ions. Other migratable ions can include magnesium, aluminium, iron, zinc, manganese, sodium, potassium, lead, mercury, silver, gold, nickel, cadmium and the like.

[0026] Examples of ion active materials are lithium iron phosphate, lithium manganese phosphate, lithium cobalt oxide, silica, manganese dioxide, cadmium, titanium dioxide and carbon.

[0027] 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 is preferred that the lithium ions comprise the majority of the ions of the mixture. 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 Fe^{2+} or Fe^{3+} .

[0028] When mixing ion active materials for attachment to the carbon 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).

[0029] 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

[0030] 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

[0031] 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

[0032] 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*.

[0033] 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

[0034] 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

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[0035] 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.

[0036] 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 TiO₂-oxidized carbon nanotube composition from titanium isopropoxide as a precursor

[0037] 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

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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 or layers of lithium ion active material attached to their surface.
2. The composition of claim 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.
3. The composition of claim 2, wherein the lithium metal salt has an olivine 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.
5. The composition of claim 1, 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.
6. The composition of claim 1, further comprising graphene or oxygenated graphene.
7. The composition of claim 6, wherein the weight ratio of graphene to carbon nanotube is in the range of 0.1:99.9 to 99.9:0.1.
8. A process for the production of the 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;

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- 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.
9. A process for the production of the 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.
10. A composition useful for lithium ion batteries, comprising discrete carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface, wherein the carbon nanotubes are in a weight ratio of carbon nanotubes to lithium salts of 0.1% to 10%.
11. A composition useful for lithium ion batteries, 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
12. A composition useful for lithium ion batteries, comprising uniformly dispersible oxidized carbon nanotubes having crystals or layers of lithium ion active materials attached to their surface.
13. The composition of claim 12, wherein the crystals or layers of lithium ion active materials are chemically attached to the surface of the dispersible oxidized carbon nanotubes.

ABSTRACT

[0038] Compositions, and methods of obtaining them, useful for lithium ion batteries comprising discrete oxidized carbon nanotubes having attached to their surface lithium ion active materials in the form of nanometer sized crystals or layers. The composition can further comprise graphene or oxygenated graphene.

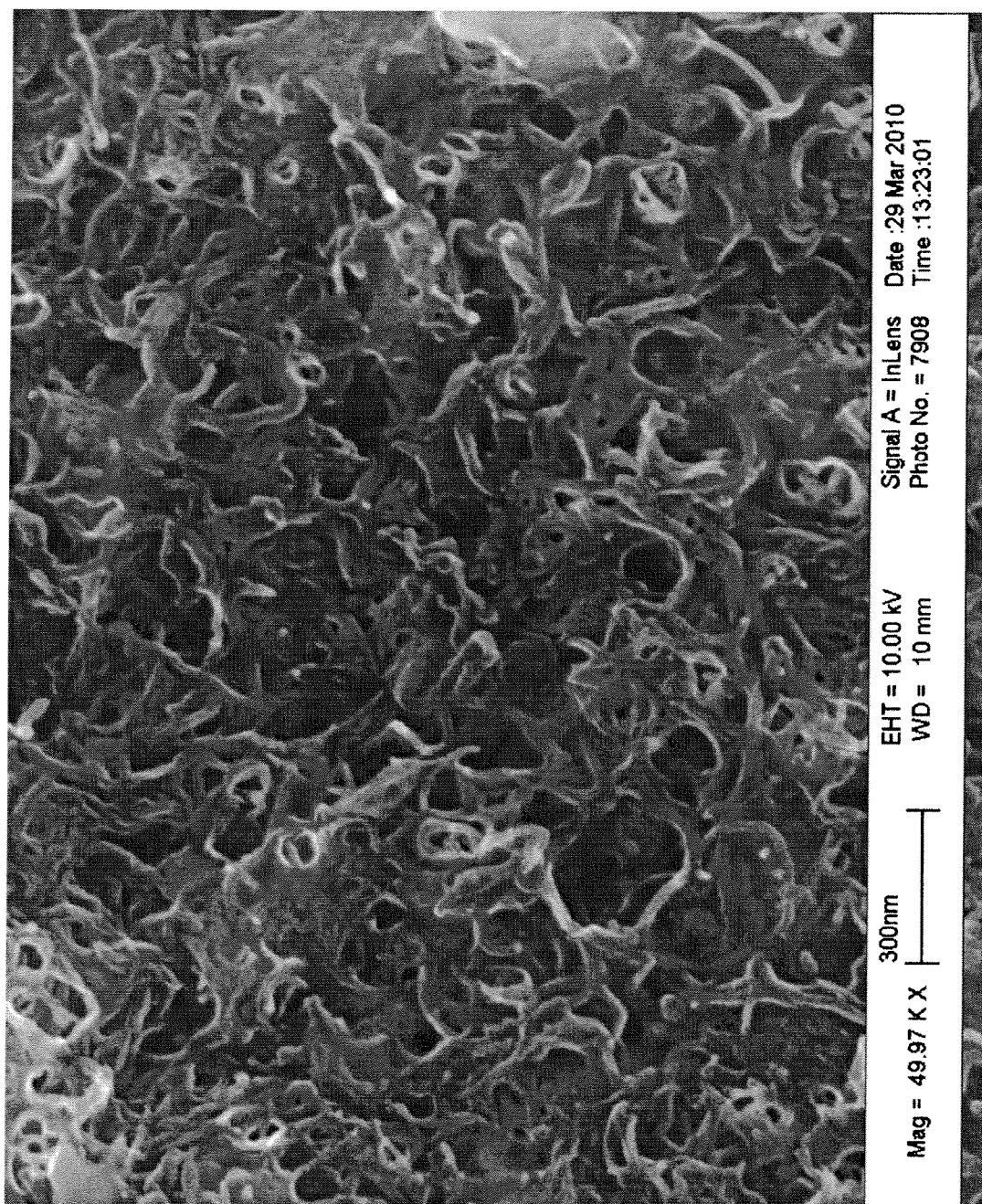


Figure 1

8237993v.1

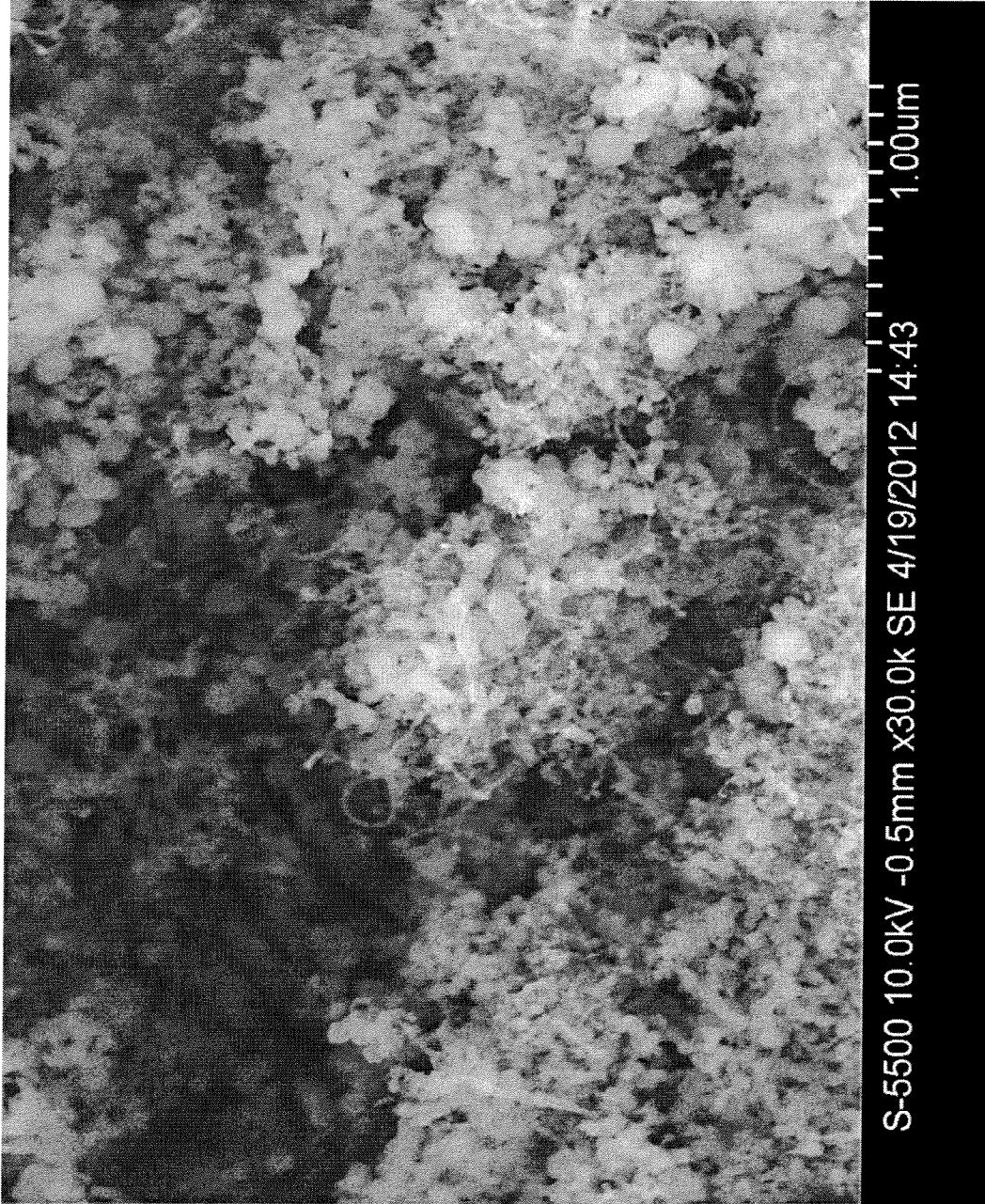


Figure 2

8237993v.1

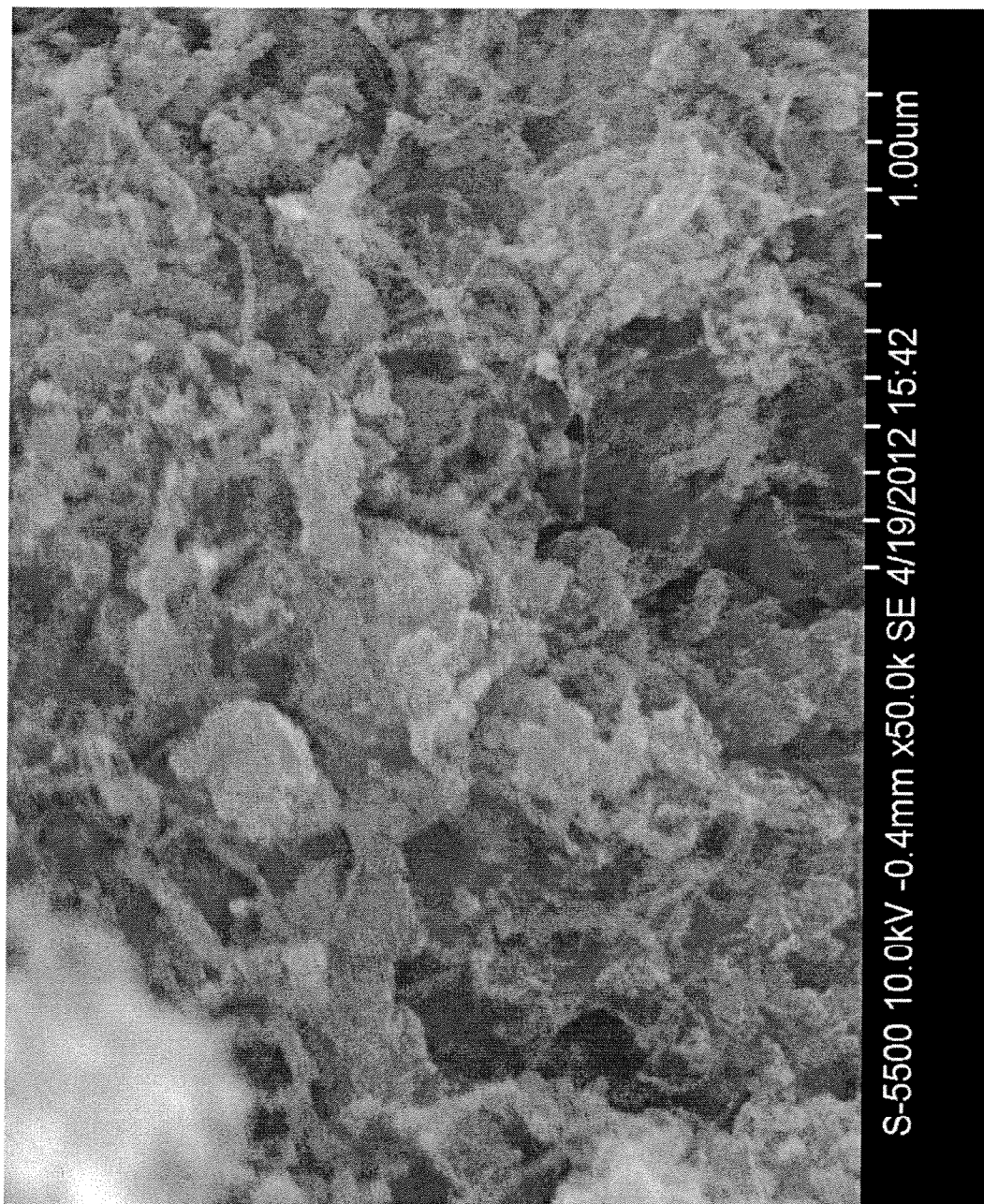


Figure 3

8237993v.1

Electronic Patent Application Fee Transmittal				
Application Number:				
Filing Date:				
Title of Invention:		LITHIUM BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM		
First Named Inventor/Applicant Name:		Designed NanoTubes, LLC		
Filer:		Amy L. Ulfers/Debra Pepper		
Attorney Docket Number:		DENA-0008WO (137124.42)		
International Application for filing in the US receiving office Filing Fees				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Transmittal fee	1601	1	240	240
Intl Filing Fee (1st-30 Pgs.) PCT Easy	1701	1	1344	1344
International Search (EPO)	1704	1	2426	2426
Pages:				
Claims:				
Miscellaneous-Filing:				
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Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
Total in USD (\$)				4010

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Title of Invention:	LITHIUM BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM
First Named Inventor/Applicant Name:	Designed NanoTubes, LLC
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Filer:	Amy L. Ulfers
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Application Type:	International Application for filing in the US receiving office

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Payment Type		Deposit Account			
Payment was successfully received in RAM		\$ 4010			
RAM confirmation Number		3607			
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File Listing:					
Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		DENA0008WOREQUEST.pdf	759041	yes	6
			c4fb0771c387dc88ce9c8de7aa2f470f392b3a3		
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	RO/101 - Request form for new IA - Conventional		1		5
	RO/101 - Annex (fee calculation sheet)		6		6
Warnings:					
Information:					
2		DENA0008WOAPPLICATION.pdf	886223	yes	15
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3	Drawings-only black and white line drawings	DENA0008WODWGS.pdf	2850970	no	3
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FEE CALCULATION SHEET

Annex to the Request

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PCT/US12/43534

International Application No.

21 JUN 2012

Date stamp of the receiving Office

Applicant's or agent's
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DENA-0008WO

Applicant

Designed NanoTubes, LLC, et al.

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE

240 ☐ T

2. SEARCH FEE

2,426 ☐ S

International search to be carried out by

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REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

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PCT/US12/43534

International Application No.

21 JUN 2012 (21.06.12)

International Filing Date

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Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) DENA-0008WO

Box No. I TITLE OF INVENTION	
LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM	
Box No. II APPLICANT ☐ This person is also inventor	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) Designed NanoTubes, LLC 4211 Waters Edge Cove Austin, Texas 78731 UNITED STATES OF AMERICA	Telephone No. 512-394-0922 Facsimile No. Applicant's registration No. with the Office
E-mail authorization: Marking one of the check-boxes below authorizes the receiving Office, the International Searching Authority, the International Bureau and the International Preliminary Examining Authority to use the e-mail address indicated in this Box to send, notifications issued in respect of this international application to that e-mail address if those offices are willing to do so. ☐ as advance copies followed by paper notifications; or ☐ exclusively in electronic form (no paper notifications will be sent). E-mail address:	
State (that is, country) of nationality: US	State (that is, country) of residence: US
This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
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Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) DUNSTAN, Amy Ulfers Jackson Walker L.L.P. 901 Main Street, Suite 6000 Dallas, Texas 75202 UNITED STATES OF AMERICA	Telephone No. 214-953-5982 Facsimile No. 214-661-6880 Agent's registration No. with the Office 61,069
E-mail authorization: Marking one of the check-boxes below authorizes the receiving Office, the International Searching Authority, the International Bureau and the International Preliminary Examining Authority to use the e-mail address indicated in this Box to send, notifications issued in respect of this international application to that e-mail address if those offices are willing to do so. ☐ as advance copies followed by paper notifications; or ☐ exclusively in electronic form (no paper notifications will be sent). E-mail address:	
☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.	

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
<i>If none of the following sub-boxes is used, this sheet should not be included in the request.</i>	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) BOSNYAK, Clive P. 12001 Settlers Trail Dripping Springs, Texas 78620 UNITED STATES OF AMERICA	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: US	State (that is, country) of residence: US
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) SWOGER, Kurt W. 4211 Waters Edge Cove Austin, Texas 78731 UNITED STATES OF AMERICA	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: US	State (that is, country) of residence: US
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.	

Supplemental Box*If the Supplemental Box is not used, this sheet should not be included in the request.*

1. If, in any of the Boxes, except Boxes Nos. VIII(i) to (v) for which a special continuation box is provided, **the space is insufficient** to furnish all the information: in such case, write "Continuation of Box No." (indicate the number of the Box) and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:
- (i) **if more than one person is to be indicated as applicant and/or inventor** and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
 - (ii) if, in Box No. II or in any of the sub-boxes of Box No. III, the indication **"the States indicated in the Supplemental Box"** is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
 - (iii) if, in Box No. II or in any of the sub-boxes of Box No. III, **the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America**: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
 - (iv) if, in addition to the agent(s) indicated in Box No. IV, there are **further agents**: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;
 - (v) if, in Box No. VI, there are **more than three earlier applications whose priority is claimed**: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI.
2. If the applicant intends to make an indication of the wish that the international application be treated, in certain designated States, as an application for a patent of addition, certificate of addition, inventor's certificate of addition or utility certificate of addition: in such case, write the name or two-letter code of each designated State concerned and the indication **"patent of addition," "certificate of addition," "inventor's certificate of addition" or "utility certificate of addition,"** the number of the parent application or parent patent or other parent grant and the date of grant of the parent patent or other parent grant or the date of filing of the parent application (Rules 4.11(a)(i) and 49bis.1(a) or (b)).
3. If the applicant intends to make an indication of the wish that the international application be treated, in the United States of America, as a continuation or continuation-in-part of an earlier application: in such case, write "United States of America" or "US" and the indication **"continuation" or "continuation-in-part"** and the number and the filing date of the parent application (Rules 4.11(a)(ii) and 49bis.1(d)).
4. If the applicant wishes to request the receiving Office or the International Bureau to obtain a priority document from a digital library but **that document is only held in a digital library in connection with another application** which also relied upon that priority document to support a priority claim (and unless that digital library is to be accessed through the Digital Access Service for Priority Documents), in such cases write "Continuation of Box No. VI", indicate for each earlier application concerned the same type of information as required in Box No. VI and indicate the number under which the application is stored (and, if known, the digital library concerned) (Section 716(a)(ii)).

Continuation of Box No. IV:

CHWANG, T. Ling, Reg. No. 33,590
 BORRELLI, Sara K., Reg. No. 50,253
 Jackson Walker L.L.P.
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 Dallas, Texas 75202
 UNITED STATES OF AMERICA
 Phone: 214-953-6000
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Box No. V DESIGNATIONS				
The filing of this request constitutes under Rule 4.9(a) the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents. However, ☐ DE Germany is not designated for any kind of national protection ☐ JP Japan is not designated for any kind of national protection ☐ KR Republic of Korea is not designated for any kind of national protection <i>(The check-boxes above may only be used to exclude (irrevocably) the designations concerned if, at the time of filing or subsequently under Rule 26bis.1, the international application contains in Box No. VI a priority claim to an earlier national application filed in the particular State concerned, in order to avoid the ceasing of the effect, under the national law, of this earlier national application.)</i>				
Box No. VI PRIORITY CLAIM				
The priority of the following earlier application(s) is hereby claimed:				
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application: regional Office	international application: receiving Office
item (1) 23 June 2011 (23.06.2011)	61/500,560	US		
item (2)				
item (3)				
☐ Further priority claims are indicated in the Supplemental Box.				
☐ The International Bureau is requested to obtain from a digital library, a certified copy of the earlier application(s) <i>(if the earlier application(s) is available to it from a digital library)</i> identified above as: *				
☐ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box				
☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) <i>(if the earlier application(s) was filed with the Office which for the purposes of this international application is the receiving Office)</i> or to obtain a certified copy of the earlier application(s) from a digital library and transmit a copy of it to the International Bureau <i>(if the earlier application(s) is available to the receiving Office from a digital library)</i> , identified above as: *				
☒ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box				
* Where the certified copy of the earlier application(s) is not stored in a digital library under the number of the earlier application indicated above but under the application number of another application which also claims priority from it, indicate that number in the supplemental sheet (item 4).				
Restore the right of priority: the receiving Office is requested to restore the right of priority for the earlier application(s) identified above or in the Supplemental Box as item(s) (_____). <i>(See also the Notes to Box No. VI; further information must be provided to support a request to restore the right of priority.)</i>				
Incorporation by reference: where an element of the international application referred to in Article 11(1)(iii)(d) or (e) or a part of the description, claims or drawings referred to in Rule 20.5(a) is not otherwise contained in this international application but is completely contained in an earlier application whose priority is claimed on the date on which one or more elements referred to in Article 11(1)(iii) were first received by the receiving Office, that element or part is, subject to confirmation under Rule 20.6, incorporated by reference in this international application for the purposes of Rule 20.6.				
Box No. VII INTERNATIONAL SEARCHING AUTHORITY				
Choice of International Searching Authority (ISA) <i>(if more than one International Searching Authority is competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):</i> ISA/ EP				

Box No. IX CHECK LIST for EFS-Web filings - this sheet is only to be used when filing an international application with RO/US via EFS-Web			
This international application contains the following: (a) request form PCT/RO/101 (including any declarations and supplemental sheets) (b) description (excluding any sequence listing part of the description, see (f), below) (c) claims (d) abstract (e) drawings (if any) (f) sequence listing part of the description in the form of an image file (e.g. PDF) Total number of sheets (including the sequence listing part of the description if filed as an image file) (g) sequence listing part of the description ☐ filed in the form of an Annex C/ST.25 text file ☐ WILL BE filed separately on physical data carrier(s), on the same day and in the form of an Annex C/ST.25 text file Indicate type and number of physical data carrier(s)	Number of sheets 5 12 2 1 3 23	This international application is accompanied by the following item(s) (<i>mark the applicable check-boxes below and indicate in right column the number of each item</i>): 1. ☒ fee calculation sheet 2. ☐ original separate power of attorney 3. ☐ original general power of attorney 4. ☐ copy of general power of attorney; reference number: 5. ☐ statement explaining lack of signature 6. ☐ priority document(s) identified in Box No. VI as item(s) 7. ☐ Translation of international application into (<i>language</i>): 8. ☐ separate indications concerning deposited microorganism or other biological material 9. ☐ (<i>only where item (f) is marked in the left column</i>) copy of the sequence listing in electronic form (Annex C/ST.25 text file) not forming part of the international application but furnished only for the purposes of international search under Rule 13ter 10. ☐ (<i>only where item (f) is marked in the left column</i>) a statement confirming that "the information recorded in electronic form submitted under Rule 13ter is identical to the sequence listing as contained in the international application" as filed via EFS-Web: 11. ☐ copy of results of earlier search(es) (Rule 12bis.1(a)) 12. ☐ other (<i>specify</i>):	Number of items 1
Figure of the drawings which should accompany the abstract:	1	Language of filing of the international application: English	
Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE <i>Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).</i>			
Amy Ulfers Dunstan Reg. 61,069 6/21/12 21-06-2012			

For receiving Office use only	
1. Date of actual receipt of the purported international application: 21 JUN 2012	2. Drawings: ☐ received: ☐ not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA / EP	
6. ☐ Transmittal of search copy delayed until search fee is paid	

For International Bureau use only
Date of receipt of the record copy by the International Bureau: