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1. <u>High-energy-density Ni-Co-based lithium ion positive electrode material and preparation method thereof</u>					
Inventor: LI XINGCUI IKEDA KAZUTAKA (+4)	Applicant: NANTONG RESHINE NEW MATERIAL CO LTD	CPC: H01M10/0525 H01M2004/028 H01M4/131 (+5)	IPC: H01M4/525 H01M4/62	Publication info: CN104701534 (A) 2015-06-10 Global Dossier	Priority date: 2015-03-31
2. <u>AQUEOUS COATING METHOD FOR HIGH-VOLTAGE LITHIUM COBALTATE POSITIVE ELECTRODE MATERIAL</u>					
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3. <u>AQUEOUS COATING METHOD FOR HIGH-VOLTAGE LITHIUM COBALTATE POSITIVE ELECTRODE MATERIAL</u>					
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High-energy-density Ni-Co-based lithium ion positive electrode material and preparation method thereof

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Abstract of CN104701534 (A)

The invention discloses a high-energy-density Ni-Co-based lithium ion positive electrode material. The chemical general formula of a base material is $\text{Li}_p\text{Ni}_x\text{Co}_{1-x}\text{MmO}_2$, M is a doping agent, and a clad material is an active material N; a positive electrode material of a lithium ion secondary battery is composed of second particles formed by gathering of primary particles, or primary particles, or mixed particles of primary particles and second particles. A preparation method of the high-energy-density Ni-Co-based lithium ion positive electrode material comprises the steps of preparation of a precursor of the lithium ion secondary battery positive electrode material and preparation of the lithium ion secondary battery positive electrode material. The Ni-Co binary precursor of the positive electrode material is subjected to a continuous coprecipitation reaction, elements are evenly mixed, the reaction is sufficient, and morphology control is facilitated; the cation mixing phenomenon is reduced through doping of proper elements in a binary high-nickel material, the structure is stabilized, safety and high-temperature performance of the battery material are improved, and the cladding active material improves first-time charge and discharge efficiency and the energy density of the material to a certain extent.



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(54) 发明名称

高能量密度的镍钴基锂离子正极材料及其制备方法

(57) 摘要

本发明公开了一种高能量密度的镍钴基锂离子正极材料,基材的化学通式为 $\text{Li}_p\text{Ni}_x\text{Co}_{1-x}\text{M}_n\text{O}_2$,M为掺杂剂,包覆材料为活性物质N;所述的锂离子二次电池的正极材料是为一次粒子聚集而成的二次粒子或一次粒子,或一次粒子与二次粒子的混合粒子构成。其制备方法为:锂离子二次电池正极材料前驱体的制备;锂离子二次电池正极材料的制备。本发明中镍钴二元前驱体为连续式共沉淀反应,元素混合均匀,反应充分,有利于形貌的控制,二元高镍材料通过掺杂适宜的元素减少阳离子混排现象,稳定了结构,提高了电池材料的安全性能和高温性能,包覆活性物质在一定程度上提高了材料的首次充放电效率和能量密度。

1. 一种高能量密度的镍钴基锂离子正极材料,其特征在于:基材的化学通式为: $\text{Li}_p\text{Ni}_x\text{Co}_{1-x}\text{M}_m\text{O}_2$,其中 $0.95 \leq p \leq 1.25$, $0.6 \leq x < 1$, $0.01 \leq m < 0.12$, M 为掺杂剂,包覆材料为活性物质 N, N 所占基材总质量的 $0.01 \sim 25\text{wt}\%$;所述的锂离子二次电池的正极材料是为一次粒子聚集而成的二次粒子或一次粒子,或一次粒子与二次粒子的混合粒子构成。

2. 根据权利要求 1 所述的高能量密度的镍钴基锂离子正极材料的制备方法,其特征在于:包括如下步骤:

第一步,锂离子二次电池正极材料前驱体的制备:

a、溶液的配制:按摩尔比 $\text{Ni}:\text{Co} = x:1-x$ 配制成混合盐溶液 A1, 使该盐溶液中金属离子浓度为 $0.5 \sim 3\text{mol/L}$;配制浓度为 $1.5 \sim 12\text{mol/L}$ 的碱溶液,配制浓度为 $0.5 \sim 5\text{mol/L}$ 的络合剂溶液,其中 $0.6 \leq x < 1$;

b、初液的配制:在反应容器中注入纯水,并用碱溶液调节溶液的 pH 值,并保持反应容器内的温度为 $40 \sim 80^\circ\text{C}$,同时通入惰性气体,并贯穿整个反应过程;

c、前驱体的反应:向反应容器内加入 A1 溶液,控制流速为 $3 \sim 20\text{L/min}$,同时缓慢加入适量络合剂和碱溶液,保持反应容器内的温度为 $40 \sim 80^\circ\text{C}$,调节搅拌速度为 $200 \sim 950\text{r/min}$;

d、固液分离:将步骤 c 中物料进行表面处理,合成的二元正极材料前驱体转至熟成槽进行固液分离,用去离子水洗涤固液分离所得的二元正极材料前驱体,干燥即得所需的二元前驱体 A2, A2 的化学式为 $\text{Ni}_x\text{Co}_{1-x}(\text{OH})_2$;

第二步,锂离子二次电池正极材料的制备:

e、一次烧结:将锂源物质、A2 和掺杂剂 M 物质按照分子式 $\text{Li}_p\text{Ni}_x\text{Co}_{1-x}\text{M}_m\text{O}_2$ 中的比例进行混合,其中 $0.95 \leq p \leq 1.25$, $0.6 \leq x < 1$, $0.01 \leq m < 0.12$, M 为掺杂剂,控制烧结温度为 $400 \sim 1050^\circ\text{C}$,烧结时间为 $4 \sim 40\text{h}$,烧结过程通入空气或者氧气,将烧结后的物料经破碎、分级、除铁等工艺处理,得到材料 A;

f、表面处理:将材料 A 进行水洗处理以降低碱含量,物质 A 与水的比例范围为 $1:1 \sim 1:6$,水洗后将物料干燥过筛;

g、包覆:以 f 处理后的物料或物质 A 为基体,在基体上包覆活性物物质 N,包覆方法为干式包覆、湿式包覆或共沉淀包覆法,其中, N 所占基材总质量的 $0.01 \sim 25\text{wt}\%$;

h、二次或多次烧结:将经过 g 包覆好的物料进行烧结,烧结主温度控制在 $400 \sim 1050^\circ\text{C}$,主温区烧结时间为 $3 \sim 35\text{h}$,烧结过程中需通入空气或者氧气,根据产品性能要求,可以进行三次以上烧结,烧结条件同二次烧结;

烧结后的物料按照需要进行破碎、分级、过筛、除铁等工艺处理。

3. 根据权利要求 1 所述的高能量密度的镍钴基锂离子正极材料的制备方法,其特征在于:所述步骤 a 中碱溶液为氢氧化钠、氢氧化钾和氢氧化锂中的一种或一种以上的混合溶液;络合剂为氨水、碳酸氢氨、硫酸铵、碳酸铵、柠檬酸和乙二胺四二酸二钠中的一种或一种以上混合溶液。

4. 根据权利要求 1 所述的高能量密度的镍钴基锂离子正极材料的制备方法,其特征在于:所述步骤 a 中镍盐、钴盐溶液为硫酸盐、硝酸盐和氯化盐中的一种或一种以上混合溶液。

5. 根据权利要求 1 所述的高能量密度的镍钴基锂离子正极材料的制备方法,其特征在

于:所述步骤 b 中 PH 值调节至 8.5 ~ 13.5。

6. 根据权利要求 1 所述的高能量密度的镍钴基锂离子正极材料的制备方法,其特征在于:所述步骤 c 中 PH 值调节至 9.5 ~ 13.5。

7. 根据权利要求 1 所述的高能量密度的镍钴基锂离子正极材料的制备方法,其特征在于:前驱体 A2 的 D50 范围为 5 ~ 22 μm 。

8. 根据权利要求 1 所述的高能量密度的镍钴基锂离子正极材料的制备方法,其特征在于:所述的锂源物质选自氢氧化锂、碳酸锂、草酸锂中的一种或多种的混合物。

9. 根据权利要求 1 所述的高能量密度的镍钴基锂离子正极材料的制备方法,其特征在于:所述的掺杂剂 M 为 Cr、La、Ce、Zr、Ni、Mg、Ti、Al、Ca、V、B、Be、Y、Mo、Tb、Ho、Tm 的氧化物、卤化物、氢氧化物、金属有机物、硝酸盐、硫酸盐、碳酸盐、磷酸盐、草酸盐或与其他金属元素的复合氧化物或金属氟化物的一种或者多种的混合物。

10. 根据权利要求 1 所述的高能量密度的镍钴基锂离子正极材料的制备方法,其特征在于:所述包覆的活性物质 N 为 Li 与 Cr、La、Ce、Zr、Ti、Al、Ca、V、B、Be、Y、Mo、Tb、Ho、Tm 的复合氧化物,或 Li 源物质:氢氧化锂、碳酸锂、草酸锂中的一种或多种的混合物;与 Cr、La、Ce、Zr、Ti、Al、Ca、V、B、Be、Y、Mo、Tb、Ho、Tm 的氧化物、卤化物、氢氧化物、金属有机物、硝酸盐、硫酸盐、碳酸盐、磷酸盐、草酸盐的混合物的一种或者多种的混合物。

高能量密度的镍钴基锂离子正极材料及其制备方法

技术领域

[0001] 本发明涉及一种锂离子电池正极材料,特别涉及一种高能量密度的镍钴基锂离子电池正极材料及其制备方法。

背景技术

[0002] 锂离子电池具有重量轻、体积小、放电平台高、容量大、循环寿命长、无记忆效应等优点,从而被广泛应用到手机、笔记本电脑等移动电子设备,同时也被应用于人造卫星、电动汽车、航天航空等领域。

[0003] $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ ($0.6 < x < 1$) 正极材料具备了钴酸锂和镍酸锂的优点,放电比容量高、循环性能好、成本低和环境污染小等优点,但是由于高镍材料存在着 Ni^{2+} 难以完全氧化成 Ni^{3+} ,而导致高温结晶过程中 Ni^{2+} 与 Ni^{3+} 之间出现阳离子混排现象,从而会出现热稳定性差以及首次充放电效率低等缺陷。

[0004] 目前为了解决此问题,对此进行掺杂包覆改性等,确实一定程度的改善了其阳离子混排现象,稳定了结构,但是由于掺杂或包覆的物质为非活性物质,在一定程度上降低了电池的比容量。

[0005] 为了解决上述问题,本文通过对 $\text{Li}_p\text{Ni}_x\text{Co}_{1-x}\text{O}_2$ 进行掺杂对其进行改性稳定材料的结构,再通过包覆活性物质,进一步改善材料的电化学性能,不仅提高了材料的稳定性和高温性能,同时还较大程度的提高了材料的电化学性能,特别是比容量和首次充放电效率有所提高。

发明内容

[0006] 发明目的:本发明提供一种高能量密度的镍钴基锂离子电池正极材料及其制备方法,从而克服现有技术的不足。

[0007] 技术方案:一种高能量密度的镍钴基锂离子正极材料,基材的化学通式为: $\text{Li}_p\text{Ni}_x\text{Co}_{1-x}\text{M}_m\text{O}_2$,其中 $0.95 \leq p \leq 1.25$, $0.6 \leq x < 1$, $0.01 \leq m < 0.12$, M 为掺杂剂,包覆材料为活性物质 N, N 所占基材总质量的 $0.01 \sim 25\text{wt}\%$;所述的锂离子二次电池的正极材料是为一次粒子聚集而成的二次粒子或一次粒子,或一次粒子与二次粒子的混合粒子构成。

[0008] 所述的高能量密度的镍钴基锂离子正极材料的制备方法,包括如下步骤:

第一步,锂离子二次电池正极材料前驱体的制备:

a、溶液的配制:按摩尔比 $\text{Ni}:\text{Co} = x:1-x$ 配制成混合盐溶液 A1,使该盐溶液中金属离子浓度为 $0.5 \sim 3\text{mol/L}$;配制浓度为 $1.5 \sim 12\text{mol/L}$ 的碱溶液,配制浓度为 $0.5 \sim 5\text{mol/L}$ 的络合剂溶液,其中 $0.6 \leq x < 1$;

b、初液的配制:在反应容器中注入纯水,并用碱溶液调节溶液的 pH 值,并保持反应容器内的温度为 $40 \sim 80^\circ\text{C}$,同时通入惰性气体,并贯穿整个反应过程;

c、前驱体的反应:向反应容器内加入 A1 溶液,控制流速为 $3 \sim 20\text{L/min}$,同时缓慢加入适量络合剂和碱溶液,保持反应容器内的温度为 $40 \sim 80^\circ\text{C}$,调节搅拌速度为 $200 \sim 950\text{r/}$

min ;

d、固液分离 :将步骤 c 中物料进行表面处理,合成的二元正极材料前驱体转至熟成槽进行固液分离,用去离子水洗涤固液分离所得的二元正极材料前驱体,干燥即得所需的二元前驱体 A2, A2 的化学式为 $\text{Ni}_x\text{Co}_{1-x}(\text{OH})_2$;

第二步,锂离子二次电池正极材料的制备 :

e、一次烧结 :将锂源物质、A2 和掺杂剂 M 物质按照分子式 $\text{Li}_p\text{Ni}_x\text{Co}_{1-x}\text{M}_m\text{O}_2$ 中的比例进行混合,其中 $0.95 \leq p \leq 1.25$, $0.6 \leq x < 1$, $0.01 \leq m < 0.12$, M 为掺杂剂,控制烧结温度为 $400 \sim 1050^\circ\text{C}$,烧结时间为 $4 \sim 40\text{h}$,烧结过程通入空气或者氧气,将烧结后的物料经破碎、分级、除铁等工艺处理,得到材料 A ;

f、表面处理 :将材料 A 进行水洗处理以降低碱含量,物质 A 与水的比例范围为 $1:1 \sim 1:6$,水洗后将物料干燥过筛 ;

g、包覆 :以 f 处理后的物料或物质 A 为基体,在基体上包覆活性物物质 N,包覆方法为干式包覆、湿式包覆或共沉淀包覆法,其中, N 所占基材总质量的 $0.01 \sim 25\text{wt}\%$;

h、二次或多次烧结 :将经过 g 包覆好的物料进行烧结,烧结主温度控制在 $400 \sim 1050^\circ\text{C}$,主温区烧结时间为 $3 \sim 35\text{h}$,烧结过程中需通入空气或者氧气,根据产品性能要求,可以进行三次以上烧结,烧结条件同二次烧结。烧结后的物料按照需要进行破碎、分级、过筛、除铁等工艺处理。

[0009] 作为优化 :所述步骤 a 中碱溶液为氢氧化钠、氢氧化钾和氢氧化锂中的一种或一种以上的混合溶液 ;络合剂为氨水、碳酸氢氨、硫酸铵、碳酸铵、柠檬酸和乙二胺四二酸二钠中的一种或一种以上混合溶液。

[0010] 作为优化 :所述步骤 a 中镍盐、钴盐溶液为硫酸盐、硝酸盐和氯化盐中的一种或一种以上混合溶液。

[0011] 作为优化 :所述步骤 b 中 PH 值调节至 $8.5 \sim 13.5$ 。

[0012] 作为优化 :所述步骤 c 中 PH 值调节至 $9.5 \sim 13.5$ 。

[0013] 作为优化 :前驱体 A2 的 D50 范围为 $5 \sim 22\mu\text{m}$ 。

[0014] 作为优化 :所述的锂源物质选自氢氧化锂、碳酸锂、草酸锂中的一种或多种的混合物。

[0015] 作为优化 :所述的掺杂剂 M 为 Cr、La、Ce、Zr、Ni、Mg、Ti、Al、Ca、V、B、Be、Y、Mo、Tb、Ho、Tm 的氧化物、卤化物、氢氧化物、金属有机物、硝酸盐、硫酸盐、碳酸盐、磷酸盐、草酸盐或与其他金属元素的复合氧化物或金属氟化物的一种或者多种的混合物。

[0016] 作为优化 :所述包覆的活性物质 N 为 Li 与 Cr、La、Ce、Zr、Ti、Al、Ca、V、B、Be、Y、Mo、Tb、Ho、Tm 的复合氧化物,或 Li 源物质 :氢氧化锂、碳酸锂、草酸锂中的一种或多种的混合物 ;与 Cr、La、Ce、Zr、Ti、Al、Ca、V、B、Be、Y、Mo、Tb、Ho、Tm 的氧化物、卤化物、氢氧化物、金属有机物、硝酸盐、硫酸盐、碳酸盐、磷酸盐、草酸盐的混合物的一种或者多种的混合物。

[0017] 有益效果 :本发明中镍钴二元前驱体为连续式共沉淀反应,元素混合均匀,反应充分,有利于形貌的控制。二元高镍材料通过掺杂适宜的元素减少阳离子混排现象,稳定了结构,提高了电池材料的安全性能和高温性能,包覆活性物质在一定程度上提高了材料的首次充放电效率和能量密度。

具体实施方式

[0018] 下面结合具体实施例对本发明作进一步说明：

实施例 1：

前驱体的制备：Ni:Co=0.6:0.4 配制成 0.5mol/L 的混合溶液 A1，配制 1.5mol/L 的氢氧化钠溶液和 0.5mol/L 硫酸铵溶液；在反应容器中注入纯水，并用 1.5mol/L 氢氧化钠溶液调节初液的 pH 值为 8.5，调节反应容器内的温度为 40℃，转速为 200 r/min，通入氮气；调节 A1 溶液的流速为 20L/min，同时缓慢滴加氢氧化钠和硫酸铵，当粒度达到要求时，进行固液分离，干燥，得到所需的前驱体 A2。

[0019] 正极材料的制备：将氢氧化锂、A2、以及氢氧化铝按照分子式 $\text{Li}_p\text{Ni}_x\text{Co}_{1-x}\text{M}_m\text{O}_2$ 中的比例进行混合，其中 $p=1.25$ ， $x=0.6$ ， $m=0.12$ ，控制烧结温度为 1050℃，烧结时间为 40h，烧结过程通入空气，将烧结后的物料经破碎、分级、除铁等工艺处理，得到材料 A；

表面处理：按照 A：水 =1:1 的比例进行水洗，干燥、过筛；

包覆：以上述处理好的样品为基体，在基体上包覆 LiCrO_2 ，包覆方法为干式包覆，N 所占基材总质量的 0.01%。

[0020] 二次烧结：将上述处理好的物料进行二次烧结，烧结主温度控制在 400℃，主温区的烧结时间为 35h，烧结过程中通入空气。

[0021] 实施例 2：

前驱体的制备：Ni:Co=0.85:0.15 配制成 3mol/L 的混合溶液 A1，配制 12mol/L 的氢氧化钠溶液和 5mol/L 硫酸铵溶液；在反应容器中注入纯水，并用 8mol/L 氢氧化钠溶液调节初液的 pH 值为 13.5，调节反应容器内的温度为 80℃，转速为 200 r/min，通入氮气；调节 A1 溶液的流速为 3L/min，同时缓慢滴加氢氧化钠和硫酸铵，当粒度达到要求时，进行固液分离，干燥，得到所需的前驱体 A2。

[0022] 正极材料的制备：将氢氧化锂、A2、以及氢氧化铝按照分子式 $\text{Li}_p\text{Ni}_x\text{Co}_{1-x}\text{M}_m\text{O}_2$ 中的比例进行混合，其中 $p=0.95$ ， $x=0.85$ ， $m=0.01$ ，控制烧结温度为 400℃，烧结时间为 4h，烧结过程通入氧气，将烧结后的物料经破碎、分级、除铁等工艺处理，得到材料 A；

表面处理：按照 A：水 =1:6 的比例进行水洗，干燥、过筛。

[0023] 包覆：以上述处理好的样品为基体，在基体上包覆氧化铝和 Li_2CO_3 的混合物，包覆方法为干式包覆，N 所占基材总质量的 0.01%。

[0024] 二次烧结：将上述处理好的物料进行二次烧结，烧结主温度控制在 1050℃，主温区的烧结时间为 3h，烧结过程中通入空气。

[0025] 实施例 3：

前驱体的制备：Ni:Co=0.80:0.20 配制成 2mol/L 的混合溶液 A1，配制 2.5mol/L 的氢氧化钠溶液和 1.8mol/L 硫酸铵溶液；在反应容器中注入纯水，并用 2.5mol/L 氢氧化钠溶液调节初液的 pH 值为 12，调节反应容器内的温度为 60℃，转速为 500 r/min，通入氮气；调节 A1 溶液的流速为 10L/min，同时缓慢滴加氢氧化钠和硫酸铵，当粒度达到要求时，进行固液分离，干燥，得到所需的前驱体 A2。

[0026] 正极材料的制备：将氢氧化锂、A2、以及氧化钴按照分子式 $\text{Li}_p\text{Ni}_x\text{Co}_{1-x}\text{M}_m\text{O}_2$ 中的比例进行混合，其中 $p=0.11$ ， $x=0.80$ ， $m=0.04$ ，控制烧结温度为 400℃，烧结时间为 4h，烧结过程通入氧气，将烧结后的物料经破碎、分级、除铁等工艺处理，得到材料 A；

包覆 :以 A 为基体,在基体上包覆 LiAlO_2 ,包覆方法为干式包覆,N 所占基材总质量的 0.08%。

[0027] 二次烧结 :将上述处理好的物料进行二次烧结,烧结主温度控制在 750°C ,主温区的烧结时间为 6h,烧结过程中通入空气。



Espacenet

Family list: KR20160092946 (A) — 2016-08-05

1 application(s) for: KR20160092946 (A)

1. POSITIVE ACTIVE MATERIAL FOR RECHARGEABLE LITHIUM BATTERY, METHOD OF PREPARING THE SAME, AND RECHARGEABLE LITHIUM BATTERY INCLUDING THE SAME					
Inventor: CHOI SU AN [KR] JEONG HO JUN [KR] (+5)	Applicant: L & F CO LTD [KR]	CPC: Y02E60/10	IPC: H01M10/052 H01M4/36 H01M4/505 (+2)	Publication info: KR20160092946 (A) 2016-08-05 KR101788561 (B1) 2017-10-20 Global Dossier	Priority date: 2015-01-28



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POSITIVE ACTIVE MATERIAL FOR RECHARGEABLE LITHIUM BATTERY,
METHOD OF PREPARING THE SAME, AND RECHARGEABLE LITHIUM BATTERY
INCLUDING THE SAME

Inventor(s): CHOI SU AN [KR]; JEONG HO JUN [KR]; JEON SANG HOON [KR]; YANG JI WOON [KR]; SHIN JUN HO [KR]; JEONG JIN SEONG [KR]; JEONG BONG JUN [KR] ± (최수안, ; 정호준, ; 전상훈, ; 양지운, ; 신준호, ; 정진성, ; 정봉준)

Applicant(s): L & F CO LTD [KR] ± (주식회사 엘 앤 에프)

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Abstract of KR20160092946 (A)

The present invention relates to a positive active material for a lithium secondary battery, a method for manufacturing the positive active material, and a lithium secondary battery comprising the positive active material. Provided is the positive active material for a lithium secondary battery, the positive active material comprising: a first positive active material which includes a compound adapted to enable reversible intercalation and deintercalation of lithium and a coating layer disposed on at least part of a surface of the compound, wherein the coating layer includes Li_3PO_4 or LiF , the coating layer is a composite coating layer further including a lithium metal oxide, a metal oxide, or a combination thereof, at least any one of the lithium metal oxide and the metal oxide independently includes metal M, and metal M includes at least one element selected from the group consisting of Mg, Ti, Al, Si, Sn, and Zr; and a second positive active material which includes a compound adapted to enable reversible intercalation and deintercalation of lithium and a coating layer disposed on at least part of a surface of this compound, wherein this coating layer includes Li_3PO_4 or LiF , this coating layer is a composite coating layer further including a lithium metal oxide, a metal oxide, or a combination thereof, at least any one of this lithium metal oxide and this metal oxide independently includes metal M, metal M includes at least one element selected from the group consisting of Mg, Ti, Al, Si, Sn, and Zr, and metal M is different from metal M in the first positive active material.



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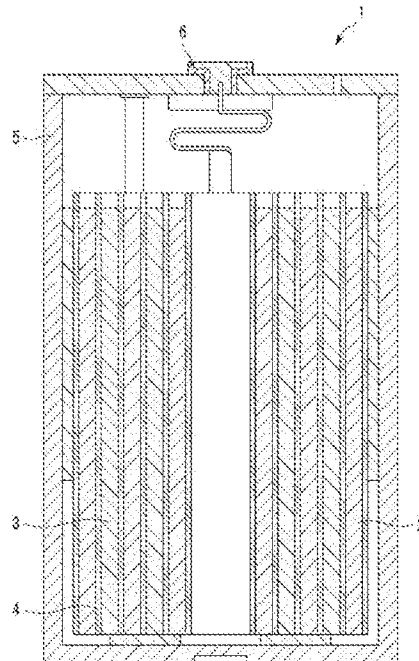
(54) 발명의 명칭 리튬 이차 전지용 양극 활물질, 이의 제조방법 및 이를 포함하는 리튬 이차 전지

(57) 요약

리튬 이차 전지용 양극 활물질, 이의 제조방법 및 이를 포함하는 리튬 이차 전지에 관한 것으로, 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물; 및 상기 화합물의 표면의 적어도 일부에 위치하는 코팅층을 포함하고, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는

(뒷면에 계속)

도 1



이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M을 포함하며, 상기 금속 M은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되는 적어도 하나의 원소를 포함하는 것인 제1 양극 활물질; 및 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물; 및 상기 화합물의 표면의 적어도 일부에 위치하는 코팅층을 포함하고, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M'을 포함하며, 상기 금속 M'은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되며, 상기 M'은 상기 제1 양극 활물질 내 M과는 서로 다른 금속인 것인 제2 양극 활물질을 포함하는 리튬 이차 전지용 양극 활물질을 제공한다.

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신준호

경상북도 칠곡군 왜관읍 2산업단지1길 135

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연구과제명 고에너지 이차전지용 전극(양극, 음극)소재 개발

가 여 율 1/1

주관기관 주식회사 엘앤에프신소재

연구기간 2010.09.01~2019.03.31

별개서

청구범위

청구항 1

리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물; 및 상기 화합물의 표면의 적어도 일부에 위치하는 코팅층을 포함하고, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M을 포함하며, 상기 금속 M은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되는 적어도 하나의 원소를 포함하는 것인 제1 양극 활물질; 및

리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물; 및 상기 화합물의 표면의 적어도 일부에 위치하는 코팅층을 포함하고, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M'을 포함하며, 상기 금속 M'은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되며, 상기 M'은 상기 제1 양극 활물질 내 M과는 서로 다른 금속인 것인 제2 양극 활물질;

을 포함하는 리튬 이차 전지용 양극 활물질.

청구항 2

제1항에 있어서,

상기 복합 코팅층 내 포함된 Li_3PO_4 또는 LiF , 또는 리튬 금속 산화물의 리튬은, 상기 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물 내에 포함되는 Li으로부터 기인되거나, 별도의 Li 공급 물질로부터 기인된 것인 리튬 이차 전지용 양극 활물질.

청구항 3

제1항에 있어서,

상기 복합 코팅층 내 LiF 의 불소는, 상기 불소가 도핑된 코어 내 포함된 불소로부터 기인되거나, 별도의 불소 공급 물질로부터 기인된 것인 리튬 이차 전지용 양극 활물질.

청구항 4

제1항에 있어서,

상기 제2 양극 활물질에 대한 제1 양극 활물질의 중량비는 95/5 내지 70/30인 것인 리튬 이차 전지용 양극 활물질.

청구항 5

제1항에 있어서,

상기 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물은, $\text{Li}_a\text{A}_{1-b}\text{X}_b\text{D}_2$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$); $\text{Li}_a\text{A}_{1-b}\text{X}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$); $\text{LiE}_{1-b}\text{X}_b\text{O}_{2-c}\text{D}_c$ ($0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$); $\text{LiE}_{2-b}\text{X}_b\text{O}_{4-c}\text{T}_c$ ($0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$); $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{X}_c\text{D}_a$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq$

$0.5, 0 \leq c \leq 0.05, 0 < a \leq 2$); $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{X}_c\text{O}_{2-a}\text{T}_2$ ($0.90 \leq a \leq 1.8, 0 \leq b \leq 0.5, 0 \leq c \leq 0.05, 0 < a < 2$); $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{X}_c\text{O}_{2-a}\text{T}_2$ ($0.90 \leq a \leq 1.8, 0 \leq b \leq 0.5, 0 \leq c \leq 0.05, 0 < a < 2$); $\text{Li}_a\text{Ni}_{1-b-c}\text{Mn}_b\text{X}_c\text{O}_{2-a}\text{T}_2$ ($0.90 \leq a \leq 1.8, 0 \leq b \leq 0.5, 0 \leq c \leq 0.05, 0 < a < 2$); $\text{Li}_a\text{Ni}_{1-b-c}\text{Mn}_b\text{X}_c\text{O}_{2-a}\text{T}_2$ ($0.90 \leq a \leq 1.8, 0 \leq b \leq 0.5, 0 \leq c \leq 0.05, 0 < a < 2$); $\text{Li}_a\text{Ni}_{1-b-c}\text{Mn}_b\text{X}_c\text{O}_{2-a}\text{T}_2$ ($0.90 \leq a \leq 1.8, 0 \leq b \leq 0.5, 0 \leq c \leq 0.05, 0 < a < 2$); $\text{Li}_a\text{Ni}_b\text{E}_c\text{G}_d\text{O}_{2-e}\text{T}_f$ ($0.90 \leq a \leq 1.8, 0 \leq b \leq 0.9, 0 \leq c \leq 0.5, 0.001 \leq d \leq 0.1, 0 \leq e \leq 0.05$); $\text{Li}_a\text{Ni}_b\text{Co}_c\text{Mn}_d\text{G}_e\text{O}_{2-f}\text{T}_f$ ($0.90 \leq a \leq 1.8, 0 \leq b \leq 0.9, 0 \leq c \leq 0.5, 0 \leq d \leq 0.5, 0.001 \leq e \leq 0.1, 0 \leq f \leq 0.05$); $\text{Li}_a\text{NiG}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8, 0.001 \leq b \leq 0.1, 0 \leq c \leq 0.05$); $\text{Li}_a\text{CoG}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8, 0.001 \leq b \leq 0.1, 0 \leq c \leq 0.05$); $\text{Li}_a\text{MnG}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8, 0.001 \leq b \leq 0.1, 0 \leq c \leq 0.05$); $\text{Li}_a\text{Mn}_2\text{G}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8, 0.001 \leq b \leq 0.1, 0 \leq c \leq 0.05$); $\text{Li}_a\text{MnG}_b\text{PO}_4$ ($0.90 \leq a \leq 1.8, 0.001 \leq b \leq 0.1$); LiNiVO_4 ; 및 $\text{Li}_{(2-f)}\text{J}_2(\text{PO}_4)_3$ ($0 \leq f \leq 2$) 로 이루어진 군에서 선택된 적어도 하나인 것인 리튬 이차 전지용 양극 활물질;

상기 화학식에 있어서, A는 Ni, Co, Mn, 및 이들의 조합으로 이루어진 군에서 선택되고; X는 Al, Ni, Co, Mn, Cr, Fe, Mg, Sr, V, 희토류 원소 및 이들의 조합으로 이루어진 군에서 선택되고; D는 O, F, S, P, 및 이들의 조합으로 이루어진 군에서 선택되고; E는 Co, Mn, 및 이들의 조합으로 이루어진 군에서 선택되고; T는 F, S, P, 및 이들의 조합으로 이루어진 군에서 선택되고; G는 Al, Cr, Mn, Fe, Mg, La, Ce, Sr, V, 및 이들의 조합으로 이루어진 군에서 선택되고; Q는 Ti, Mo, Mn, 및 이들의 조합으로 이루어진 군에서 선택되고; Z는 Cr, V, Fe, Sc, Y, 및 이들의 조합으로 이루어진 군에서 선택되며; J는 V, Cr, Mn, Co, Ni, Cu, 및 이들의 조합으로 이루어진 군에서 선택된다.

청구항 6

제1항에 있어서,

상기 제1 양극 활물질 및 제2 양극 활물질에 있어서,

서로 독립적으로, 상기 양극 활물질의 총 중량에 대한 상기 복합 코팅층의 함량은 0.2 내지 2.0 중량% 인 것인 리튬 이차 전지용 양극 활물질.

청구항 7

리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물:을 준비하는 단계;

인 또는 불소 공급원: 및 금속 공급원:을 준비하는 단계;

상기 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물에 상기 인 또는 불소 공급원: 또는 금속 공급원을 혼합하여, 상기 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물의 표면에 인 또는 불소 공급원: 또는 금속 공급원을 균일하게 부착시키는 단계; 및

상기 인 또는 불소 공급원: 또는 금속 공급원이 부착된 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물을 열처리하여 코팅층을 형성시키는 단계:를 포함하는 양극 활물질의 제조 방법이며,

상기 제조 방법은 독립적으로 수행되어, 제1 양극 활물질 및 제2 양극 활물질을 제조하고,

상기 제1 양극 활물질의 제조에 있어서, 상기 코팅층을 형성시키는 단계에 의해, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M을 포함하며, 상기 금속 M은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되는 적어도 하나의 원소를 포함하고,

상기 제2 양극 활물질의 제조에 있어서, 상기 코팅층을 형성시키는 단계에 의해, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M' 을 포

함하며, 상기 금속 M' 는 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되며, 상기 M' 는 상기 제1 양극 활물질 내 M과는 서로 다른 금속이고,

상기 제2 양극 활물질에 대한 제1 양극 활물질의 중량비는 95/5 내지 70/30 인 것인 리튬 이차전지용 양극 활물질의 제조 방법.

청구항 8

제7항에 있어서,

상기 인 또는 불소 공급원; 또는 금속 공급원이 부착된 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물을 열처리하여 코팅층을 형성시키는 단계;에서,

열처리 온도는, 650 내지 950℃인 것인 리튬 이차전지용 양극 활물질의 제조 방법.

청구항 9

제1항 내지 제6항 중 어느 한 항에 따른 리튬 이차 전지용 양극 활물질을 포함하는 양극;

음극 활물질을 포함하는 음극; 및

전해질;

을 포함하는 리튬 이차 전지.

발명의 설명

기술 분야

[0001] 리튬 이차 전지용 양극 활물질, 이의 제조방법 및 이를 포함하는 리튬 이차 전지에 관한 것이다.

배경 기술

[0002] 최근 휴대용 전자기기의 소형화 및 경량화 추세와 관련하여 이들 기기의 전원으로 사용되는 전지의 고성능화 및 대용량화에 대한 필요성이 높아지고 있다.

[0003] 전지는 양극과 음극에 전기 화학 반응이 가능한 물질을 사용함으로써 전력을 발생시키는 것이다. 이러한 전지 중 대표적인 예로는 양극 및 음극에서 리튬 이온이 인터칼레이션/디인터칼레이션될 때의 화학전위(chemical potential)의 변화에 의하여 전기 에너지를 생성하는 리튬 이차 전지가 있다.

[0004] 상기 리튬 이차 전지는 리튬 이온의 가역적인 인터칼레이션/디인터칼레이션이 가능한 물질을 양극과 음극 활물질로 사용하고, 상기 양극과 음극 사이에 유기 전해액 또는 폴리머 전해액을 충전시켜 제조한다.

[0005] 리튬 이차 전지의 양극 활물질로는 리튬 복합금속 화합물이 사용되고 있으며, 그 예로 LiCoO_2 , LiMn_2O_4 , LiNiO_2 , LiMnO_2 등의 복합금속 산화물들이 연구되고 있다.

[0006] 상기 양극 활물질 중 LiMn_2O_4 , LiMnO_2 등의 Mn계 양극 활물질은 합성하기도 쉽고, 값이 비교적 싸며, 과충전시 다른 활물질에 비하여 열적 안정성이 가장 우수하고, 환경에 대한 오염이 낮아 매력에 있는 물질이기는 하나, 용량이 적다는 단점을 가지고 있다.

[0007] LiCoO_2 는 양호한 전기 전도도와 약 3.7V 정도의 높은 전지 전압을 가지며, 사이클 수명 특성, 안정성 또한 방전 용량 역시 우수하므로, 현재 상업화되어 시판되고 있는 대표적인 양극 활물질이다. 그러나 LiCoO_2 는 가격이 비싸기 때문에 전지 가격의 30% 이상을 차지하므로 가격 경쟁력이 떨어지는 문제점이 있다.

[0008] 또한 LiNiO_2 는 위에서 언급한 양극 활물질 중 가장 높은 방전 용량의 전지 특성을 나타내고 있으나, 합성하기 어려운 단점이 있다. 또한 니켈의 높은 산화상태는 전지 및 전극 수명 저하의 원인이 되며, 자기 방전이 심하고 가역성이 떨어지는 문제가 있다. 아울러, 안정성 확보가 완전하지 않아서 상용화에 어려움을 겪고 있다.

[0009] 상기와 같이 종전의 기술들에서 전지 특성을 향상 시키기 위한 다양한 코팅층을 포함하는 리튬 이차 전지용 양극 활물질이 제공되어 왔었다.

발명의 내용

해결하려는 과제

[0010] 고용량, 고효율 및 수명특성이 우수한 리튬 이차 전지용 양극 활물질을 제공하며, 이의 제조 방법 및 상기 양극 활물질을 포함하는 양극을 포함하는 리튬 이차 전지를 제공하는 것이다.

과제의 해결 수단

[0011] 본 발명의 일 구현예에서는, 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물; 및 상기 화합물의 표면의 적어도 일부에 위치하는 코팅층을 포함하고, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M을 포함하며, 상기 금속 M은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되는 적어도 하나의 원소를 포함하는 것인 제1 양극 활물질; 및

[0012] 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물; 및 상기 화합물의 표면의 적어도 일부에 위치하는 코팅층을 포함하고, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M' 을 포함하며, 상기 금속 M' 은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되며, 상기 M' 는 상기 제1 양극 활물질 내 M과는 서로 다른 금속인 것인 제2 양극 활물질;을 포함하는 리튬 이차 전지용 양극 활물질을 제공한다.

[0013] 상기 복합 코팅층 내 포함된 Li_3PO_4 또는 LiF , 또는 리튬 금속 산화물의 리튬은, 상기 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물 내에 포함되는 Li로부터 기인되거나, 별도의 Li 공급 물질로부터 기인될 수 있다.

[0014] 상기 복합 코팅층 내 LiF 의 불소는, 상기 불소가 도핑된 코어 내 포함된 불소로부터 기인되거나, 별도의 불소 공급 물질로부터 기인될 수 있다.

[0015] 상기 제2 양극 활물질에 대한 제1 양극 활물질의 중량비는 95/5 내지 70/30 일 수 있다.

[0016] 상기 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물은, $\text{Li}_a\text{A}_{1-b}\text{X}_b\text{D}_2$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$); $\text{Li}_a\text{A}_{1-b}\text{X}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$); $\text{LiE}_{1-b}\text{X}_b\text{O}_{2-c}\text{D}_c$ ($0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$); $\text{LiE}_{2-b}\text{X}_b\text{O}_{2-c}\text{T}_c$ ($0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$); $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{X}_c\text{D}_a$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$, $0 < a < 2$); $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{X}_c\text{O}_{2-a}\text{T}_a$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$, $0 < a < 2$); $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{X}_c\text{O}_{2-a}\text{T}_2$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$, $0 < a < 2$); $\text{Li}_a\text{Ni}_{1-b-c}\text{Mn}_b\text{X}_c\text{D}_a$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$, $0 < a < 2$); $\text{Li}_a\text{Ni}_{1-b-c}\text{Mn}_b\text{X}_c\text{O}_{2-a}\text{T}_a$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$, $0 < a < 2$); $\text{Li}_a\text{Ni}_{1-b-c}\text{Mn}_b\text{X}_c\text{O}_{2-a}\text{T}_2$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$, $0 < a < 2$); $\text{Li}_a\text{Ni}_b\text{E}_c\text{G}_d\text{O}_{2-c}\text{T}_e$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.9$, $0 \leq c \leq 0.5$, $0.001 \leq d \leq 0.1$, $0 \leq e \leq 0.05$); $\text{Li}_a\text{Ni}_b\text{Co}_c\text{Mn}_d\text{G}_e\text{O}_{2-f}\text{T}_f$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.9$, $0 \leq c \leq 0.5$, $0 \leq d \leq 0.5$, $0.001 \leq e \leq 0.1$, $0 \leq f \leq 0.05$); $\text{Li}_a\text{NiG}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8$, $0.001 \leq b \leq 0.1$, $0 \leq c \leq 0.05$); $\text{Li}_a\text{CoG}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8$, $0.001 \leq b \leq 0.1$, $0 \leq c \leq 0.05$); $\text{Li}_a\text{MnG}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8$, $0.001 \leq b \leq 0.1$, $0 \leq c \leq 0.05$); $\text{Li}_a\text{Mn}_b\text{G}_c\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8$, $0.001 \leq b \leq 0.1$, $0 \leq c \leq 0.05$); $\text{Li}_a\text{MnG}_b\text{PO}_4$ ($0.90 \leq a \leq 1.8$, $0.001 \leq b \leq 0.1$); LiNiVO_4 ; 및 $\text{Li}_{13-f}\text{J}_f(\text{PO}_4)_3$ ($0 \leq f \leq 2$) 로 이루어진 군에서 선택된 적어도 하나일 수 있다.

[0017] 상기 화학식에 있어서, A는 Ni, Co, Mn, 및 이들의 조합으로 이루어진 군에서 선택되고; X는 Al, Ni, Co, Mn, Cr, Fe, Mg, Sr, V, 희토류 원소 및 이들의 조합으로 이루어진 군에서 선택되고; D는 O, F, S, P, 및 이들의 조합으로 이루어진 군에서 선택되고; E는 Co, Mn, 및 이들의 조합으로 이루어진 군에서 선택되고; T는 F, S, P,

및 이들의 조합으로 이루어진 군에서 선택되고; G는 Al, Cr, Mn, Fe, Mg, La, Ce, Sr, V, 및 이들의 조합으로 이루어진 군에서 선택되고; Q는 Ti, Mo, Mn, 및 이들의 조합으로 이루어진 군에서 선택되고; Z는 Cr, V, Fe, Sc, Y, 및 이들의 조합으로 이루어진 군에서 선택되며; J는 V, Cr, Mn, Co, Ni, Cu, 및 이들의 조합으로 이루어진 군에서 선택된다.

[0018] 상기 제1 양극 활물질 및 제2 양극 활물질에 있어서, 서로 독립적으로, 상기 양극 활물질의 총 중량에 대한 상기 복합 코팅층의 함량은 0.2 내지 2.0 중량% 일 수 있다.

[0019] 본 발명의 다른 일 구현예에서는, 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물;을 준비하는 단계; 인 또는 불소 공급원; 및 금속 공급원;을 준비하는 단계; 상기 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물에 상기 인 또는 불소 공급원; 또는 금속 공급원을 혼합하여, 상기 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물의 표면에 인 또는 불소 공급원; 또는 금속 공급원을 균일하게 부착시키는 단계; 및 상기 인 또는 불소 공급원; 또는 금속 공급원이 부착된 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물을 열처리하여 코팅층을 형성시키는 단계;를 포함하는 양극 활물질의 제조 방법 이되, 상기 제조 방법은 독립적으로 수행되어, 제1 양극 활물질 및 제2 양극 활물질을 제조하고, 상기 제1 양극 활물질의 제조에 있어서, 상기 코팅층을 형성시키는 단계에 의해, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M을 포함하며, 상기 금속 M은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되는 적어도 하나의 원소를 포함하고, 상기 제2 양극 활물질의 제조에 있어서, 상기 코팅층을 형성시키는 단계에 의해, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M' 을 포함하며, 상기 금속 M' 은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되며, 상기 M' 는 상기 제1 양극 활물질 내 M과는 서로 다른 금속이고, 상기 제2 양극 활물질에 대한 제1 양극 활물질의 중량비는 95/5 내지 70/30 인 것인 리튬 이차전지용 양극 활물질의 제조 방법을 제공한다.

[0020] 상기 인 또는 불소 공급원; 또는 금속 공급원이 부착된 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물을 열처리하여 코팅층을 형성시키는 단계;에서, 열처리 온도는, 650 내지 950℃일 수 있다.

[0021] 본 발명의 또 다른 일 구현예에서는, 전술한 본 발명의 일 구현예에 따른 리튬 이차 전지용 양극 활물질을 포함하는 양극; 음극 활물질을 포함하는 음극; 및 전해질;을 포함하는 리튬 이차 전지를 제공한다.

발명의 효과

[0022] 우수한 전지 특성을 갖는 양극 활물질 및 이를 포함하는 리튬 이차 전지를 제공할 수 있다.

도면의 간단한 설명

[0023] 도 1은 리튬 이차 전지의 개략도이다.

발명을 실시하기 위한 구체적인 내용

[0024] 이하, 본 발명의 구현예를 상세히 설명하기로 한다. 다만, 이는 예시로서 제시되는 것으로, 이에 의해 본 발명이 제한되지는 않으며 본 발명은 후술할 청구범위의 범주에 의해 정의될 뿐이다.

[0025] 본 발명의 일 구현예에서는, 본 발명의 일 구현예에서는, 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물; 및 상기 화합물의 표면의 적어도 일부에 위치하는 코팅층을 포함하고, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M을 포함하며, 상기 금속 M은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되는 적어도 하나의 원소를 포함하는 것인 제1 양극 활물질; 및 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물; 및 상기 화합물의 표면의 적어도 일부에 위치하는 코팅층을 포함하고, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M' 을 포함하며, 상기 금속 M' 은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되며, 상기 M' 는 상기 제1 양극 활물질 내 M과는 서로 다른 금속인 것인 제2 양

극 활물질;을 포함하는 리튬 이차 전지용 양극 활물질을 제공한다.

- [0026] 상기 코팅층의 화합물은 열처리 반응으로 인하여 발생한 화합물일 수 있다.
- [0027] 또한, 상기 복합 코팅층 내 포함된 Li_3PO_4 또는 LiF , 또는 리튬 금속 산화물의 리튬은, 상기 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물 내에 포함되는 Li으로부터 기인되거나, 별도의 Li 공급 물질로부터 기인될 것일 수 있다.
- [0028] 또한, 상기 복합 코팅층 내 LiF 의 불소는, 상기 불소가 도핑된 코어 내 포함된 불소로부터 기인되거나, 별도의 불소 공급 물질로부터 기인될 수 있다.
- [0029] 상기 Li_3PO_4 또는 LiF 를 포함하고, 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층을 포함하는 양극 활물질은 리튬 이차 전지의 전지적 특성을 향상시킬 수 있다. 보다 구체적으로, 기존의 양극 활물질 보다 높은 초기 용량, 향상된 효율 특성 및 뛰어난 수명특성을 가지는 양극 활물질을 제공할 수 있다.
- [0030] 상기 복합 코팅층의 Li를 포함하는 금속화합물은 양극 활물질 내의 Li이온의 확산도를 높이는 역할(Driving Force)을 수행하여 Li 이온의 이동을 용이하게 하여 전기 특성 향상에 기여할 수 있다.
- [0031] 또한 상기의 Li_3PO_4 역시 이온전도성을 향상 시키며, 효율 특성 향상에 효과가 있다. 더욱이 LiF 를 더 포함할 경우 전해액과의 부반응 억제 하여 표면구조 안정화에 기여하여 전기 특성 향상에 더 유리하다.
- [0032] 보다 구체적으로, 상기 복합 코팅층은 양극 활물질 표면에서 서로 간의 복잡한 결합을 통하여 표면 개질에 있어서 상승 작용을 일으킨다.
- [0033] 또한, 상기 본 발명의 일 구현예에 따른 양극 활물질은 리튬 이차 전지의 전지적 특성을 향상시킬 수 있다. 향상된 전지적 특성의 예로, 고전압 특성에서 전지의 초기 용량, 향상된 효율 특성, 뛰어난 수명특성 등이 있다.
- [0034] 상기의 서로 다른 복합 코팅층을 가지는 제1 양극 활물질과 제2 양극 활물질을 포함하는 양극 활물질은 상기의 상승 작용을 보다 일으켜 전기 특성을 보다 더 향상시킬 수 있다.
- [0035] 상기 제2 양극 활물질에 대한 제1 양극 활물질의 중량비는 95/5 내지 70/30일 수 있다.
- [0036] 상기 양극 활물질의 총 중량에 대한 상기 복합 코팅층의 함량은 0.2 내지 2.0 중량%일 수 있다. 상기 중량비가 0.2 미만의 경우 코팅층의 역할이 감소할 수 있으며, 2.0 초과이면 초기용량 감소 및 충방전 효율의 감소가 나타날 수 있다. 다만, 이에 제한되는 것은 아니다.
- [0037] 구체적인 예를 들어, 상기 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물은, $\text{Li}_a\text{Al}_{1-b}\text{X}_b\text{D}_2$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$); $\text{Li}_a\text{Al}_{1-b}\text{X}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$); $\text{LiE}_{1-b}\text{X}_b\text{O}_{2-c}\text{D}_c$ ($0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$); $\text{LiE}_{1-b}\text{X}_b\text{O}_{4-c}\text{T}_c$ ($0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$); $\text{Li}_2\text{Ni}_{1-b-c}\text{Co}_b\text{X}_c\text{D}_a$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$, $0 < a \leq 2$); $\text{Li}_2\text{Ni}_{1-b-c}\text{Co}_b\text{X}_c\text{O}_{2-a}\text{T}_a$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$, $0 < a < 2$); $\text{Li}_2\text{Ni}_{1-b-c}\text{Co}_b\text{X}_c\text{O}_{2-a}\text{T}_2$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$, $0 < a < 2$); $\text{Li}_2\text{Ni}_{1-b-c}\text{Mn}_b\text{X}_c\text{D}_a$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$, $0 < a \leq 2$); $\text{Li}_2\text{Ni}_{1-b-c}\text{Mn}_b\text{X}_c\text{O}_{2-a}\text{T}_a$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$, $0 < a < 2$); $\text{Li}_2\text{Ni}_{1-b-c}\text{Mn}_b\text{X}_c\text{O}_{2-a}\text{T}_2$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.5$, $0 \leq c \leq 0.05$, $0 < a < 2$); $\text{Li}_2\text{Ni}_b\text{E}_c\text{G}_d\text{O}_{2-e}\text{T}_e$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.9$, $0 \leq c \leq 0.5$, $0.001 \leq d \leq 0.1$, $0 \leq e \leq 0.05$); $\text{Li}_2\text{Ni}_b\text{Co}_c\text{Mn}_d\text{G}_e\text{O}_{2-f}\text{T}_f$ ($0.90 \leq a \leq 1.8$, $0 \leq b \leq 0.9$, $0 \leq c \leq 0.5$, $0 \leq d \leq 0.5$, $0.001 \leq e \leq 0.1$, $0 \leq f \leq 0.05$); $\text{Li}_2\text{NiG}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8$, $0.001 \leq b \leq 0.1$, $0 \leq c \leq 0.05$); $\text{Li}_2\text{CoG}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8$, $0.001 \leq b \leq 0.1$, $0 \leq c \leq 0.05$); $\text{Li}_2\text{MnG}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8$, $0.001 \leq b \leq 0.1$, $0 \leq c \leq 0.05$); $\text{Li}_2\text{Mn}_2\text{G}_b\text{O}_{2-c}\text{T}_c$ ($0.90 \leq a \leq 1.8$, $0.001 \leq b \leq 0.1$, $0 \leq c \leq 0.05$); $\text{Li}_2\text{MnG}_b\text{PO}_4$ ($0.90 \leq a \leq 1.8$, $0.001 \leq b \leq 0.1$); LiNiVO_4 ; 및 $\text{Li}_{(3-f)}\text{J}_2(\text{PO}_4)_3$ ($0 \leq f \leq 2$) 로 이루어진 군에서 선택된 적어도 하나일 수 있다. .
- [0038] 상기 화학식에 있어서, A는 Ni, Co, Mn, 및 이들의 조합으로 이루어진 군에서 선택되고; X는 Al, Ni, Co, Mn, Cr, Fe, Mg, Sr, V, 희토류 원소 및 이들의 조합으로 이루어진 군에서 선택되고; D는 O, F, S, P, 및 이들의 조

합으로 이루어진 군에서 선택되고; E는 Co, Mn, 및 이들의 조합으로 이루어진 군에서 선택되고; T는 F, S, P, 및 이들의 조합으로 이루어진 군에서 선택되고; G는 Al, Cr, Mn, Fe, Mg, La, Ce, Sr, V, 및 이들의 조합으로 이루어진 군에서 선택되고; Q는 Ti, Mo, Mn, 및 이들의 조합으로 이루어진 군에서 선택되고; Z는 Cr, V, Fe, Sc, Y, 및 이들의 조합으로 이루어진 군에서 선택되며; J는 V, Cr, Mn, Co, Ni, Cu, 및 이들의 조합으로 이루어진 군에서 선택된다.

[0039] 본 발명의 다른 일 구현예에서는, 본 발명의 다른 일 구현예에서는, 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물:을 준비하는 단계; 인 또는 불소 공급원; 및 금속 공급원:을 준비하는 단계; 상기 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물에 상기 인 또는 불소 공급원; 또는 금속 공급원을 혼합하여, 상기 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물의 표면에 인 또는 불소 공급원; 또는 금속 공급원을 균일하게 부착시키는 단계; 및 상기 인 또는 불소 공급원; 또는 금속 공급원이 부착된 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물을 열처리하여 코팅층을 형성시키는 단계;를 포함하는 양극 활물질의 제조 방법이다. 상기 제조 방법은 독립적으로 수행되어, 제1 양극 활물질 및 제2 양극 활물질을 제조하고, 상기 제1 양극 활물질의 제조에 있어서, 상기 코팅층을 형성시키는 단계에 의해, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M을 포함하며, 상기 금속 M은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되는 적어도 하나의 원소를 포함하고, 상기 제2 양극 활물질의 제조에 있어서, 상기 코팅층을 형성시키는 단계에 의해, 상기 코팅층은 Li_3PO_4 또는 LiF 를 포함하며, 상기 코팅층은 리튬 금속 산화물, 금속 산화물, 또는 이들의 조합을 더 포함하는 복합 코팅층이고, 상기 리튬 금속 산화물 및 금속 산화물 중 적어도 어느 하나는 서로 독립적으로, 금속 M'을 포함하며, 상기 금속 M'은 Mg, Ti, Al, Si, Sn 및 Zr로 이루어진 군에서 선택되며, 상기 M'은 상기 제1 양극 활물질 내 M과는 서로 다른 금속이고, 상기 제2 양극 활물질에 대한 제1 양극 활물질의 중량비는 95/5 내지 70/30 인 것인 리튬 이차전지용 양극 활물질의 제조 방법을 제공한다.

[0040] 상기 인 또는 불소 공급원; 또는 금속 공급원이 부착된 리튬의 가역적인 인터칼레이션 및 디인터칼레이션이 가능한 화합물을 열처리하여 코팅층을 형성시키는 단계;에서, 열처리 온도는, 650 내지 950℃일 수 있다. 상기 온도 범위인 경우 양극 활물질 표면에 형성된 코팅층이 안정적인 역할을 수행 할 수 있다.

[0041] 나머지 구성에 대한 설명은 전술한 본 발명의 일 구현예와 동일하기 때문에 그 설명을 생략하도록 한다.

[0042] 본 발명의 또 다른 일 구현예에서는, 양극, 음극 및 전해질을 포함하는 리튬 이차 전지이며, 상기 양극은 전류 집전체 및 상기 전류 집전체 상에 형성된 양극 활물질층을 포함하며, 상기 양극 활물질층은, 전술한 양극 활물질을 포함하는 것인 리튬 이차 전지를 제공한다.

[0043] 상기 양극 활물질과 관련된 설명은 전술한 본 발명의 일 구현예와 동일하기 때문에 생략하도록 한다.

[0044] 상기 양극 활물질층은 바인더 및 도전재를 포함할 수 있다.

[0045] 상기 바인더는 양극 활물질 입자들을 서로 잘 부착시키고, 또한 양극 활물질을 전류 집전체에 잘 부착시키는 역할을 하며, 그 대표적인 예로는 폴리비닐알콜, 카르복시메틸셀룰로오스, 히드록시프로필셀룰로오스, 디아세틸셀룰로오스, 폴리비닐클로라이드, 카르복실화된 폴리비닐클로라이드, 폴리비닐플루오라이드, 에틸렌 옥사이드를 포함하는 폴리머, 폴리비닐피롤리돈, 폴리우레탄, 폴리테트라플루오로에틸렌, 폴리비닐리덴 플루오라이드, 폴리에틸렌, 폴리프로필렌, 스티렌-부타디엔 러버, 아크릴레이트 스티렌-부타디엔 러버, 에폭시 수지, 나일론 등을 사용할 수 있으나, 이에 한정되는 것은 아니다.

[0046] 상기 도전재는 전극에 도전성을 부여하기 위해 사용되는 것으로서, 구성되는 전지에 있어서, 화학변화를 야기하지 않고 전자 전도성 재료이면 어떠한 것도 사용가능하며, 그 예로 천연 흑연, 인조 흑연, 카본 블랙, 아세틸렌 블랙, 케첸블랙, 탄소섬유 등의 탄소계 물질; 구리, 니켈, 알루미늄, 은 등의 금속 분말 또는 금속 섬유 등의 금속계 물질; 폴리페닐렌 유도체 등의 도전성 폴리머; 또는 이들의 혼합물을 포함하는 도전성 재료를 사용할 수 있다.

[0047] 상기 음극은 집전체 및 상기 집전체 위에 형성된 음극 활물질층을 포함하며, 상기 음극 활물질층은 음극 활물질을 포함한다.

[0048] 상기 음극 활물질로는 리튬 이온을 가역적으로 인터칼레이션/디인터칼레이션할 수 있는 물질, 리튬 금속, 리튬 금속의 합금, 리튬을 도프 및 탈도프할 수 있는 물질, 또는 전이 금속 산화물을 포함한다.

- [0049] 상기 리튬 이온을 가역적으로 인터칼레이션/디인터칼레이션할 수 있는 물질로는 탄소 물질로서, 리튬 이온 이차 전지에서 일반적으로 사용되는 탄소계 음극 활물질은 어떠한 것도 사용할 수 있으며, 그 대표적인 예로는 결정질 탄소, 비정질 탄소 또는 이들을 함께 사용할 수 있다. 상기 결정질 탄소의 예로는 무정형, 판상, 린편상(flake), 구형 또는 섬유형의 천연 흑연 또는 인조 흑연과 같은 흑연을 들 수 있고, 상기 비정질 탄소의 예로는 소프트 카본(soft carbon: 작은 소성 탄소) 또는 하드 카본(hard carbon), 매조페이스 피치 탄화물, 소성된 코크스 등을 들 수 있다.
- [0050] 상기 리튬 금속의 합금으로는 리튬과 Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Si, Sb, Pb, In, Zn, Ba, Ra, Ge, Al 및 Sn으로 이루어진 군에서 선택되는 금속의 합금이 사용될 수 있다.
- [0051] 상기 리튬을 도프 및 탈도프할 수 있는 물질로는 Si, SiO_x ($0 < x < 2$), Si-Y 합금(상기 Y는 알칼리 금속, 알칼리 토금속, 13족 원소, 14족 원소, 전이금속, 희토류 원소 및 이들의 조합으로 이루어진 군에서 선택되는 원소이며, Si은 아님), Sn, SnO_2 , Sn-Y(상기 Y는 알칼리 금속, 알칼리 토금속, 13족 원소, 14족 원소, 전이금속, 희토류 원소 및 이들의 조합으로 이루어진 군에서 선택되는 원소이며, Sn은 아님) 등을 들 수 있고, 또한 이들 중 적어도 하나와 SiO_2 를 혼합하여 사용할 수도 있다. 상기 원소 Y로는 Mg, Ca, Sr, Ba, Ra, Sc, Y, Ti, Zr, Hf, Rf, V, Nb, Ta, Db, Cr, Mo, W, Sg, Tc, Re, Bh, Fe, Pb, Ru, Os, Hs, Rh, Ir, Pd, Pt, Cu, Ag, Au, Zn, Cd, B, Al, Ga, Sn, In, Ti, Ge, P, As, Sb, Bi, S, Se, Te, Po, 및 이들의 조합으로 이루어진 군에서 선택될 수 있다.
- [0052] 상기 전이 금속 산화물로는 바나듐 산화물, 리튬 바나듐 산화물 등을 들 수 있다.
- [0053] 상기 음극 활물질 층은 또한 바인더를 포함하며, 선택적으로 도전재를 더욱 포함할 수도 있다.
- [0054] 상기 바인더는 음극 활물질 입자들을 서로 잘 부착시키고, 또한 음극 활물질을 전류 집전체에 잘 부착시키는 역할을 하며, 그 대표적인 예로 폴리비닐알콜, 카르복시메틸셀룰로오스, 히드록시프로필셀룰로오스, 폴리비닐클로라이드, 카르복실화된 폴리비닐클로라이드, 폴리비닐플루오라이드, 에틸렌 옥사이드를 포함하는 폴리머, 폴리비닐피롤리돈, 폴리우레탄, 폴리테트라플루오로에틸렌, 폴리비닐리덴 플루오라이드, 폴리에틸렌, 폴리프로필렌, 스티렌-부타디엔 러버, 아크릴레이터드 스티렌-부타디엔 러버, 에폭시 수지, 나일론 등을 사용할 수 있으나, 이에 한정되는 것은 아니다.
- [0055] 상기 도전재는 전극에 도전성을 부여하기 위해 사용되는 것으로서, 구성되는 전지에 있어서, 화학변화를 야기하지 않고 전자 전도성 재료이면 어떠한 것도 사용가능하며, 그 예로 천연 흑연, 인조 흑연, 카본 블랙, 아세틸렌 블랙, 캐헨블랙, 탄소섬유 등의 탄소계 물질; 구리, 니켈, 알루미늄, 은 등의 금속 분말 또는 금속 섬유 등의 금속계 물질; 폴리페닐렌 유도체 등의 도전성 폴리머; 또는 이들의 혼합물을 포함하는 도전성 재료를 사용할 수 있다.
- [0056] 상기 집전체로는 구리 박, 니켈 박, 스테인레스강 박, 티타늄 박, 니켈 발포체(foam), 구리 발포체, 전도성 금속이 코팅된 폴리머 기재, 및 이들의 조합으로 이루어진 군에서 선택되는 것을 사용할 수 있다.
- [0057] 상기 전류 집전체로는 Al을 사용할 수 있으나 이에 한정되는 것은 아니다.
- [0058] 상기 음극과 양극은 활물질, 도전재 및 결합제를 용매 중에서 혼합하여 활물질 조성물을 제조하고, 이 조성물을 전류 집전체에 도포하여 제조한다. 이와 같은 전극 제조 방법은 당해 분야에 널리 알려진 내용이므로 본 명세서에서 상세한 설명은 생략하기로 한다. 상기 용매로는 N-메틸피롤리돈 등을 사용할 수 있으나 이에 한정되는 것은 아니다.
- [0059] 상기 전해질은 비수성 유기 용매와 리튬염을 포함한다.
- [0060] 상기 비수성 유기 용매는 전지의 전기화학적 반응에 관여하는 이온들이 이동할 수 있는 매질 역할을 한다.
- [0061] 상기 비수성 유기용매로는 카보네이트계, 에스테르계, 에테르계, 케톤계, 알코올계, 또는 비양성자성 용매를 사용할 수 있다. 상기 카보네이트계 용매로는 디메틸 카보네이트(DMC), 디에틸 카보네이트(DEC), 디프로필 카보네이트(DPC), 메틸프로필 카보네이트(MPC), 에틸프로필 카보네이트(EPC), 메틸에틸 카보네이트(MEC), 에틸렌 카보네이트(EC), 프로필렌 카보네이트(PC), 부틸렌 카보네이트(BC) 등이 사용될 수 있으며, 상기 에스테르계 용매로는 메틸 아세테이트, 에틸 아세테이트, n-프로필 아세테이트, 디메틸아세테이트, 메틸프로피오네이트, 에틸프로피오네이트, γ-부티로락톤, 데카놀라이드(decanolide), 발레로락톤, 메발로노락톤(mevalonolactone), 카프로락톤(caprolactone), 등이 사용될 수 있다. 상기 에테르계 용매로는 디부틸 에테르, 테트라글라이드, 디글라이드,

디테트시아에탄, 2-메틸테트라하드로퓨란, 테트라하드로퓨란 등이 사용될 수 있으며, 상기 캐톤계 용매로는 시클로헥산은 등이 사용될 수 있다. 또한 상기 알코올계 용매로는 에틸알코올, 이소프로필 알코올 등이 사용될 수 있으며, 상기 비양성자성 용매로는 R-CN(R은 탄소수 2 내지 20의 직쇄상, 분지상, 또는 환 구조의 탄화수소기이며, 이중결합 방향 환 또는 에테르 결합을 포함할 수 있다) 등의 니트릴류 디메틸포름아미드 등의 아미드류, 1,3-디옥솔란 등의 디옥솔란류 설폴란(sulfolane)류 등이 사용될 수 있다.

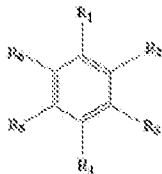
[0062] 상기 비수성 유기 용매는 단독으로 또는 하나 이상 혼합하여 사용할 수 있으며, 하나 이상 혼합하여 사용하는 경우의 혼합 비율은 목적하는 전지 성능에 따라 적절하게 조절할 수 있고, 이는 당해 분야에 종사하는 사람들에게는 널리 이해될 수 있다.

[0063] 또한, 상기 카보네이트계 용매의 경우 환형(cyclic) 카보네이트와 사슬형(chain) 카보네이트를 혼합하여 사용하는 것이 좋다. 이 경우 환형 카보네이트와 사슬형 카보네이트는 1:1 내지 1:9의 부피비로 혼합하여 사용하는 것이 전해액의 성능이 우수하게 나타날 수 있다.

[0064] 본 발명의 일 구현예에 따른 비수성 유기용매는 상기 카보네이트계 용매에 방향족 탄화수소계 유기용매를 더 포함할 수도 있다. 이때 상기 카보네이트계 용매와 방향족 탄화수소계 유기용매는 1:1 내지 30:1의 부피비로 혼합될 수 있다.

[0065] 상기 방향족 탄화수소계 유기용매로는 하기 화학식 1의 방향족 탄화수소계 화합물이 사용될 수 있다.

[0066] [화학식 1]



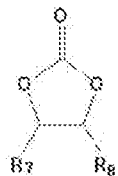
[0067]

[0068] (상기 화학식 1에서, R₁ 내지 R₆는 각각 독립적으로 수소, 할로젠, C₁ 내지 C₁₀ 알킬기, 할로알킬기 또는 이들의 조합이다.)

[0069] 상기 방향족 탄화수소계 유기용매는 벤젠, 플루오로벤젠, 1,2-디플루오로벤젠, 1,3-디플루오로벤젠, 1,4-디플루오로벤젠, 1,2,3-트리플루오로벤젠, 1,2,4-트리플루오로벤젠, 클로로벤젠, 1,2-디클로로벤젠, 1,3-디클로로벤젠, 1,4-디클로로벤젠, 1,2,3-트리클로로벤젠, 1,2,4-트리클로로벤젠, 아이오도벤젠, 1,2-다이아이오도벤젠, 1,3-다이아이오도벤젠, 1,4-다이아이오도벤젠, 1,2,3-트리아이오도벤젠, 1,2,4-트리아이오도벤젠, 톨루엔, 플루오로톨루엔, 1,2-디플루오로톨루엔, 1,3-디플루오로톨루엔, 1,4-디플루오로톨루엔, 1,2,3-트리플루오로톨루엔, 1,2,4-트리플루오로톨루엔, 클로로톨루엔, 1,2-디클로로톨루엔, 1,3-디클로로톨루엔, 1,4-디클로로톨루엔, 1,2,3-트리클로로톨루엔, 1,2,4-트리클로로톨루엔, 아이오도톨루엔, 1,2-다이아이오도톨루엔, 1,3-다이아이오도톨루엔, 1,4-다이아이오도톨루엔, 1,2,3-트리아이오도톨루엔, 1,2,4-트리아이오도톨루엔, 자일렌, 및 이들의 조합으로 이루어진 군에서 선택되는 것이다.

[0070] 상기 비수성 전해질은 전지 수명을 향상시키기 위하여 비닐렌 카보네이트 또는 하기 화학식 2의 에틸렌 카보네이트계 화합물을 더욱 포함할 수도 있다.

[0071] [화학식 2]



[0072]

[0073] (상기 화학식 2에서, R₇ 및 R₈는 각각 독립적으로 수소, 할로젠기, 시아노기(CN), 니트로기(NO₂) 또는 C₁ 내지 C₅ 플루오로알킬기이고, 상기 R₇과 R₈중 적어도 하나는 할로젠기, 시아노기(CN), 니트로기(NO₂) 또는 C₁ 내지 C₅

의 플루오로알킬기이다.)

- [0074] 상기 에틸렌 카보네이트계 화합물의 대표적인 예로는 디플루오로 에틸렌카보네이트, 클로로에틸렌 카보네이트, 디클로로에틸렌 카보네이트, 브로모에틸렌 카보네이트, 디브로모에틸렌 카보네이트, 니트로에틸렌 카보네이트, 시아노에틸렌 카보네이트 또는 플루오로에틸렌 카보네이트 등을 들 수 있다. 이러한 수명 향상 첨가제를 더욱 사용하는 경우 그 사용량은 적절하게 조절할 수 있다.
- [0075] 상기 리튬염은 유기 용매에 용해되어, 전지 내에서 리튬 이온의 공급원으로 작용하여 기본적인 리튬 이차 전지의 작동을 가능하게 하고, 양극과 음극 사이의 리튬 이온의 이동을 촉진하는 역할을 하는 물질이다. 이러한 리튬염의 대표적인 예로는 LiPF_6 , LiBF_4 , LiSbF_6 , LiAsF_6 , $\text{LiC}_4\text{F}_9\text{SO}_3$, LiClO_4 , LiAlO_2 , LiAlCl_4 , $\text{LiN}(\text{C}_x\text{F}_{2x+1}\text{SO}_2)(\text{C}_y\text{F}_{2y+1}\text{SO}_2)$ (여기서, x 및 y는 자연수임), LiCl , LiI 및 $\text{LiB}(\text{C}_2\text{O}_4)_2$ (리튬 비스옥살레이트 보레이트 (lithium bis(oxalato) borate: LiBOB)로 이루어진 군에서 선택되는 하나 또는 둘 이상을 지지(supporting) 전해염으로 포함한다. 리튬염의 농도는 0.1 내지 2.0M 범위 내에서 사용하는 것이 좋다. 리튬염의 농도가 상기 범위에 포함되면, 전해질이 적절한 전도도 및 점도를 가지므로 우수한 전해질 성능을 나타낼 수 있고, 리튬 이온이 효과적으로 이동할 수 있다.
- [0076] 리튬 이차 전지의 종류에 따라 양극과 음극 사이에 세퍼레이터가 존재할 수 도 있다. 이러한 세퍼레이터로는 폴리에틸렌, 폴리프로필렌, 폴리비닐리덴 플루오라이드 또는 이들의 2층 이상의 다층막이 사용될 수 있으며, 폴리에틸렌/폴리프로필렌 2층 세퍼레이터, 폴리에틸렌/폴리프로필렌/폴리에틸렌 3층 세퍼레이터, 폴리프로필렌/폴리에틸렌/폴리프로필렌 3층 세퍼레이터 등과 같은 혼합 다층막이 사용될 수 있음은 물론이다.
- [0077] 리튬 이차 전지는 사용하는 세퍼레이터와 전해질의 종류에 따라 리튬 이온 전지, 리튬 이온 폴리머 전지 및 리튬 폴리머 전지로 분류될 수 있고, 형태에 따라 원통형, 각형, 코인형, 파우치형 등으로 분류될 수 있으며, 사이즈에 따라 벌크 타입과 박막 타입으로 나눌 수 있다. 이들 전지의 구조와 제조방법은 이 분야에 널리 알려져 있으므로 상세한 설명은 생략한다.
- [0078] 도 1에 본 발명의 리튬 이차 전지의 대표적인 구조를 개략적으로 나타내었다. 도 1에 나타난 것과 같이 상기 리튬 이차 전지(1)는 양극(3), 음극(2) 및 상기 양극(3)과 음극(2) 사이에 존재하는 세퍼레이터(4)에 함침된 전해액을 포함하는 전지 용기(5)와, 상기 전지 용기(5)를 봉입하는 봉입 부재(6)를 포함한다.
- [0079] 이하 본 발명의 실시예 및 비교예를 기재한다. 그러나 하기의 실시예는 본 발명의 일 실시예 일뿐 본 발명이 하기한 실시예에 한정되는 것은 아니다.
- [0080] **실시예**
- [0081] **제조예1**
- [0082] Co_3O_4 와 Li_2CO_3 의 화학양론적 비율의 혼합물에 활물질 기준으로 MgCO_3 (0.01%), CaF_2 (0.005%), 및, TiO_2 (0.005%)가 되게 혼합물과 건식 혼합한 후, 이를 1000℃로 10 시간 동안 열처리하여 양극 활물질을 제조하였다.
- [0083] **제조예2**
- [0084] $\text{Ni}_{0.66}\text{Co}_{0.26}\text{Mn}_{0.26}(\text{OH})_2$ 와 Li_2CO_3 의 화학양론적 비율의 혼합물에 활물질 기준으로 MgCO_3 (0.01%), CaF_2 (0.005%), 및, TiO_2 (0.005%)가 되게 혼합물과 건식 혼합한 후, 이를 890℃로 12 시간 동안 열처리하여 양극 활물질을 제조하였다.
- [0085] **실시예 1**
- [0086] 믹서에 상기 제조예 1에서 제조 된 양극 활물질 100g과 $\text{Al}(\text{OH})_3$ 분말 0.027g과 TiO_2 분말 0.159g과 $(\text{NH}_4)_2\text{HPO}_4$ 분말 0.465g을 건식 혼합하여 상기 분말이 양극 활물질 본체의 표면에 부착된 혼합물을 제조 한 후 상기 혼합물을 800 ℃로 6시간 열처리하여 제1 양극 활물질을 제조하였다.
- [0087] 믹서에 상기 제조예 1에서 제조 된 양극 활물질 100g과 $\text{Zr}(\text{OH})_4$ 분말 0.172g과 SiO_2 분말 0.054g과 $(\text{NH}_4)_2\text{HPO}_4$ 분말 0.387g을 건식 혼합하여 상기 분말이 양극 활물질 본체의 표면에 부착된 혼합물을 제조 한 후 상기 혼합물을 800 ℃로 6시간 열처리하여 제2 양극 활물질을 제조하였다.
- [0088] 상기 제조 된 제1 양극 활물질과 제2 양극 활물질을 리본 믹서에 80/20의 중량비로 15분간 혼합하여 제1양극 활

물질과 제2 양극 활물질을 포함하는 양극 활물질을 제조하였다.

[0089] 실시예 2

[0090] 믹서에 상기 제조예 1에서 제조된 양극 활물질 100g과 $Zr(OH)_4$ 분말 0.172g과 SiO_2 분말 0.054g과 $(NH_4)_2HPO_4$ 분말 0.387g을 건식 혼합하여 상기 분말이 양극 활물질 본체의 표면에 부착된 혼합물을 제조한 후 상기 혼합물을 800 ℃로 6시간 열처리하여 제1 양극 활물질을 제조하였다.

[0091] 믹서에 상기 제조예 1에서 제조된 양극 활물질 100g과 $MgCO_3$ 분말 0.259g, TiO_2 분말 0.615g, $(NH_4)_2HPO_4$ 분말 1.426g 및 LiF 0.132g을 건식 혼합하여 상기 분말이 양극 활물질 본체의 표면에 부착된 혼합물을 제조한 후 상기 혼합물을 800 ℃로 6시간 열처리하여 제2 양극 활물질을 제조하였다.

[0092] 상기 제조된 제1 양극 활물질과 제2 양극 활물질을 리본 믹서에 80/20의 중량비로 15분간 혼합하여 제1 양극 활물질과 제2 양극 활물질을 포함하는 양극 활물질을 제조하였다.

[0093] 실시예 3

[0094] 믹서에 상기 제조예 2에서 제조된 양극 활물질 100g과 $Al(OH)_3$ 분말 0.027g과 $SnSO_4$ 분말 0.00044g과 $(NH_4)_2HPO_4$ 분말 1.331g을 건식 혼합하여 상기 분말이 양극 활물질 본체의 표면에 부착된 혼합물을 제조한 후 상기 혼합물을 650 ℃로 6시간 열처리하여 제1 양극 활물질을 제조하였다.

[0095] 믹서에 상기 제조예 2에서 제조된 양극 활물질 100g과 $MgCO_3$ 분말 0.259g, TiO_2 분말 0.615g, $(NH_4)_2HPO_4$ 분말 1.426g 및 LiF 0.132g을 건식 혼합하여 상기 분말이 양극 활물질 본체의 표면에 부착된 혼합물을 제조한 후 상기 혼합물을 650 ℃로 6시간 열처리하여 제2 양극 활물질을 제조하였다.

[0096] 상기 제조된 제1 양극 활물질과 제2 양극 활물질을 리본 믹서에 80/20의 중량비로 15분간 혼합하여 제1 양극 활물질과 제2 양극 활물질을 포함하는 양극 활물질을 제조하였다.

[0097] 비교예 1

[0098] 믹서에 상기 제조예 1에서 제조된 양극 활물질 100g과 $Al(OH)_3$ 분말 0.027g과 TiO_2 분말 0.159g과 $(NH_4)_2HPO_4$ 분말 0.465g을 건식 혼합하여 상기 분말이 양극 활물질 본체의 표면에 부착된 혼합물을 제조한 후 상기 혼합물을 800 ℃로 6시간 열처리하여 양극 활물질을 제조하였다.

[0099] 비교예 2

[0100] 믹서에 상기 제조예 1에서 제조된 양극 활물질 100g과 $Zr(OH)_4$ 분말 0.172g과 SiO_2 분말 0.054g과 $(NH_4)_2HPO_4$ 분말 0.387g을 건식 혼합하여 상기 분말이 양극 활물질 본체의 표면에 부착된 혼합물을 제조한 후 상기 혼합물을 800 ℃로 6시간 열처리하여 양극 활물질을 제조하였다.

[0101] 비교예 3

[0102] 믹서에 상기 제조예 1에서 제조된 양극 활물질 100g과 $MgCO_3$ 분말 0.259g, TiO_2 분말 0.615g, $(NH_4)_2HPO_4$ 분말 1.426g 및 LiF 0.132g을 건식 혼합하여 상기 분말이 양극 활물질 본체의 표면에 부착된 혼합물을 제조한 후 상기 혼합물을 800 ℃로 6시간 열처리하여 양극 활물질을 제조하였다.

[0103] 비교예 4

[0104] 믹서에 상기 제조예 2에서 제조된 양극 활물질 100g과 $Al(OH)_3$ 분말 0.027g과 $SnSO_4$ 분말 0.00044g과 $(NH_4)_2HPO_4$ 분말 1.331g을 건식 혼합하여 상기 분말이 양극 활물질 본체의 표면에 부착된 혼합물을 제조한 후 상기 혼합물을 650 ℃로 6시간 열처리하여 양극 활물질을 제조하였다.

[0105] 코인셀의 제조

[0106] 상기 실시예 및 비교예에서 제조된 양극 활물질 95 중량%, 도전제로 카본 블랙(carbon black) 2.5 중량%, 결합제로 PVDF 2.5 중량%를 용매(솔벤트)인 N-메틸-2 피롤리돈(NMP) 5.0 중량%에 첨가하여 양극 슬러리를 제조하였다. 상기 양극 슬러리를 두께 20 내지 40 μm의 양극 집전체인 알루미늄(Al) 박막에 도포 및 진공 건조하고 롤 프레스(roll press)를 실시하여 양극을 제조하였다.

[0107] 음극으로는 Li-금속을 이용하였다.

[0108] 이와 같이 제조된 양극과 Li-금속을 대극으로, 전해액으로는 1.15M LiPF₆EC:DMC(1:1vol%)을 사용하여 코인 셀 타입의 반쪽 전지를 제조하였다.

[0109] 충방전은 4.5-3.0V 범위에서 실시하였다.

[0110] 실험예 1: 전지 특성 평가

[0111] 하기 표 1은 상기의 실시예 및 비교예의 4.5V 초기 Formation, 율특성, 1cycle, 20cycle, 30cycle 용량 및 수명 특성 데이터이다. 상기의 실시예 및 비교예의 코팅 원소 및 코팅층 화합물에 대한 정보를 표 2에 기재하였다.

표 1

	Formation 방전용량 (mAh/g)	효율	1CY 방전용량	20CY 방전용량	30CY 방전용량	수명특성 (20CY/ 1CY, %)	수명특성 (30CY/ 1CY, %)	율특성 (1.0/0.2C, %)
실시예1	192.57	97.68	187.04	182.11	180.21	97.36	96.35	96.69
실시예2	192.66	98.04	186.99	182.51	181.27	97.60	96.94	96.81
실시예3	203.04	90.21	197.45	185.37	180.27	93.88	91.30	90.71
비교예1	191.79	97.44	186.73	182.02	179.54	97.48	96.15	96.75
비교예2	192.75	97.77	187.10	180.03	176.21	96.22	94.18	96.66
비교예3	191.03	98.05	186.34	184.81	183.06	99.18	98.24	96.66
비교예4	203.56	88.91	197.51	182.11	177.17	92.20	89.70	89.14

표 2

	제 1양극 활물질 코팅 원소	제 2양극 활물질 코팅 원소	제 1양극 활물질 코팅층 화합물	제 2양극 활물질 코팅층 화합물
실시예1	Al, Ti, P	Zr, Si, P	Li ₃ PO ₄ , LiAlO ₂ , Li ₂ TiO ₃ , Al ₂ O ₃ , TiO ₂	Li ₃ PO ₄ , Li ₂ ZrO ₃ , Li ₂ SiO ₃ , ZrO ₂ , SiO ₂
실시예2	Zr, Si, P	Mg, Ti, P, F	Li ₃ PO ₄ , Li ₂ ZrO ₃ , Li ₂ SiO ₃ , ZrO ₂ , SiO ₂	Li ₃ PO ₄ , LiF, Li ₂ TiO ₃ , MgO, TiO ₂
실시예3	Al, Sn, P	Mg, Ti, P, F	Li ₃ PO ₄ , LiAlO ₂ , Al ₂ O ₃ , SnO ₂	Li ₃ PO ₄ , LiF, Li ₂ TiO ₃ , MgO, TiO ₂
비교예1	Al, Ti, P	-	Li ₃ PO ₄ , LiAlO ₂ , Li ₂ TiO ₃ , Al ₂ O ₃ , TiO ₂	-
비교예2	Zr, Si, P	-	Li ₃ PO ₄ , Li ₂ ZrO ₃ , Li ₂ SiO ₃ , ZrO ₂ , SiO ₂	-

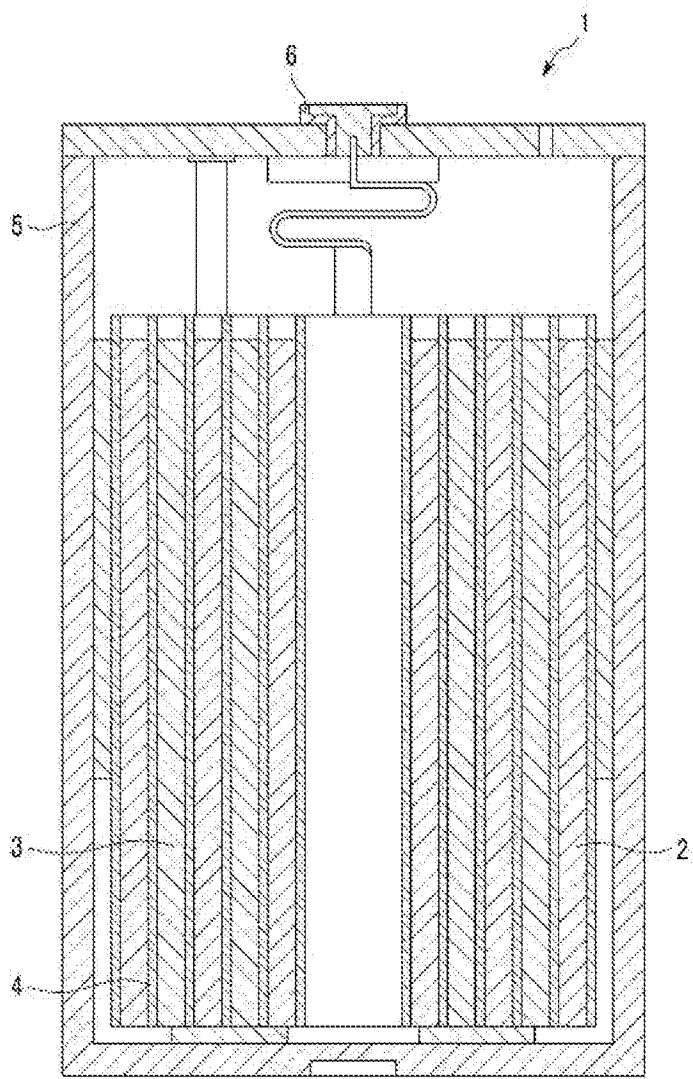
비교예3	Mg, Ti, P, F	-	Li ₃ PO ₄ , LiF, Li ₂ TiO ₃ , MgO, TiO ₂	-
비교예4	Al, Sn, P	-	Li ₃ PO ₄ , LiAlO ₂ , Al ₂ O ₃ , SnO ₂	-

[0114] 상기 표 1에서 제1 양극 활물질과 제2 양극 활물질을 포함하는 실시예 1 내지 3은 상응하는 비교예와 비교시 뛰어난 전지 특성이 확인된다.

[0115] 본 발명은 상기 실시예들에 한정되는 것이 아니라 서로 다른 다양한 형태로 제조될 수 있으며, 본 발명이 속하는 기술분야에서 통상의 지식을 가진 자는 본 발명의 기술적 사상이나 필수적인 특징을 변경하지 않고서 다른 구체적인 형태로 실시될 수 있다는 것을 이해할 수 있을 것이다. 그러므로 이상에서 기술한 실시예들은 모든 면에서 예시적인 것이며 한정적이 아닌 것으로 이해해야만 한다.

도면

도면



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

First Named Inventor :	Teruaki OCHIAI	Art Unit :	1725
Application No. :	16/923,494	Examiner :	Sean P. Cullen
Filed :	July 8, 2020	Conf. No. :	3273
Title :	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY		

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

REPLY TO ACTION OF SEPTEMBER 21, 2020

Please consider the following reply.

Amendments to the Specification

Please replace the title with the following amended title:

POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING LITHIUM COBALTATE
COATED WITH LITHIUM TITANATE AND MAGNESIUM OXIDE, METHOD FOR
MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY
BATTERY

Please replace paragraph [0310] with the following amended paragraph:

FIG. 12D is a top view of the module 615. The conductive plate 613 is shown by a dotted line for clarity of the drawing. As illustrated in FIG. 12D, the module 615 may include a wiring 616 which electrically connects the plurality of cylindrical secondary batteries 600 to each other. It is possible to provide the conductive plate 613 over the wiring 616 to overlap with each other. In addition, a temperature control device 617 may be provided between the plurality of ~~cylindrical~~ cylindrical secondary batteries 600. When the cylindrical secondary batteries 600 are overheated, the temperature control device 617 can cool them, and when the ~~cylindrical~~ cylindrical secondary batteries 600 are cooled too much, the temperature control device 617 can heat them. Thus, the performance of the module 615 is not easily influenced by the outside air temperature.

Please replace paragraph [0367] with the following amended paragraph:

Specifically, when the total thickness of the stacked positive electrodes 11a and negative electrodes 11b and the separators [[214]] 14 (not illustrated in FIGS. 22B1, 22B2, 22C, or 22D) is referred to as a thickness t, the distance La is preferably 0.8 times or more and 3.0 times or less, further preferably 0.9 times or more and 2.5 times or less, still further preferably 1.0 times or more and 2.0 times or less as large as the thickness t. When the distance La is in the above-described range, a compact battery which is highly reliable for bending can be obtained.

Please replace paragraph [0615] with the following amended paragraph:

11a: positive electrode, 11b: negative electrode, 12a: lead, 12b: lead, 14: separator, 15a: bonding portion, 15b: bonding portion, 17: fixing member, 50: secondary battery, 51: exterior body, 61: folded portion, 62: seal portion, 63: seal portion, 71: crest line, 72: trough line, 73: space, 100: positive electrode active material, 101: first region, 101p: crystal plane, 102: second region, 102p: crystal plane, 103: third region, 103p: crystal plane, 104: fourth region, 105: coating film, 106: crack portion, 110: particle, 111: region, 112: layer containing titanium, 114: cobalt oxide layer, 120: particle, 121: region, 122: layer containing titanium, 124: cobalt oxide layer, 125: layer containing lithium titanate, 200: active material layer, 201: graphene compound, ~~214: separator~~, 280: spray dry apparatus, 281: chamber, 282: nozzle, 283: tube, 284: suspension, 285: heater, 286: collection container, 288: arrow, 300: coin-type secondary battery, 301: positive electrode can, 302: negative electrode can, 303: gasket, 304: positive electrode, 305: positive electrode current collector, 306: positive electrode active material layer, 307: negative electrode, 308: negative electrode current collector, 309: negative electrode active material layer, 310: separator, 500: laminated laminated secondary battery, 501: positive electrode current collector, 502: positive electrode active material layer, 503: positive electrode, 504: negative electrode current collector, 505: negative electrode active material layer, 506: negative electrode, 507: separator, 508: electrolyte solution, 509: exterior body, 510: positive electrode lead electrode, 511: negative electrode lead electrode, 600: cylindrical secondary battery, 601: positive electrode cap, 602: battery can, 603: positive electrode terminal, 604: positive electrode, 605: separator, 606: negative electrode, 607: negative electrode terminal, 608: insulating plate, 609: insulating plate, 611: PTC element, 612: safety valve mechanism, 613: conductive plate, 614: conductive plate, 615: module, 616: wiring, 617: temperature control device, 900: circuit board, 910: label, 911: terminal, 912: circuit, 913: secondary battery, 914: antenna, 915: antenna, 916: layer, 917: layer, 918: antenna, 920: display device, 921: sensor, 922: terminal, 930: housing, 930a: housing, 930b: housing, 931: negative electrode, 932: positive electrode, 933: separator, 950: wound body, 951: terminal, 952: terminal, 980: laminated secondary battery, 981: film, 982: film, 993: wound body, 994: negative electrode, 995: positive electrode, 996: separator, 997: lead electrode, 998: lead electrode, 7100: portable display device, 7101: housing, 7102: display portion, 7103: operation button, 7104: secondary battery, 7200: portable information terminal, 7201:

housing, 7202: display portion, 7203: band, 7204: buckle, 7205: operation button, 7206: input output terminal, 7207: icon, 7300: display device, 7304: display portion, 7400: mobile phone, 7401: housing, 7402: display portion, 7403: operation button, 7404: external connection port, 7405: speaker, 7406: microphone, 7407: secondary battery, 7408: lead electrode, 7409: current collector, 7500: vaporizer, 7501: atomizer, 7502: cartridge, 7504: secondary battery, 8000: display device, 8001: housing, 8002: display portion, 8003: speaker portion, 8004: secondary battery, 8021: ground-based charging apparatus, 8022: cable, 8024: secondary battery, 8100: lighting device, 8101: housing, 8102: light source, 8103: secondary battery, 8104: ceiling, 8105: wall, 8106: floor, 8107: window, 8200: indoor unit, 8201: housing, 8202: air outlet, 8203: secondary battery, 8204: outdoor unit, 8300: electric refrigerator-freezer, 8301: housing, 8302: refrigerator door, 8303: freezer door, 8304: secondary battery, 8400: automobile, 8401: headlight, 8406: electric motor, 8500: automobile, 8600: motor scooter, 8601: side mirror, 8602: secondary battery, 8603: indicator, 8604: storage unit under seat, 9600: tablet terminal, 9625: power saving mode changing switch, 9626: display mode changing switch, 9627: power switch, 9628: operation switch, 9629: fastener, 9630: housing, 9630a: housing, 9630b: housing, 9631: display portion, 9631a: display portion, 9631b: display portion, 9633: solar cell, 9634: charge and discharge control circuit, 9635: power storage unit, 9636: DCDC converter, 9637: converter, 9640: movable portion.

Amendments to the Claims

Listing of Claims (replacing prior versions)

1. (Currently Amended) A lithium-ion secondary battery comprising a positive electrode, the positive electrode comprising a positive electrode active material particle comprising lithium cobaltate, wherein the positive electrode active material particle comprises a first region and a second region,

wherein the first region comprises a layered rock-salt crystal structure,

wherein the second region comprises a rock-salt crystal structure,

wherein the positive electrode active material particle comprises titanium, magnesium, fluorine, and oxygen in the second region, ~~a range from a surface of the positive electrode active material particle to an inside of the positive electrode active material particle where a concentration of the magnesium which is detected by analysis in a depth direction is 1/5 of a peak.~~

wherein the second region extends from a surface of the positive electrode active material particle to an inside of the positive electrode active material particle where magnesium detected by a line analysis of energy dispersive X-ray spectroscopy (EDX) in a depth direction is 1/5 of a maximum peak of the magnesium in the line analysis, and

wherein a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned.

2. (Canceled)

3. (Previously Presented) The lithium-ion secondary battery according to claim 1, wherein a relative value of a concentration of the titanium is greater than or equal to 0.05 and less than or equal to 0.4 when the surface of the positive electrode active material particle is subjected to an XPS analysis and a concentration of cobalt is defined as 1.

4. (Previously Presented) The lithium-ion secondary battery according to claim 1, wherein a relative value of a concentration of the magnesium is greater than or equal to 0.4 and less than or equal to 1.5 when the surface of the positive electrode active material particle is subjected to an XPS analysis and a concentration of cobalt is defined as 1.

5. (Original) The lithium-ion secondary battery according to claim 1,
wherein the titanium, the magnesium, the fluorine, and the oxygen are provided in a range from
the surface of the positive electrode active material particle to a depth of 5 nm.

6. (Original) The lithium-ion secondary battery according to claim 1,
wherein the positive electrode further comprises a conductive additive, and
wherein the conductive additive comprises carbon fiber, graphene or multilayer graphene.

7. (Currently Amended) A lithium-ion secondary battery comprising a positive electrode, the
positive electrode comprising a positive electrode active material particle comprising lithium cobaltate,
wherein the positive electrode active material particle comprises a first region and a second
region,
wherein the first region comprises a layered rock-salt crystal structure,
wherein the second region comprises a crystal structure which is different from the layered rock-
salt crystal structure,

wherein the positive electrode active material particle comprises titanium, magnesium, fluorine,
and oxygen in the second region, ~~a range from a surface of the positive electrode active material particle~~
~~to an inside of the positive electrode active material particle where a concentration of the magnesium~~
~~which is detected by analysis in a depth direction is 1/5 of a peak, and~~

wherein the second region extends from a surface of the positive electrode active material
particle to an inside of the positive electrode active material particle where magnesium detected by a line
analysis of energy dispersive X-ray spectroscopy (EDX) in a depth direction is 1/5 of a maximum peak of
the magnesium in the line analysis, and

~~wherein a concentration of the magnesium is larger than a concentration of the titanium when~~
~~the surface of the positive electrode active material particle is subjected to an XPS analysis.~~

wherein a crystal orientation of at least a part of the first region and a crystal orientation of at
least a part of the second region are substantially aligned.

8. (Canceled)

9. (Previously Presented) The lithium-ion secondary battery according to claim 7,

wherein a relative value of the concentration of the titanium is greater than or equal to 0.05 and less than or equal to 0.4 when the surface of the positive electrode active material particle is subjected to the XPS analysis and a concentration of cobalt is defined as 1.

10. (Previously Presented) The lithium-ion secondary battery according to claim 7,
wherein a relative value of the concentration of the magnesium is greater than or equal to 0.4 and less than or equal to 1.5 when the surface of the positive electrode active material particle is subjected to the XPS analysis and a concentration of cobalt is defined as 1.

11. (Previously Presented) The lithium-ion secondary battery according to claim 7,
wherein the titanium, the magnesium, the fluorine, and the oxygen are provided in a range from the surface of the positive electrode active material particle to a depth of 5 nm.

12. (Original) The lithium-ion secondary battery according to claim 7,
wherein the positive electrode further comprises a conductive additive, and
wherein the conductive additive comprises carbon fiber, graphene or multilayer graphene.

13. (Currently Amended) ~~An electronic device comprising a~~ A lithium-ion secondary battery;
~~the lithium-ion secondary battery comprising~~[[:]]

~~a positive electrode, the positive electrode~~ comprising a positive electrode active material particle comprising lithium cobaltate[[:]],

~~a negative electrode; and~~

~~an electrolyte;~~

wherein the positive electrode active material particle comprises a first region and a second region,

wherein the first region comprises a layered rock-salt crystal structure,

wherein the second region comprises a rock-salt crystal structure,

wherein the second region covers at least a part of the first region,

wherein the positive electrode active material particle comprises titanium, magnesium, fluorine, and oxygen in the second region, and ~~a range from a surface of the positive electrode active material particle to an inside of the positive electrode active material particle where a concentration of the magnesium which is detected by analysis in a depth direction is 1/5 of a peak.~~

wherein a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned.

14. (Canceled)

15. (Currently Amended) The ~~electronic device~~ lithium-ion secondary battery according to claim 13,

wherein a relative value of a concentration of the titanium is greater than or equal to 0.05 and less than or equal to 0.4 when the surface of the positive electrode active material particle is subjected to an XPS analysis and a concentration of cobalt is defined as 1.

16. (Currently Amended) The ~~electronic device~~ lithium-ion secondary battery according to claim 13,

wherein a relative value of a concentration of the magnesium is greater than or equal to 0.4 and less than or equal to 1.5 when the surface of the positive electrode active material particle is subjected to an XPS analysis and a concentration of cobalt is defined as 1.

17. (Currently Amended) The ~~electronic device~~ lithium-ion secondary battery according to claim 13,

wherein the titanium, the magnesium, the fluorine, and the oxygen are provided in a range from the surface of the positive electrode active material particle to a depth of 5 nm.

18. (Currently Amended) The ~~electronic device~~ lithium-ion secondary battery according to claim 13,

wherein the positive electrode further comprises a conductive additive, and

wherein the conductive additive comprises carbon fiber, graphene or multilayer graphene.

19. (Currently Amended) ~~An electronic device comprising a~~ A lithium-ion secondary battery;
~~the lithium-ion secondary battery~~ comprising[[:]]

a positive electrode, the positive electrode comprising a positive electrode active material particle comprising lithium cobaltate[[:]],

~~a negative electrode; and~~

~~an electrolyte,~~
wherein the positive electrode active material particle comprises a first region and a second region,
wherein the first region comprises a layered rock-salt crystal structure,
wherein the second region comprises a crystal structure which is different from the layered rock-salt crystal structure,
~~wherein the first region comprises cobalt,~~
wherein the second region covers at least a part of the first region,
wherein ~~the second region~~ the positive electrode active material particle comprises titanium, magnesium, fluorine, and oxygen in the second region, and
~~wherein the second region covers at least a part of the first region, and~~
~~wherein the second region is in a range from a surface of the positive electrode active material particle to an inside of the positive electrode active material particle where a concentration of the magnesium which is detected by analysis in a depth direction is 1/5 of a peak.~~
wherein a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned.

20. (Canceled)

21. (Currently Amended) The ~~electronic device~~ lithium-ion secondary battery according to claim 19,

wherein a relative value of a concentration of the titanium is greater than or equal to 0.05 and less than or equal to 0.4 when the surface of the positive electrode active material particle is subjected to an XPS analysis and a concentration of cobalt is defined as 1.

22. (Currently Amended) The ~~electronic device~~ lithium-ion secondary battery according to claim 19,

wherein a relative value of a concentration of the magnesium is greater than or equal to 0.4 and less than or equal to 1.5 when the surface of the positive electrode active material particle is subjected to an XPS analysis and a concentration of cobalt is defined as 1.

23. (Currently Amended) The ~~electronic device~~ lithium-ion secondary battery according to claim 19,

wherein the titanium, the magnesium, the fluorine, and the oxygen are provided in a range from the surface of the positive electrode active material particle to a depth of 5 nm.

24. (Currently Amended) The ~~electronic device~~ lithium-ion secondary battery according to claim 19,

wherein the positive electrode further comprises a conductive additive, and

wherein the conductive additive comprises carbon fiber, graphene or multilayer graphene.

25. (New) The lithium-ion secondary battery according to claim 7,

wherein a concentration of the magnesium is larger than a concentration of the titanium when the surface of the positive electrode active material particle is subjected to an XPS analysis.

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FIG. 22A

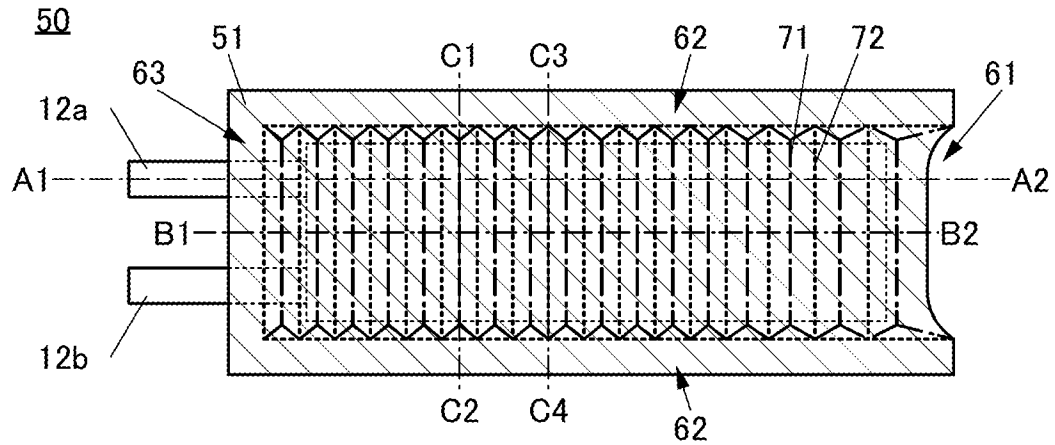


FIG. 22B1

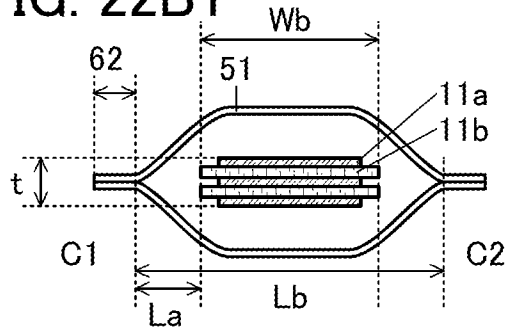


FIG. 22B2

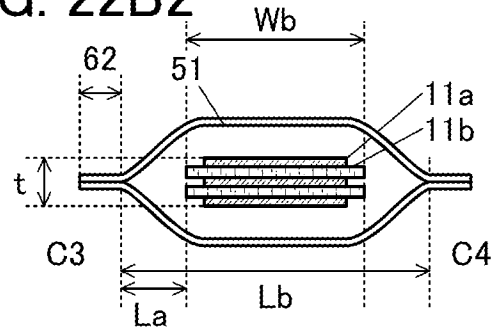


FIG. 22C

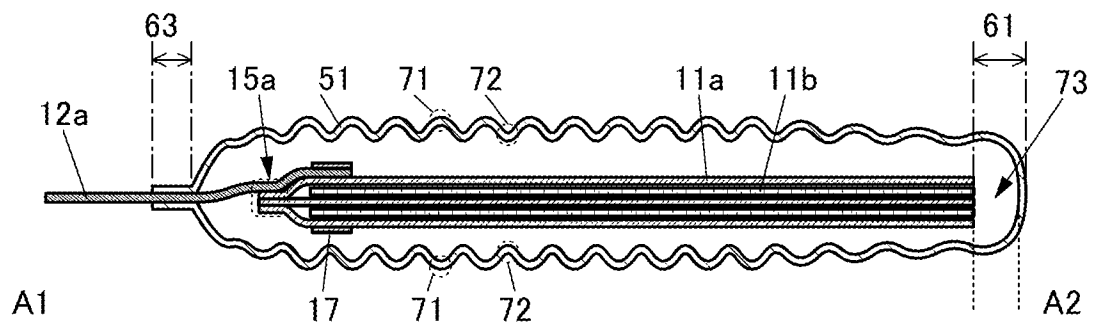
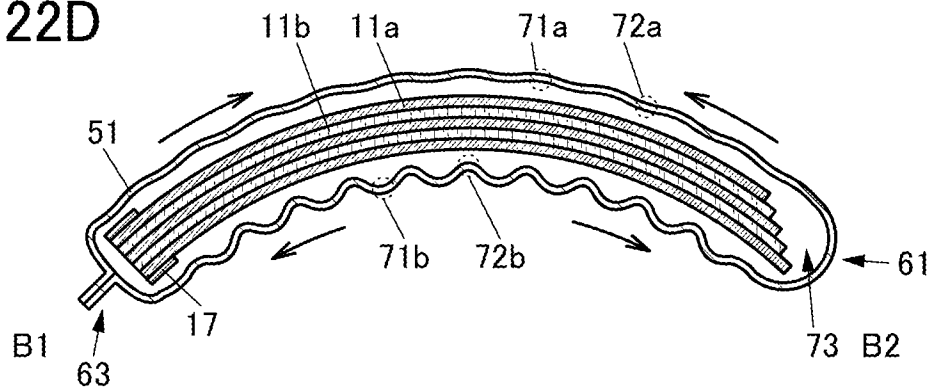


FIG. 22D



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before Ti heating (Sample06)

FIG. 37A

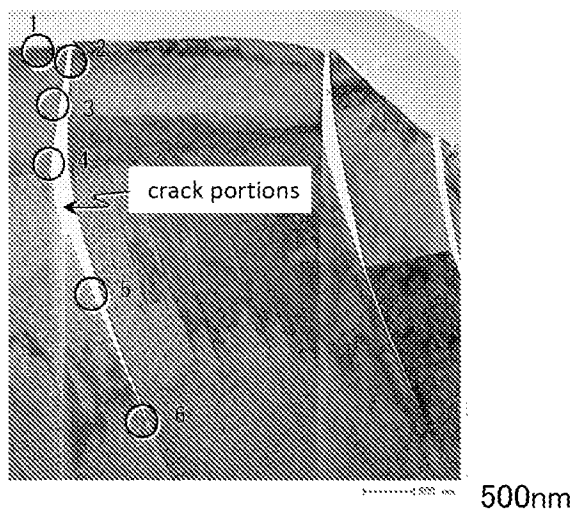


FIG. 37B1

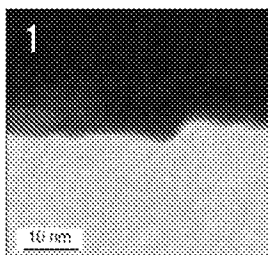
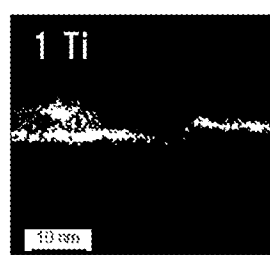


FIG. 37B2

FIG. 37C1

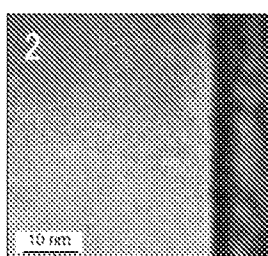


FIG. 37C2

FIG. 37D1

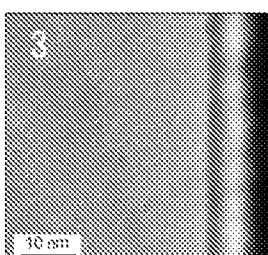
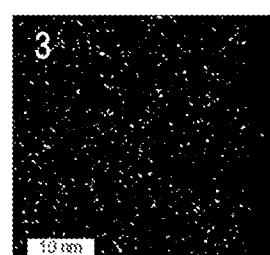


FIG. 37D2

FIG. 37E1

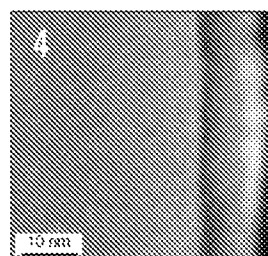
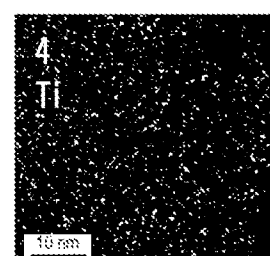


FIG. 37E2

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after Ti heating (Sample07)

FIG. 38A

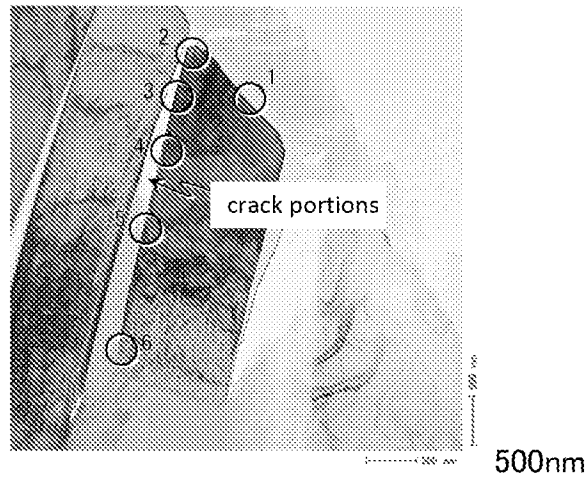


FIG. 38B1

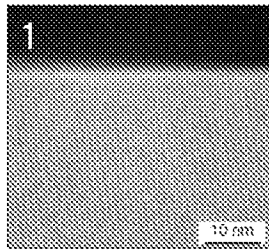
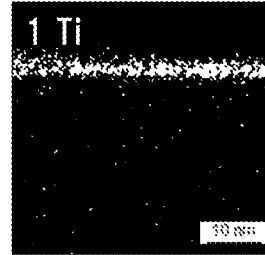


FIG. 38B2

FIG. 38C1

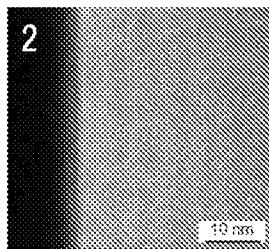
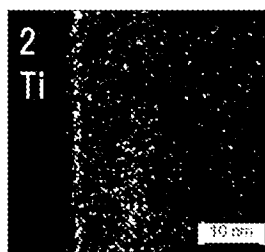


FIG. 38C2

FIG. 38D1

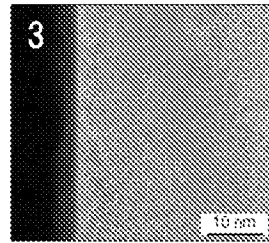
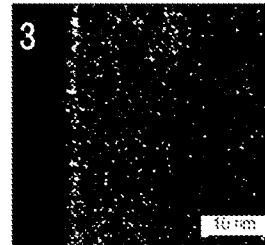


FIG. 38D2

FIG. 38E1

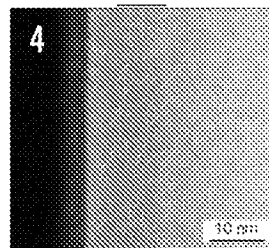
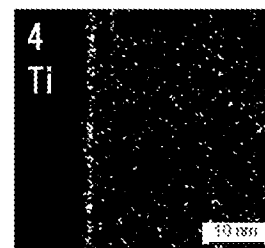


FIG. 38E2

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before Mg heating (Sample06)

FIG. 39A

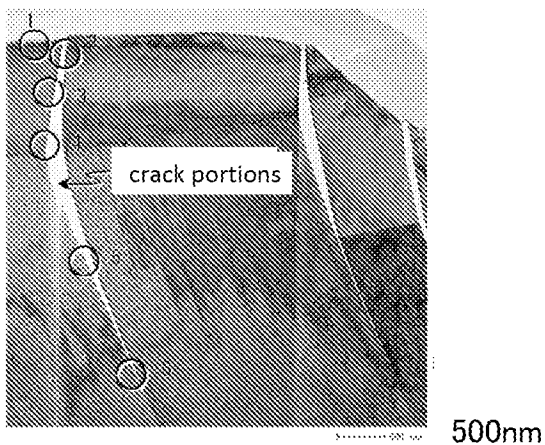


FIG. 39B1

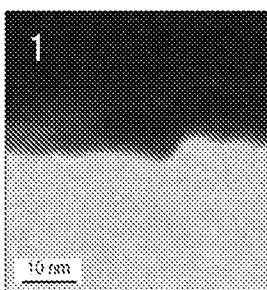
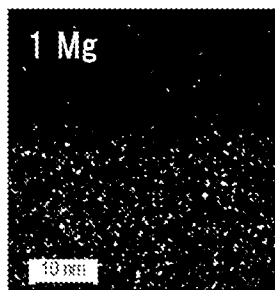


FIG. 39B2

FIG. 39C1

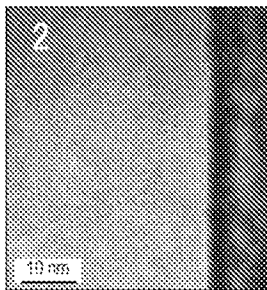
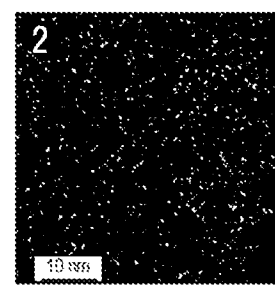


FIG. 39C2

FIG. 39D1

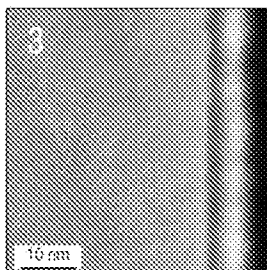
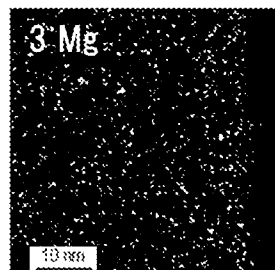


FIG. 39D2

FIG. 39E1

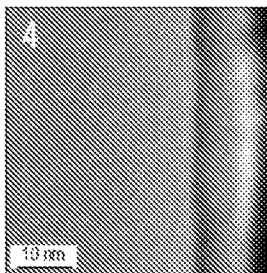
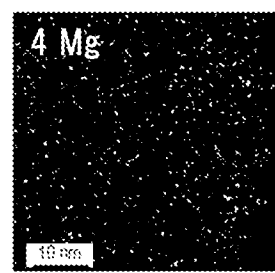


FIG. 39E2

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after Mg heating (Sample07)

FIG. 40A

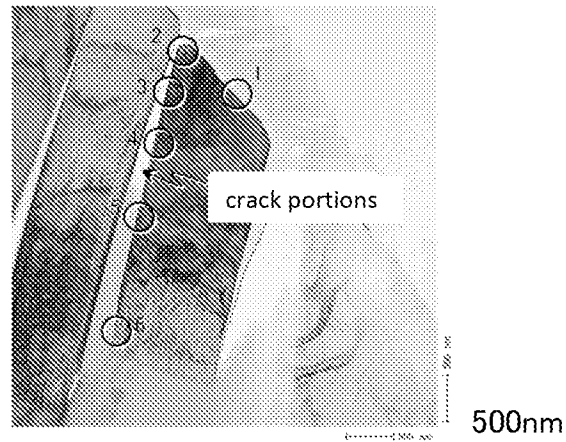


FIG. 40B1

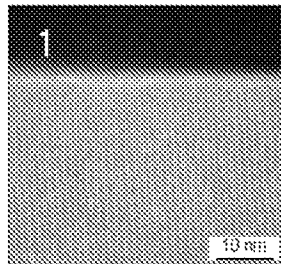
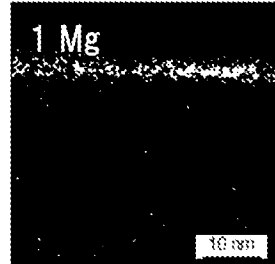


FIG. 40B2

FIG. 40C1

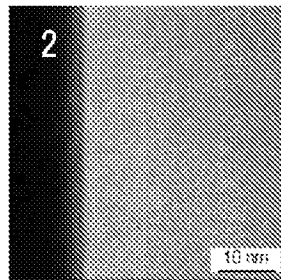
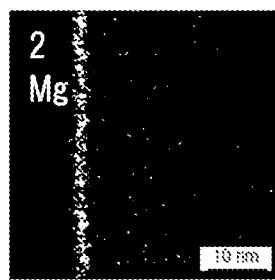


FIG. 40C2

FIG. 40D1

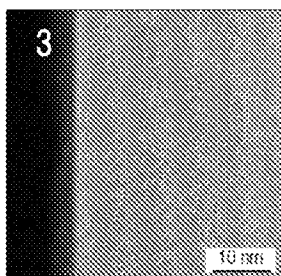
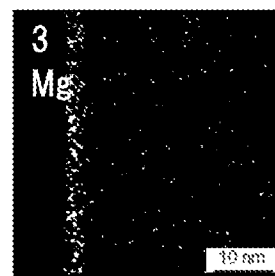


FIG. 40D2

FIG. 40E1

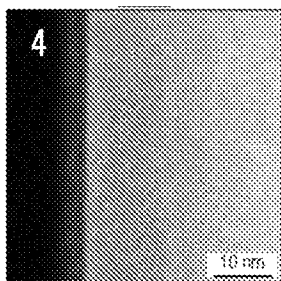
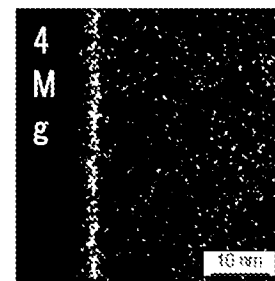


FIG. 40E2

Electronic Patent Application Fee Transmittal

Application Number:	16923494			
Filing Date:	08-Jul-2020			
Title of Invention:	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY			
First Named Inventor/Applicant Name:	Teruaki OCHIAI			
Filer:	Heather L. Flanagan/Sharon Allen			
Attorney Docket Number:	12732-2003004			
Filed as Large Entity				
Filing Fees for Utility under 35 USC 111(a)				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Pages:				
Claims:				
CLAIMS IN EXCESS OF 20	1202	1	100	100
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Extension-of-Time:				
Miscellaneous:				
Total in USD (\$)				100

Electronic Acknowledgement Receipt

EFS ID:	41443974
Application Number:	16923494
International Application Number:	
Confirmation Number:	3273
Title of Invention:	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY
First Named Inventor/Applicant Name:	Teruaki OCHIAI
Customer Number:	26171
Filer:	Heather L. Flanagan/Sharon Allen
Filer Authorized By:	Heather L. Flanagan
Attorney Docket Number:	12732-2003004
Receipt Date:	21-DEC-2020
Filing Date:	08-JUL-2020
Time Stamp:	11:03:37
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	\$ 100
RAM confirmation Number	E2020BKB03584298
Deposit Account	061050
Authorized User	Sharon Allen

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:
37 CFR 1.16 (National application filing, search, and examination fees)

File Listing:					
Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		12732-2003004-Response.pdf	137866	yes	15
			05b992aa9db15011aa3d54045b2467f4e6858923		
	Multipart Description/PDF files in .zip description				
	Document Description		Start	End	
	Amendment/Req. Reconsideration-After Non-Final Reject		1	1	
	Specification		2	4	
	Claims		5	10	
	Drawings-only black and white line drawings		11	11	
	Applicant Arguments/Remarks Made in an Amendment		12	15	
Warnings:					
Information:					
2	Drawings-only black and white line drawings	ReplacementFig-22.pdf	471603	no	1
			5ccbfe26bec8e9177f012019a853b546ba331cbc		
Warnings:					
Information:					
3	Drawings-only black and white line drawings	ReplacementFig37-40.pdf	4540464	no	4
			fb0b608a9b787dbcdf8eabd12af66211700ca755		
Warnings:					
Information:					
4	Fee Worksheet (SB06)	fee-info.pdf	30442	no	2
			ca147f2ab4b290ba9d0e10939a998f173137cc77		
Warnings:					
Information:					
AMPEREX Ex. 10					

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

First Named Inventor : Teruaki OCHIAI
Application No. : 16/923,494
Filed : July 8, 2020
Page : 11 of 15

Attorney Docket: 12732-
2003004 / US24652/.../26813-C4

Amendments to the Drawings

The attached replacement sheets of drawings includes changes to FIGS. 22A-22D and 37A-40E2 and replaces the original sheets including FIGS. 22A-22D and 37A-40E2.

Reference character 10 has been removed from FIGS. 22A, 22B1, 22B2, and 22D, and reference character 10a has been removed from FIG. 22C. FIGS. 37A-40E2 have been replaced with higher resolution images.

Attachments following last page of this Amendment:

Replacement Sheets (5 pages)

REMARKS

Claims 1, 3-7, 9-13, 15-19, and 21-25 are pending, with claims 1, 7, 13, and 19 being independent. Claims 1, 5, 7, 13, 15-19, and 21-24 have been amended, and claim 25 has been added. The specification and drawings have been amended to overcome objections. Support for the amendments and new claim is found throughout the specification and drawings as filed.

Information Disclosure Statement

A copy of KR 10-0696619 was provided with the Information Disclosure Statement filed on October 21, 2020.

Drawings

Replacement drawing sheets for FIGS. 22A-22D are provided, in which reference character 10 has been removed from FIGS. 22A, 22B1, 22B2, and 22D, and reference character 10a has been removed from FIG. 22C. Replacement drawing sheets for FIGS. 37A-40E2 are provided. These drawings are of sufficient quality so that all details in the photographs are reproducible in the printed patent. Paragraphs [0367] and [0615] have been amended to remove reference character 214. Applicant therefore requests withdrawal of the objections to the drawings.

Specification

Paragraphs [0310] and [0615] have been amended to remove the underlined words “cylindrical” and “laminated,” respectively. Paragraph [0367] has been amended to replace reference character 214 with reference character 14, which is shown at least in FIG. 23A and referred to at least in paragraphs [0356], [0357], and [0359] of the specification.

Title

The title has been amended as suggested by the Examiner.

Claim Rejections - 35 USC § 102

Claims 1, 3-5, 7, 9-11, 13, 15-17, 19, and 21-23 were rejected under 35 U.S.C. § 102(a)(1) over CN 102610806 B (Liu).

Applicant requests withdrawal of this rejection because Liu does not describe or suggest a positive electrode active material particle comprising a first region and a second region, “wherein the first region comprises a layered rock-salt crystal structure,” “wherein the second region comprises a rock-salt crystal structure” or “wherein the second region comprises a crystal structure which is different from the layered rock-salt crystal structure,” and “wherein a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned,” as recited by amended independent claims 1, 7, 13, and 19. Nor does Liu describe or suggest “wherein the second region covers at least a part of the first region,” as recited by claims 13 and 19.

Applicant further requests withdrawal of this rejection of claims 1 and 7 and their dependent claims because Liu does not describe or suggest “wherein the second region extends from a surface of the positive electrode active material particle to an inside of the positive electrode active material particle where magnesium detected by a line analysis of energy dispersive X-ray spectroscopy (EDX) in a depth direction is 1/5 of a maximum peak of the magnesium in the line analysis.” Rather, paragraph [0012] of Liu discloses a positive electrode active material for a lithium ion battery with the structural formula $\text{Li}_a\text{CO}_{1-b-c}\text{A}_b\text{B}_c\text{O}_{2-d}\text{C}_d$, where the element A, which can be magnesium, is evenly distributed in the bulk phase of the positive active electrode material. Paragraph [0013] of Liu explains that an inhomogeneity in element A would cause local structural instability and affect overall performance. A uniform distribution of magnesium would not result in the positive electrode active material particle with the distribution of magnesium recited by claims 1 and 7. Thus, for this additional reason, this rejection of claims 1 and 7 as well as their dependent claims should be withdrawn.

Claims dependent from independent claims 1, 7, 13, and 19 are also separately patentable. For example, Liu does not describe or suggest “wherein a relative value of a concentration of the titanium is greater than or equal to 0.05 and less than or equal to 0.4 when the surface of the positive electrode active material particle is subjected to an XPS analysis and a concentration of cobalt is defined as 1,” as recited by claims 3, 9, 15, and 21. In the structural

formula of Liu ($\text{Li}_a\text{CO}_{1-b-c}\text{A}_b\text{B}_c\text{O}_{2-d}\text{C}_d$), only element B can be titanium. Although paragraph [0014] of Liu describes a distribution of the B element, Liu does not describe the recited relative value of a concentration of B with respect to cobalt. As such, a *prima facie* case of anticipation has not been established, the rejection of claims 3, 9, 15, and 21 of Liu should be withdrawn.

Claim Rejections - 35 USC § 103

Claims 6, 12, 18, and 24 were rejected under 35 U.S.C. § 103 over Liu as applied to claims 1, 7, 13, and 19, respectively, and further in view of US 2016/0104880 (Gao). The Office Action relies on Gao to disclose a positive electrode comprising at least one of carbon fiber, graphene, or multilayer graphene as a conductive additive to improve the conductivity of the positive electrode. However, Gao does not cure the deficiencies of Liu with respect to independent claims 1, 7, 13, and 19. Applicant therefore requests withdrawal of this rejection.

New Claim

New claim 25 depends from claim 7 and recites: “wherein a concentration of the magnesium is larger than a concentration of the titanium when the surface of the positive electrode active material particle is subjected to an XPS analysis.” Claim 25 is allowable at least for reasons described above with respect to claim 7.

First Named Inventor : Teruaki OCHIAI
Application No. : 16/923,494
Filed : July 8, 2020
Page : 15 of 15

Attorney Docket: 12732-
2003004 / US24652/.../26813-C4

Conclusion

All claims are in condition for allowance. The fee for one excess dependent claim is being paid with this reply on the Electronic Filing System. Apply those fees and any other necessary charges or credits to Deposit Account 06-1050, referencing the above attorney docket number.

Respectfully submitted,

Date: December 21, 2020

/Heather L. Flanagan/

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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875				Application or Docket Number 16/923,494		Filing Date 07/08/2020		☐ To be Mailed		
ENTITY: ☒ LARGE ☐ SMALL ☐ MICRO										
APPLICATION AS FILED - PART I										
		(Column 1)	(Column 2)							
FOR		NUMBER FILED	NUMBER EXTRA	RATE (\$)		FEE (\$)				
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))		N/A	N/A	N/A						
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))		N/A	N/A	N/A						
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))		N/A	N/A	N/A						
TOTAL CLAIMS (37 CFR 1.16(i))		minus 20 =	*	x \$100 =						
INDEPENDENT CLAIMS (37 CFR 1.16(h))		minus 3 =	*	x \$460 =						
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))		If the specification and drawings exceed 100 sheets of paper, the application size fee due is \$310 (\$155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).								
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))										
* If the difference in column 1 is less than zero, enter "0" in column 2.				TOTAL						
APPLICATION AS AMENDED - PART II										
		(Column 1)	(Column 2)	(Column 3)						
AMENDMENT	12/21/2020	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE (\$)		ADDITIONAL FEE (\$)		
	Total (37 CFR 1.16(i))	* 21	Minus	** 24	= 0	x \$100 =		0		
	Independent (37 CFR 1.16(h))	* 4	Minus	*** 4	= 0	x \$480 =		0		
	☐ Application Size Fee (37 CFR 1.16(s))									
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))									
						TOTAL ADD'L FEE		0		
		(Column 1)	(Column 2)	(Column 3)						
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE (\$)		ADDITIONAL FEE (\$)		
	Total (37 CFR 1.16(i))	*	Minus	**	=	x \$0 =				
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x \$0 =				
	☐ Application Size Fee (37 CFR 1.16(s))									
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))									
						TOTAL ADD'L FEE				
* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.						LIE				
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".						/VERONICA EVERETTE/				
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".										
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.										

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/923,494	07/08/2020	Teruaki OCHIAI	12732-2003004	3273
26171	7590	01/11/2021		
FISH & RICHARDSON P.C. (DC)			EXAMINER	
P.O. BOX 1022			CULLEN, SEAN P	
MINNEAPOLIS, MN 55440-1022				
			ART UNIT	PAPER NUMBER
			1725	
			NOTIFICATION DATE	DELIVERY MODE
			01/11/2021	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

PATDOCTC@fr.com

DETAILED ACTION

Notice of Pre-AIA or AIA Status

1. The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Status of Claims and Other Notes

2. **Claim(s) 1, 3–7, 9–13, 15–19, and 21–25** is/are pending.
3. **Claim(s) 2, 8, 14, and 20** is/are canceled.
4. The paragraph numbers cited in this Office Action in reference to the instant application are referring to the paragraph numbering of the PG-Pub of the instant application. See US 2020/0343530 A1.
5. The text of those sections of Title 35, U.S. Code not included in this action can be found in a prior Office action.

Information Disclosure Statement

6. The information disclosure statement (IDS) submitted on 18 September 2020 was filed before the mailing of a first Office Action on the merits. The submission complies with the provisions of 37 CFR 1.97. Accordingly, the information disclosure statement is being considered by the examiner.
7. The information disclosure statement (IDS) submitted on 24 September 2020 was filed after the mailing date of the non-final Office Action on 21 September 2020. The submission complies with the provisions of 37 CFR 1.97. Accordingly, the information disclosure statement is being considered by the examiner.

8. The information disclosure statement (IDS) submitted on 21 October 2020 was filed after the mailing date of the non-final Office Action on 21 September 2020. The submission complies with the provisions of 37 CFR 1.97. Accordingly, the information disclosure statement is being considered by the examiner.

9. The information disclosure statement (IDS) submitted on 21 December 2020 was filed after the mailing date of the non-final Office Action on 21 September 2020. The submission complies with the provisions of 37 CFR 1.97. Accordingly, the information disclosure statement is being considered by the examiner.

Drawings

10. The drawings were received on 21 December 2020. These drawings are acceptable.

11. Applicants' amendment(s) have overcome the objection(s) to the drawing(s).

Specification

12. Applicants' amendment(s) have overcome the objection(s) to the specification.

Claim Rejections - 35 USC § 112

13. The following is a quotation of the first paragraph of 35 U.S.C. 112(a):

(a) IN GENERAL.—The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same, and shall set forth the best mode contemplated by the inventor or joint inventor of carrying out the invention.

The following is a quotation of the first paragraph of pre-AIA 35 U.S.C. 112:

The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person

skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same, and shall set forth the best mode contemplated by the inventor of carrying out his invention.

14. **Claim(s) 7, 9–12, 19, and 21–25** is/are rejected under 35 U.S.C. 112(a) or 35 U.S.C. 112 (pre-AIA), first paragraph, because the specification, while being enabling for a second region comprising a rock-salt crystal structure, does not reasonably provide enablement for a second region comprising a crystal structure which is different from a layered rock-salt crystal structure. The specification does not enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make the invention commensurate in scope with these claims.

Claim 7 recites the limitation "wherein the second region comprises a crystal structure which is different from the layered rock-salt crystal structure." The breadth of the claims is large. The limitation "wherein the second region comprises a crystal structure which is different from the layered rock-salt crystal structure" encompasses a second region with any crystal structure other than a layered rock-salt crystal structure. The nature of the invention is complex. The manufacturing of active material particles include many factors, such as, concentration, temperature, pressure, additives, solvents, and post treatments. The level of predictability in the art is low because many factors affect a crystal structure of an active material particle, such as, concentration, temperature, pressure, reactants, additives, solvents, and post treatments. The amount of direction provided by the inventor is low. The inventor provides direction to manufacture only a second region with a rock-salt crystal structure. The working examples provided only have a second region with a rock-salt crystal structure. Therefore, the amount of experimentation is undue to make the invention commensurate in scope with claim 7.

Claims 9–12 are directly dependent from claim 7 and include all the limitations of claim 7. Claims 9–12 also fail to further limit the scope of the second region. Therefore, the amount of experimentation is undue to make the invention commensurate in scope with claims 9–12.

Claim 19 recites the limitation "wherein the second region comprises a crystal structure which is different from the layered rock-salt crystal structure." The breadth of the claims is large. The limitation "wherein the second region comprises a crystal structure which is different from the layered rock-salt crystal structure" encompasses a second region with any crystal structure other than a layered rock-salt crystal structure. The nature of the invention is complex. The manufacturing of active material particles include many factors, such as, concentration, temperature, pressure, reactants, additives, solvents, and post treatments. The level of predictability in the art is low because many factors affect a crystal structure of an active material particle, such as, concentration, temperature, pressure, reactants, additives, solvents, and post treatments. The amount of direction provided by the inventor is low. The inventor provides direction to manufacture only a second region with a rock-salt crystal structure. The working examples provided only have a second region with a rock-salt crystal structure. Therefore, the amount of experimentation is undue to make the invention commensurate in scope with claim 19.

Claims 22–24 are directly dependent from claim 19 and include all the limitations of claim 19. Claims 22–24 also fail to further limit the scope of the second region. Therefore, the amount of experimentation is undue to make the invention commensurate in scope with claims 22–24.

Claim 25 is directly dependent from claim 7 and includes all the limitations of claim 7. Claim 25 also fails to further limit the scope of the second region. Therefore, the amount of experimentation is undue to make the invention commensurate in scope with claim 25.

15. The following is a quotation of 35 U.S.C. 112(b):

(b) CONCLUSION.—The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.

The following is a quotation of 35 U.S.C. 112 (pre-AIA), second paragraph:
The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

16. **Claim(s) 1, 3–7, 9–13, 15–19, and 21–24** is/are rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor (or for applications subject to pre-AIA 35 U.S.C. 112, the applicant), regards as the invention.

Claim 1 recites the limitation "wherein a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned." It is unclear with what a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned. Are a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region substantially aligned with each other?

Claims 3–6 are directly dependent from claim 1 and include all the limitations of claim 1. Therefore, claims 3–6 are also indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor (or for applications subject to pre-AIA 35 U.S.C. 112, the applicant), regards as the invention.

Claim 7 recites the limitation "wherein a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned." It is unclear with what a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned. Are a crystal

orientation of at least a part of the first region and a crystal orientation of at least a part of the second region substantially aligned with each other?

Claims 9–12 are directly dependent from claim 1 and include all the limitations of claim 7. Therefore, claims 9–12 are also indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor (or for applications subject to pre-AIA 35 U.S.C. 112, the applicant), regards as the invention.

Claim 13 recite the limitation "a part of the first region" in line 16. Claim 13 has previously recited the limitation "a part of the first region" in line 11. It is unclear if "a part of the first region" recited in line 16 is further limiting "a part of the first region" recited in line 11.

Claim 13 recites the limitation "wherein a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned." It is unclear with what a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned. Are a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region substantially aligned with each other?

Claims 15–18 are directly dependent from claim 13 and include all the limitations of claim 13. Therefore, claims 15–18 are also indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor (or for applications subject to pre-AIA 35 U.S.C. 112, the applicant), regards as the invention.

Claim 19 recites the limitation "a part of the first region" in line 20. Claim 19 has previously recited the limitation "a part of the first region" in line 13. It is unclear if "a part of the first region" recited in line 20 is further limiting "a part of the first region" recited in line 13.

Claim 19 recites the limitation "wherein a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned." It is unclear with what a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned. Are a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region substantially aligned with each other?

Claims 21–24 are directly dependent from claim 19 and include all the limitations of claim 19. Therefore, claims 21–24 are also indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor (or for applications subject to pre-AIA 35 U.S.C. 112, the applicant), regards as the invention.

Response to Arguments

17. Applicant's arguments with respect to **claim(s) 1, 3–7, 9–13, 15–19, and 21–25** have been considered but are moot because the new ground of rejection does not rely on any reference applied in the prior rejection of record for any teaching or matter specifically challenged in the argument.

Conclusion

18. The prior art made of record and not relied upon is considered pertinent to applicant's disclosure.

Yura (US 2012/0258358 A1) discloses a lithium-ion secondary battery (1) comprising a positive electrode (2), the positive electrode (2) comprising a positive electrode active material particle (222) comprising lithium cobaltate (see LiCoO_2 , [0018]), wherein the positive electrode

active material particle (222) comprising a first region (222a) and a second region (222a, [0061]), wherein the first region (222a) comprises a layered rock-salt crystal structure (Fig. 3, [0061]), wherein the second region (222a) comprises a rock-salt crystal structure (Fig. 3, [0061]), wherein a crystal orientation of at least part of the first region (222a) and a crystal orientation of at least a part of the second region (222a) are substantially aligned with each other (Fig. 3, [0062]).

19. Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire **THREE MONTHS** from the mailing date of this action. In the event a first reply is filed within **TWO MONTHS** of the mailing date of this final action and the advisory action is not mailed until after the end of the **THREE-MONTH** shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than **SIX MONTHS** from the date of this final action.

20. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Sean P Cullen, Ph.D. whose telephone number is (571)270-1251. The examiner can normally be reached on Monday to Thursday 6:00 am to 4:00 pm CT, Friday 6:00 am to 12:00 pm CT.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at <http://www.uspto.gov/interviewpractice>.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Basia A Ridley can be reached on (571)272-1453. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <https://ppair-my.uspto.gov/pair/PrivatePair>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Sean P Cullen, Ph.D./
Primary Examiner, Art Unit 1725

Notice of References Cited	Application/Control No. 16/923,494		Applicant(s)/Patent Under Reexamination OCHIAI et al.	
	Examiner Sean P Cullen, Ph.D.		Art Unit 1725	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
*	A	US-20120258358-A1	10-2012	YURA; Yukinobu	H01M4/02	429/209
	B					
	C					
	D					
	E					
	F					
	G					
	H					
	I					
	J					
	K					
	L					
	M					

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

<i>Index of Claims</i> 	Application/Control No. 16/923,494	Applicant(s)/Patent Under Reexamination OCHIAI et al.
	Examiner Sean P Cullen, Ph.D.	Art Unit 1725

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS										
☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47										
CLAIM		DATE								
Final	Original	09/14/2020	01/05/2021							
	1	✓	✓							
	2	-	-							
	3	✓	✓							
	4	✓	✓							
	5	✓	✓							
	6	✓	✓							
	7	✓	✓							
	8	-	-							
	9	✓	✓							
	10	✓	✓							
	11	✓	✓							
	12	✓	✓							
	13	✓	✓							
	14	-	-							
	15	✓	✓							
	16	✓	✓							
	17	✓	✓							
	18	✓	✓							
	19	✓	✓							
	20	-	-							
	21	✓	✓							
	22	✓	✓							
	23	✓	✓							
	24	✓	✓							
	25		✓							

Search Notes 	Application/Control No. 16/923,494	Applicant(s)/Patent Under Reexamination OCHIAI et al.
	Examiner Sean P Cullen, Ph.D.	Art Unit 1725

CPC - Searched*		
Symbol	Date	Examiner
H01M4/131, 1315, 1391, 13915, 625, 8657	09/14/2020	SPC
Updated CPC search	01/05/2021	SPC

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner
429	231.3, 231.5, 231.6, 231.95	09/14/2020	SPC
	Updated USPC search	01/05/2021	SPC

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	Date	Examiner
H01M4/131, 1315, 1391, 13915, 625, 8657	09/14/2020	SPC
429/231.3, 231.5, 231.6, 231.95	09/14/2020	SPC
Inventor/applicant search, PALM	09/14/2020	SPC
PE2E SEARCH text search, see search history	09/14/2020	SPC
Updated inventor/applicant search, PALM	01/05/2021	SPC
Updated PE2E SEARCH text search, see search history	01/05/2021	SPC

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<i>Search Notes</i> 	Application/Control No. 16/923,494	Applicant(s)/Patent Under Reexamination OCHIAI et al.
	Examiner Sean P Cullen, Ph.D.	Art Unit 1725

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner

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PTO/SB/08A (07-06)

Approved for use through 03/31/2007. OMB 0651-0031

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Use as many sheets as necessary)				Complete if Known	
				Application Number	16/923,494
				Filing Date	July 8, 2020
				First Named Inventor	Teruaki OCHIAI
				Art Unit	1725
				Examiner Name	S.CULLEN
Sheet	1	of	1	Attorney Docket Number	12732-2003004

U. S. PATENT DOCUMENTS					
Examiner Initials*	Cite No. ¹	Document Number	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		Number-Kind Code ² (if known)			
		US-2016/0013478	01-14-2016	Satow.T et al.	
		US-2013/0230770	09-05-2013	Oya.M et al.	

FOREIGN PATENT DOCUMENTS						
Examiner Initials*	Cite No. ¹	Foreign Patent Document	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	T ⁶
		Country Code ³ -Number ⁴ -Kind Code ⁵ (if known)				
		CN-105024047A	11-04-2015			FULL
		KR-10-0696619	03-19-2007			Abst.

Examiner Signature	/Sean P Cullen, Ph.D./	Date Considered	01/05/2021
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*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. 1 Applicant's unique citation designation number (optional). 2 See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. 3 Enter Office that issued the document, by the two-letter code (WPO Standard ST.3). 4 For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. 5 Kind of document by the appropriate symbols as indicated on the document under WPO Standard ST.16 if possible. 6 Applicant is to place a check mark here if English language Translation is attached.

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

First Named Inventor : Teruaki OCHIAI Art Unit : 1725
Application No. : 16/923,494 Examiner : Sean P. Cullen
Filed : July 8, 2020 Conf. No. : 3273
Title : POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR
MANUFACTURING POSITIVE ELECTRODE ACTIVE
MATERIAL, AND SECONDARY BATTERY

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

INFORMATION DISCLOSURE STATEMENT

Please consider the references listed on the enclosed disclosure form. Copies of the documents required under 37 C.F.R. § 1.98(a)(2) are being submitted with this statement.

Applicant notes that this information disclosure statement includes KR-10-0696619, which was listed on the information disclosure statement filed on August 3, 2020. As noted by the Examiner in the office action dated September 21, 2020, that information disclosure statement erroneously indicated that this reference had been provided in the parent application. Applicant is providing a copy of the reference now to correct that error.

This statement is being filed after a first action on the merits, but before receipt of a final action or a notice of allowance. A late submission fee in the amount of \$260 specified by 37 CFR §1.17(p), is being paid with this statement. Please apply any charges or credits to Deposit Account No. 06-1050, referencing the above attorney docket number.

Respectfully submitted,

Date: October 21, 2020

/John F. Hayden/

John F. Hayden

Reg. No. 37640

Customer Number 26171
Fish & Richardson P.C.
Telephone: (202) 783-5070
Facsimile: (877) 769-7945

100275944.doc

PE2E SEARCH - Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	British Equivalents	Time Stamp
L190	1	16/923494.app.	US-PGPUB; USPAT; USOCR; FIT (AU, AP, AT, CA, CH, CN, DD, DE, EA, EP, ES, FR, GB, JP, KR, OA, RU, SU, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/01/05 11:37 AM
L191	6	(US-20110269023-\$ US-20110300441-\$ US-20120258358-\$).did.	US-PGPUB; USPAT; USOCR; FIT (AU, AP, AT, CA, CH, CN, DD, DE, EA, EP, ES, FR, GB, JP, KR, OA, RU, SU, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/01/05 02:11 PM
L192	1	L191 AND (rock 3m R3m Fd3m Fm3m Fm Fd)	US-PGPUB; USPAT; USOCR; FIT (AU, AP, AT, CA, CH, CN, DD, DE, EA, EP, ES, FR, GB, JP, KR, OA, RU, SU, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/01/05 02:17 PM
L193	6	L191 AND (Ti titanium Mg magnesium F fluorine)	US-PGPUB; USPAT; USOCR; FIT (AU, AP, AT, CA, CH, CN, DD, DE, EA, EP, ES, FR, GB, JP, KR, OA, RU, SU, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/01/05 02:18 PM
L194	94	(US-20040023113-\$ US-20040175618-\$ US-20040191161-\$ US-20070212602-\$ US-20070248883-\$ US-20090011334-\$ US-20140272562-\$ US-20150086787-\$ US-20150093580-\$ US-20160056453-\$ US-20160118658-\$ US-20160218350-\$ US-20160268594-\$ US-20180013130-\$ US-20180366726-\$).DID. (CN-104051740-\$ CN-107112582-\$ EP-3582298-\$ EP-3582299-	US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, CA, CH, CN, DD, DE, EA, EP, ES, FR, GB, JP, KR, OA, RU, SU, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/01/05 04:25 PM

		\$ JP-07037576-\$ JP-08055624-\$ JP-2000195514-\$ JP-2001167761-\$ JP-2002279985-\$ JP-2008258160-\$ JP-2012009193-\$ JP-2012084502-\$ JP-2014129188-\$ JP-2015076397-\$ JP-2018045759-\$ WO-2010074302-\$ WO-2011162251-\$ WO-2014038394-\$ WO-2014061399-\$ WO-2014061579-\$ WO-2014061580-\$ WO-2015108163-\$ WO-2016039511-\$ WO-2016067142-\$ WO-2019027215-\$ WO-2019058681-\$).DID.					
L195	5	L194 AND (mismatch mismatch mis ADJ match align\$4 distort\$4) near4 (lattice crystal)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/01/05 04:26 PM
L196	60	(US-20070212602-\$ US-20070248883-\$ US-20090104517-\$ US-20120258369-\$ US-20160181597-\$ US-20160268594-\$ US-20180166687-\$).DID. (CN-106716689-\$ CN-108183233-\$ CN-110729458-\$ JP-2003229124-\$ JP-2005005105-\$ JP-2006253119-\$ JP-2007173210-\$ JP-2008257992-\$ JP-2009081130-\$ JP-2009099418-\$ JP-2009117241-\$ JP-2009158489-\$ JP-2009295514-\$ KR-20190076746-\$ WO-2010074304-\$ WO-2011162253-\$ WO-2012137391-\$ WO-2012137534-\$ WO-2015108163-\$ WO-2016048862-\$).DID.	US-PGPUB; USPAT; USOCR; FIT (AP, AT, AU, CA, CH, CN, DD, DE, EA, EP, ES, FR, GB, JP, KR, OA, RU, SU, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/01/05 04:34 PM
L197	5	L195 AND (mismatch mis-	US-PGPUB; USPAT;	OR	ON	ON	2021/01/05

		match mis ADJ match align\$4 distort\$4) near4 (lattice crystal)	USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB				04:34 PM
L198	5	L195 AND (mismatch mis- match mis ADJ match align\$4 distort\$4 orientat\$4) near4 (lattice crystal)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/01/05 04:35 PM
L200	9	L194 AND (mismatch mis- match mis ADJ match align\$4 distort\$4 orientat\$4) near4 (lattice crystal)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/01/05 04:35 PM

PE2E SEARCH - Search History (Interference)

There are no Interference searches to show.

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Substitute for form 1449/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Use as many sheets as necessary)				Application Number	16/923,494
				Filing Date	July 8, 2020
				First Named Inventor	Teruaki OCHIAI
				Art Unit	1725
				Examiner Name	S.CULLEN
				Attorney Docket Number	12732-2003004
Sheet	1	of	3		

[illegible]

FOREIGN PATENT DOCUMENTS						
Examiner Initials*	Cite No. ¹	Foreign Patent Document	Publication Date	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	T ⁶
		Country Code ³ -Number ⁴ -Kind Code ⁵ (if known)	MM-DD-YYYY			
		JP-2011-082133A	04-21-2011			Abst.
		JP-2011-210694A	10-20-2011			Full
		JP-2014-116111A	06-26-2014			Abst.
		JP-2018-147726A	09-20-2018			Abst.
		JP-2012-043794A	03-01-2012			Abst.
		WO-2014/061653	04-24-2014			Abst.

Examiner Signature	/Sean P Cullen, Ph.D./	Date Considered	01/05/2021
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				Examiner Name	S.CULLEN
				Attorney Docket Number	12732-2003004
Sheet	2	of	3		

[illegible]

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		Country Code ³ -Number ⁴ -Kind Code ⁵ (if known)				
		WO-2015/163356	10-29-2015			Full
		WO-2015/136881	09-17-2015			Abst.
		JP-2004-288579A	10-14-2004			Abst.

Examiner Signature	/Sean P Cullen, Ph.D./	Date Considered	01/05/2021
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			Examiner Name	S.CULLEN	
Sheet	3	of	3	Attorney Docket Number	12732-2003004

NON PATENT LITERATURE DOCUMENTS			
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		Xia.H et al., "Phase Transitions and High-Voltage Electrochemical Behavior of LiCoO ₂ Thin Films Grown by Pulsed Laser Deposition", J. ELECTROCHEM. SOC. (JOURNAL OF THE ELECTROCHEMICAL SOCIETY), 2007, Vol. 154, No. 4, pp. A337-A342.	Eng.
		Sun.Y et al., "Role of AlF ₃ Coating on LiCoO ₂ Particles during Cycling to Cutoff Voltage above 4.5 V", J. ELECTROCHEM. SOC. (JOURNAL OF THE ELECTROCHEMICAL SOCIETY), 2009, Vol. 156, No. 12, pp. A1005-A1010.	Eng.
		Araki.K et al., "Electrochemical properties of LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂ cathode material modified by coating with Al ₂ O ₃ nanoparticles", JOURNAL OF POWER SOURCES, 2014, Vol. 269, pp. 236-243.	Eng.
		Kim.H et al., "Capacity fading behavior of Ni-rich layered cathode materials in Li-ion full cells", Journal of Electroanalytical Chemistry, 2016, Vol. 782, pp. 168-173.	Eng.
		Lin.F et al., "Surface reconstruction and chemical evolution of stoichiometric layered cathode materials for lithium-ion batteries", NATURE COMMUNICATIONS, March 27, 2014, Vol. 5, pp. 3529-1-3529-9.	Eng.
		Yano.A et al., "Surface Structure and High-Voltage Charge/Discharge Characteristics of Al-Oxide Coated LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂ Cathodes", J. ELECTROCHEM. SOC. (JOURNAL OF THE ELECTROCHEMICAL SOCIETY), 2015, Vol. 162, No. 2, pp. A3137-A3144.	Eng.
		Yano.A et al., "Surface Structure and High-Voltage Charging/Discharging Performance of Low-Content Zr-Oxide-Coated LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂ ", J. ELECTROCHEM. SOC. (JOURNAL OF THE ELECTROCHEMICAL SOCIETY), 2016, Vol. 163, No. 2, pp. A75-A82.	Eng.

Examiner Signature	/Sean P Cullen, Ph.D./	Date Considered	01/05/2021
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

First Named Inventor : Teruaki OCHIAI Art Unit : 1725
Application No. : 16/923,494 Examiner : Sean P. Cullen
Filed : July 8, 2020 Conf. No. : 3273
Title : POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR
MANUFACTURING POSITIVE ELECTRODE ACTIVE
MATERIAL, AND SECONDARY BATTERY

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

INFORMATION DISCLOSURE STATEMENT

Please consider the references listed on the enclosed disclosure form. Copies of the documents required under 37 C.F.R. § 1.98(a)(2) are being submitted with this statement.

This statement is being filed within three months of the filing date of the application and before the receipt of a first action on the merits. Please apply any charges or credits to Deposit Account No. 06-1050, referencing the above attorney docket number.

Respectfully submitted,

Date: September 18, 2020

/John F. Hayden/

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			Application Number	16/923,494	
			Filing Date	July 8, 2020	
			First Named Inventor	Teruaki OCHIAI	
			Art Unit	1725	
			Examiner Name	S. CULLEN	
Sheet	1	of	3	Attorney Docket Number	12732-2003004

U. S. PATENT DOCUMENTS					
Examiner Initials*	Cite No. ¹	Document Number	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		Number-Kind Code ² (if known)			
		US-9,105,926	08-11-2015	Fujiki.S et al.	
		US-2014/0212759	07-31-2014	Blangero.M et al.	
		US-8,951,448	02-10-2015	Toyama.T et al.	
		US-10,777,815	09-15-2020	Kanada.S et al.	
		US-2016/0336595	11-17-2016	Choi.S et al.	
		US-7,504,180	03-17-2009	Tatsumi.K et al.	
		US-9,614,225	04-04-2017	Park.J	
		US-9,812,709	11-07-2017	Endoh.K et al.	
		US-2004/0142241	07-22-2004	Nagayama.M	
		US-2006/0263690	11-23-2006	Suhara.M et al.	
		US-2009/0017383	01-15-2009	Suhara.M et al.	
		US-2010/0294985	11-25-2010	Suhara.M et al.	
		US-2016/0276659	09-22-2016	Choi.S et al.	
		US-2018/0034045	02-01-2018	Xia.X et al.	
		US-2013/0052534	02-28-2013	Fujiki.S et al.	
		US-2013/0089786	04-11-2013	Jeong.C et al.	
		US-2018/0190976	07-05-2018	Blangero.M et al.	
		US-2010/0086854	04-08-2010	Kumar.S et al.	
		US-9,871,246	01-16-2018	Kim.J et al.	

FOREIGN PATENT DOCUMENTS						
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		Country Code ³ - Number ⁴ - Kind Code ⁵ (if known)				
		CN-001715193A	01-04-2006			Abst.
		CN-103490060A	01-01-2014			Abst.
		JP-2003-068306A	03-07-2003			Abst.
		JP-2008-060033A	03-13-2008			Abst.
		JP-2013-087040A	05-13-2013			Abst.
		KR-2016-0092946A	08-05-2016			Abst.

Examiner Signature	/Sean P Cullen, Ph.D./	Date Considered	01/05/2021
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Sheet	2	of	3	Attorney Docket Number	12732-2003004

U. S. PATENT DOCUMENTS

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		Country Code ² -Number ³ -Kind Code ⁵ (if known)				
		CN-102779976A	11-14-2012			Abst.
		CN-102339998A	02-01-2012			Abst.
		CN-102447107A	05-09-2012			Abst.
		CN-103022502A	04-03-2013			Abst.
		CN-104701534A	06-10-2015			Abst.
		CN-106099098A	11-09-2016			Abst.

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Sheet	3	of	3	Attorney Docket Number	12732-2003004

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		Antolini.E, "LiCoO ₂ : formation, structure, lithium and oxygen nonstoichiometry, electrochemical behaviour and transport properties", Solid State Ionics, 2004, Vol. 170, No. 3-4, pp. 159-171.	Eng.
		Ceder.G et al., "Identification of cathode materials for lithium batteries guided by first-principles calculations", NATURE, April 16, 1998, Vol. 392, pp. 694-696.	Eng.
		Gopukumar.S et al., "Synthesis and electrochemical performance of tetravalent doped LiCoO ₂ in lithium rechargeable cells", Solid State Ionics, 2003, Vol. 159, pp. 223-232, ELSEVIER.	Eng.

Examiner Signature	/Sean P Cullen, Ph.D./	Date Considered	01/05/2021
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Use as many sheets as necessary)			Complete if Known		
			Application Number	16/923,494	
			Filing Date	July 8, 2020	
			First Named Inventor	Teruaki OCHIAI	
			Art Unit	1725	
			Examiner Name	S. CULLEN	
Sheet	1	of	1	Attorney Docket Number	12732-2003004

U. S. PATENT DOCUMENTS					
Examiner Initials*	Cite No. ¹	Document Number	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		Number-Kind Code ² (if known)			
		US-9,385,366	07-05-2016	Yamakaji.M et al.	

FOREIGN PATENT DOCUMENTS						
Examiner Initials*	Cite No. ¹	Foreign Patent Document	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	T ⁶
		Country Code ³ -Number ⁴ -Kind Code ⁵ (if known)				
		KR-2009-0111130A	10-26-2009			Abst.

Examiner Signature	/Sean P Cullen, Ph.D./	Date Considered	01/05/2021
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

First Named Inventor : Teruaki OCHIAI Art Unit : 1725
Application No. : 16/923,494 Examiner : Sean P. Cullen
Filed : July 8, 2020 Conf. No. : 3273
Title : POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR
MANUFACTURING POSITIVE ELECTRODE ACTIVE
MATERIAL, AND SECONDARY BATTERY

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

INFORMATION DISCLOSURE STATEMENT

Please consider the references listed on the enclosed disclosure form. Copies of the documents required under 37 C.F.R. § 1.98(a)(2) are being submitted with this statement.

This statement is being filed after a first action on the merits, but before receipt of a final action or a notice of allowance. A late submission fee in the amount of \$260 specified by 37 CFR §1.17(p), is being paid with this statement. Please apply any charges or credits to Deposit Account No. 06-1050, referencing the above attorney docket number.

Respectfully submitted,

Date: December 21, 2020

/Heather L. Flanagan/

Heather L. Flanagan
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Fish & Richardson P.C.
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62490932.doc

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Substitute for form 1449/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Use as many sheets as necessary)				Application Number	16/923,494
				Filing Date	July 8, 2020
				First Named Inventor	Teruaki OCHIAI
				Art Unit	1725
				Examiner Name	S. CULLEN
				Attorney Docket Number	12732-2003004
Sheet	1	of	2		

[illegible]

FOREIGN PATENT DOCUMENTS						
Examiner Initials*	Cite No. ¹	Foreign Patent Document	Publication Date	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	T ⁶
		Country Code ³ -Number ⁴ -Kind Code ⁵ (if known)	MM-DD-YYYY			
		KR-2013-0033154A	04-03-2013			Abst.
		KR-2011-0134852A	12-15-2011			Abst.
		EP-2763218A	08-06-2014			Eng.
		WO-2011/155781	12-15-2011			Abst.
		JP-2015-088450A	05-07-2015			Abst.

Examiner Signature	/Sean P Cullen, Ph.D./	Date Considered	01/05/2021
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PTO/SB/08A (07-06)

Approved for use through 03/31/2007. OMB 0651-0031

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Substitute for form 1449/PTO				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Use as many sheets as necessary)				Application Number	16/923,494
				Filing Date	July 8, 2020
				First Named Inventor	Teruaki OCHIAI
				Art Unit	1725
				Examiner Name	S.CULLEN
				Attorney Docket Number	12732-2003004
Sheet	2	of	2		

[illegible]

Examiner Signature	/Sean P Cullen, Ph.D./	Date Considered	01/05/2021
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*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered.

Include copy of this form with next communication to applicant.

1 Applicant's unique citation designation number (optional). 2 Applicant is to place a check mark here if English language Translation is attached.

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 (1-800-786-9199) and select option 2.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

First Named Inventor : Teruaki OCHIAI Art Unit : 1725
Application No. : 16/923,494 Examiner : Sean P. Cullen
Filed : July 8, 2020 Conf. No. : 3273
Title : POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR
MANUFACTURING POSITIVE ELECTRODE ACTIVE
MATERIAL, AND SECONDARY BATTERY

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

INFORMATION DISCLOSURE STATEMENT

Please consider the references listed on the enclosed disclosure form. Copies of the documents required under 37 C.F.R. § 1.98(a)(2) are being submitted with this statement.

Each item of information in this information disclosure statement, with the exception of EP2763218, US2014/0242463, and WO2011/155781, was first cited in communications from foreign patent offices in counterpart foreign applications dated July 27, 2020, and August 18, 2020, neither of which is more than three months prior to the filing of this information disclosure statement. See 37 CFR 1.97(e)(1).

KR2013-0033154, KR2011-0134852, and Ding.Y et al., "Preparation of nano-structured LiFePO₄/graphene composites by co-precipitation method", ELECTROCHEMISTRY COMMUNICATIONS, 2010, Vol. 12, No. 1, pp. 10-13, ELSEVIER, were cited in an office action dated July 27, 2020, from the Korea Intellectual Property Office in counterpart Korean Application No. 2019-7034933.

JP2015-088450 was cited in office actions dated August 18, 2020, from the Japan Patent Office in counterpart Japanese Application Nos. 2020-067736 and 2020-088842.

EP2763218 and US2014/0242463 are English-language documents corresponding to KR2013-0033154; and WO2011/155781 corresponds to KR2011-0134852.

First Named Inventor : Teruaki OCHIAI
Application No. : 16/923,494
Filed : July 8, 2020
Page : 2 of 2

Attorney Docket: 12732-2003004 /
US24652/.../26813-C4

This statement is being filed within three months of the filing date of the application.
Please apply any charges or credits to Deposit Account No. 06-1050, referencing the above
attorney docket number.

Respectfully submitted,

Date: September 24, 2020

/John F. Hayden/

John F. Hayden
Reg. No. 37640

Customer Number 26171
Fish & Richardson P.C.
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CD Submission Review Results

Internal Worksheet Only - Do Not Scan

Application Number

16923494

Receipt Date

Dec 21, 2020

☒New
Application☐Response To
Notice

Date Of Response

☐

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☒**There are no problems with the CDs in the submission.****Items checked below are to be selected in the PALM Pre-Exam CD problem list.**

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☐	Files on compact disc are unreadable:
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☐	Disc(s) do not contain file names listed:
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☐	Copy of file directory listing is attached and should be mailed to applicant
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Additional Comments

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Application Number: 16923494

Document Date: 12/21/2020

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Application	Document	Mailroom Date	Attorney Docket No.
16923494	CTFR	01/11/2021	12732-2003004
	892	01/11/2021	12732-2003004
	1449	01/11/2021	12732-2003004
	1449	01/11/2021	12732-2003004
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/923,494	07/08/2020	Teruaki OCHIAI	12732-2003004	3273
26171	7590	02/04/2021		
FISH & RICHARDSON P.C. (DC)			EXAMINER	
P.O. BOX 1022			CULLEN, SEAN P	
MINNEAPOLIS, MN 55440-1022				
			ART UNIT	PAPER NUMBER
			1725	
			NOTIFICATION DATE	DELIVERY MODE
			02/04/2021	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

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<i>Applicant-Initiated Interview Summary</i>	Application No. 16/923,494	Applicant(s) OCHIAI et al.		
	Examiner Sean P Cullen, Ph.D	Art Unit 1725	AIA (First Inventor to File) Status Yes	Page 1 of 2

All Participants (applicant, applicants representative, PTO personnel)	Title	Type
Sean P Cullen, Ph.D.	Primary Examiner	Telephonic
Heather Flanagan	Attorney	

Date of Interview: 29 January 2021

Issues Discussed:

35 U.S.C. 112

It was agreed that the proposed amendments would overcome the 112a and 112 b rejections.

Proposed Amendment(s)

Applicant proposed canceling claims 7, 9–12, 19, and 21–25.

Applicant further proposed amending claims 1 and 13 from "wherein a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned" to "wherein a crystal orientation of at least a second part of the first region and a crystal orientation of at least a part of the second region are substantially aligned with each other."

Applicant further proposed amending claim 13 from "wherein the second region covers at least a part of the first region" to "wherein the second region covers at least a first part of the first region."

/Sean P Cullen, Ph.D./ Primary Examiner, Art Unit 1725	
<p>Applicant is reminded that a complete written statement as to the substance of the interview must be made of record in the application file. It is the applicants responsibility to provide the written statement, unless the interview was initiated by the Examiner and the Examiner has indicated that a written summary will be provided. See MPEP 713.04</p> <p>Please further see: MPEP 713.04 Title 37 Code of Federal Regulations (CFR) § 1.133 Interviews, paragraph (b) 37 CFR § 1.2 Business to be transacted in writing</p>	

Applicant recordation instructions: The formal written reply to the last Office action must include the substance of the interview. (See MPEP section 713.04). If a reply to the last Office action has already been filed, applicant is given a non-extendable period of the longer of one month or thirty days from this interview date, or the mailing date of this interview summary form, whichever is later, to file a statement of the substance of the interview.

Examiner recordation instructions: Examiners must summarize the substance of any interview of record. A complete and proper recordation of the substance of an interview should include the items listed in MPEP 713.04 for complete

<i>Applicant-Initiated Interview Summary</i>	Application No. 16/923,494	Applicant(s) OCHIAI et al.		
	Examiner Sean P Cullen, Ph.D	Art Unit 1725	AIA (First Inventor to File) Status Yes	Page 2 of 2

and proper recordation including the identification of the general thrust of each argument or issue discussed, a general indication of any other pertinent matters discussed regarding patentability and the general results or outcome of the interview, to include an indication as to whether or not agreement was reached on the issues raised.

To: PATDOCTC@fr.com,,
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Application	Document	Mailroom Date	Attorney Docket No.
16923494	EXIN	02/04/2021	12732-2003004

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First Named Inventor :	Teruaki OCHIAI	Art Unit :	1725
Application No. :	16/923,494	Examiner :	Sean P. Cullen
Filed :	July 8, 2020	Conf. No. :	3273
Title :	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY		

MAIL STOP AF

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INTERVIEW SUMMARY AND REPLY TO ACTION OF JANUARY 11, 2021

Please consider the following reply.

Amendments to Claims

Listing of Claims

1. (Currently Amended) A lithium-ion secondary battery comprising a positive electrode, the positive electrode comprising a positive electrode active material particle comprising lithium cobaltate,

wherein the positive electrode active material particle comprises a first region and a second region,

wherein the first region comprises a layered rock-salt crystal structure,

wherein the second region comprises a rock-salt crystal structure,

wherein the positive electrode active material particle comprises titanium, magnesium, fluorine, and oxygen in the second region, wherein the second region extends from a surface of the positive electrode active material particle to an inside of the positive electrode active material particle where magnesium detected by a line analysis of energy dispersive X-ray spectroscopy (EDX) in a depth direction is 1/5 of a maximum peak of the magnesium in the line analysis, and

wherein a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned with each other.

2. (Canceled)

3. (Previously Presented) The lithium-ion secondary battery according to claim 1, wherein a relative value of a concentration of the titanium is greater than or equal to 0.05 and less than or equal to 0.4 when the surface of the positive electrode active material particle is subjected to an XPS analysis and a concentration of cobalt is defined as 1.

4. (Previously Presented) The lithium-ion secondary battery according to claim 1, wherein a relative value of a concentration of the magnesium is greater than or equal to 0.4 and less than or equal to 1.5 when the surface of the positive electrode active material particle is subjected to an XPS analysis and a concentration of cobalt is defined as 1.

5. (Original) The lithium-ion secondary battery according to claim 1,
wherein the titanium, the magnesium, the fluorine, and the oxygen are provided in a
range from the surface of the positive electrode active material particle to a depth of 5 nm.

6. (Original) The lithium-ion secondary battery according to claim 1,
wherein the positive electrode further comprises a conductive additive, and
wherein the conductive additive comprises carbon fiber, graphene or multilayer graphene.

7-12. (Cancelled)

13. (Currently Amended) A lithium-ion secondary battery comprising
a positive electrode, the positive electrode comprising a positive electrode active material
particle comprising lithium cobaltate,
wherein the positive electrode active material particle comprises a first region and a
second region,
wherein the first region comprises a layered rock-salt crystal structure,
wherein the second region comprises a rock-salt crystal structure,
wherein the second region covers at least a first part of the first region,
wherein the positive electrode active material particle comprises titanium, magnesium,
fluorine, and oxygen in the second region, and
wherein a crystal orientation of at least a second part of the first region and a crystal
orientation of at least a part of the second region are substantially aligned with each other.

14. (Canceled)

15. (Previously Presented) The lithium-ion secondary battery according to claim 13,
wherein a relative value of a concentration of the titanium is greater than or equal to 0.05 and
less than or equal to 0.4 when the surface of the positive electrode active material particle is
subjected to an XPS analysis and a concentration of cobalt is defined as 1.

16. (Previously Presented) The lithium-ion secondary battery according to claim 13, wherein a relative value of a concentration of the magnesium is greater than or equal to 0.4 and less than or equal to 1.5 when the surface of the positive electrode active material particle is subjected to an XPS analysis and a concentration of cobalt is defined as 1.

17. (Previously Presented) The lithium-ion secondary battery according to claim 13, wherein the titanium, the magnesium, the fluorine, and the oxygen are provided in a range from the surface of the positive electrode active material particle to a depth of 5 nm.

18. (Previously Presented) The lithium-ion secondary battery according to claim 13, wherein the positive electrode further comprises a conductive additive, and wherein the conductive additive comprises carbon fiber, graphene or multilayer graphene.

19. (Cancelled)

REMARKS

Claims 1, 3-6, 13, and 15-18 are pending, with claims 1 and 13 being independent. Claims 1 and 13 have been amended, and claims 7, 9-12, 19, and 21-25 have been cancelled. No new matter has been introduced.

Interview Summary

The undersigned thanks Examiner Cullen for courtesies extended in an applicant-initiated telephonic interview on January 29, 2021, in which the amendments presented in this paper were discussed. It was agreed that these amendments overcome the rejections of record.

Claim Rejections - 35 USC § 112

Claims 7, 9-12, 19, and 21-25 were rejected under 35 U.S.C. § 112(a). Claims 1, 3-7, 9-13, 15-19, and 21-24 were rejected under 35 U.S.C. § 112(b). As noted above, claims 7, 9-12, 19, and 21-25 have been cancelled. Claim 1 has been amended as discussed during the interview to recite “wherein a crystal orientation of at least a part of the first region and a crystal orientation of at least a part of the second region are substantially aligned with each other.” Claim 13 has been amended as discussed during the interview to recite: “wherein the second region covers at least a first part of the first region” and “wherein a crystal orientation of at least a second part of the first region and a crystal orientation of at least a part of the second region are substantially aligned with each other.” Withdrawal of these rejections is therefore requested.

First Named Inventor : Teruaki OCHIAI
Application No. : 16/923,494
Filed : July 8, 2020
Page : 6 of 6

Attorney Docket: 12732-2003004 /
US24652/.../26813-C4

All claims are in condition for allowance. No fees are believed to be due. Please apply any necessary charges or credits to Deposit Account 06-1050, referencing the above attorney docket number.

Respectfully submitted,

Date: February 10, 2021

/Heather L. Flanagan/

Heather L. Flanagan
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41501395.doc

Electronic Acknowledgement Receipt

EFS ID:	41887414
Application Number:	16923494
International Application Number:	
Confirmation Number:	3273
Title of Invention:	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY
First Named Inventor/Applicant Name:	Teruaki OCHIAI
Customer Number:	26171
Filer:	Heather L. Flanagan/Sharon Allen
Filer Authorized By:	Heather L. Flanagan
Attorney Docket Number:	12732-2003004
Receipt Date:	10-FEB-2021
Filing Date:	08-JUL-2020
Time Stamp:	12:20:58
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no
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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		12732-2003004-Response.pdf	106345	yes	6
			27f92f69335225c3a97853004c12f5cc6d03239c		

Multipart Description/PDF files in .zip description			
Document Description	Start	End	
Response After Final Action	1	1	
Claims	2	4	
Applicant Arguments/Remarks Made in an Amendment	5	6	

Warnings:

Information:

Total Files Size (in bytes):	106345
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This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875				Application or Docket Number 16/923,494		Filing Date 07/08/2020		☐ To be Mailed		
ENTITY: ☒ LARGE ☐ SMALL ☐ MICRO										
APPLICATION AS FILED - PART I										
		(Column 1)	(Column 2)							
FOR		NUMBER FILED	NUMBER EXTRA	RATE (\$)		FEE (\$)				
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))		N/A	N/A	N/A						
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))		N/A	N/A	N/A						
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))		N/A	N/A	N/A						
TOTAL CLAIMS (37 CFR 1.16(i))		minus 20 =	*	x \$100 =						
INDEPENDENT CLAIMS (37 CFR 1.16(h))		minus 3 =	*	x \$460 =						
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))		If the specification and drawings exceed 100 sheets of paper, the application size fee due is \$310 (\$155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).								
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))										
* If the difference in column 1 is less than zero, enter "0" in column 2.				TOTAL						
APPLICATION AS AMENDED - PART II										
		(Column 1)		(Column 2)	(Column 3)					
AMENDMENT	02/10/2021	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE (\$)		ADDITIONAL FEE (\$)		
	Total (37 CFR 1.16(i))	* 10	Minus	** 24	= 0	x \$100 =		0		
	Independent (37 CFR 1.16(h))	* 2	Minus	*** 4	= 0	x \$480 =		0		
	☐ Application Size Fee (37 CFR 1.16(s))									
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))									
						TOTAL ADD'L FEE		0		
		(Column 1)		(Column 2)	(Column 3)					
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE (\$)		ADDITIONAL FEE (\$)		
	Total (37 CFR 1.16(i))	*	Minus	**	=	x \$0 =				
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x \$0 =				
	☐ Application Size Fee (37 CFR 1.16(s))									
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))									
						TOTAL ADD'L FEE				
* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.						LIE				
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".						/SHAREILL A COLES/				
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".										
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.										

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

26171 7590 02/22/2021
FISH & RICHARDSON P.C. (DC)
P.O. BOX 1022
MINNEAPOLIS, MN 55440-1022

EXAMINER

CULLEN, SEAN P

ART UNIT

PAPER NUMBER

1725

DATE MAILED: 02/22/2021

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/923,494	07/08/2020	Teruaki OCHIAI	12732-2003004	3273

TITLE OF INVENTION: POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING LITHIUM COBALTATE COATED WITH LITHIUM TITANATE AND MAGNESIUM OXIDE

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	\$1200	\$0.00	\$0.00	\$1200	05/24/2021

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

26171 7590 02/22/2021
FISH & RICHARDSON P.C. (DC)
P.O. BOX 1022
MINNEAPOLIS, MN 55440-1022

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/923,494	07/08/2020	Teruaki OCHIAI	12732-2003004	3273

TITLE OF INVENTION: POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING LITHIUM COBALTATE COATED WITH LITHIUM TITANATE AND MAGNESIUM OXIDE

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	\$1200	\$0.00	\$0.00	\$1200	05/24/2021

EXAMINER	ART UNIT	CLASS-SUBCLASS
CULLEN, SEAN P	1725	429-488000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list

(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,

1 _____

(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

2 _____

3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE

(B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☐ Corporation or other private group entity ☐ Government

4a. Fees submitted: ☐ Issue Fee ☐ Publication Fee (if required) ☐ Advance Order - # of Copies _____

4b. Method of Payment: (Please first reapply any previously paid fee shown above)

☐ Electronic Payment via EFS-Web ☐ Enclosed check ☐ Non-electronic payment by credit card (Attach form PTO-2038)

☐ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. Change in Entity Status (from status indicated above)

☐ Applicant certifying micro entity status. See 37 CFR 1.29

☐ Applicant asserting small entity status. See 37 CFR 1.27

☐ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.

NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____

Date _____

Typed or printed name _____

Registration No. _____



UNITED STATES PATENT AND TRADEMARK OFFICE

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United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
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www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/923,494	07/08/2020	Teruaki OCHIAI	12732-2003004	3273
26171	7590	02/22/2021	EXAMINER	
FISH & RICHARDSON P.C. (DC)			CULLEN, SEAN P	
P.O. BOX 1022				
MINNEAPOLIS, MN 55440-1022				
			ART UNIT	PAPER NUMBER
			1725	
DATE MAILED: 02/22/2021				

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b) (Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 16/923,494	Applicant(s) OCHIAI et al.	
	Examiner Sean P Cullen, Ph.D.	Art Unit 1725	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to the communication(s) 10 February 2021.
☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☒ The allowed claim(s) is/are 1,3-6,13 and 15-18. As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

4. ☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a) ☒ All b) ☐ Some *c) ☐ None of the:

1. ☐ Certified copies of the priority documents have been received.

2. ☒ Certified copies of the priority documents have been received in Application No. 15/638,449.

3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

* Certified copies not received: _____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____.

Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892) 2. ☐ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____. 3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____. 4. ☐ Interview Summary (PTO-413), Paper No./Mail Date _____.	5. ☒ Examiner's Amendment/Comment 6. ☒ Examiner's Statement of Reasons for Allowance 7. ☐ Other _____.
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/Sean P Cullen, Ph.D./
Primary Examiner, Art Unit 1725

DETAILED ACTION

Notice of Pre-AIA or AIA Status

1. The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Status of Claims

2. **Claim(s) 1, 3–6, 13, and 15–18** is/are pending.
3. **Claim(s) 2, 7–12, 14, and 19–25** is/are canceled.

Claim Rejections - 35 USC § 112

4. Applicants' amendment(s) have overcome the rejection(s) of **claim(s) 7, 9–12, 19, 21–25** under 35 U.S.C. 112(a) or 35 U.S.C. 112 (pre-AIA), first paragraph.
5. Applicants' amendment(s) have overcome the rejection(s) of **claim(s) 1, 3–7, 9–13, 15–19, and 21–24** under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph.

EXAMINER'S AMENDMENT

6. An examiner's amendment to the record appears below. Should the changes and/or additions be unacceptable to applicant, an amendment may be filed as provided by 37 CFR 1.312. To ensure consideration of such an amendment, it **MUST** be submitted no later than the payment of the issue fee.

Authorization for this examiner's amendment was given in an interview with Heather L Flanagan (Reg. No. 54,101) on 12 February 2021.

7. The application has been amended as follows:

IN THE CLAIMS:

Please cancel claims 21–25.

Allowable Subject Matter

8. **Claim(s) 1, 3–6, 13, and 15–18** is/are allowed.

9. The following is an examiner's statement of reasons for allowance:

The closest prior art of record is Yura (US 2012/0258358 A1).

Yura discloses a lithium-ion secondary battery (1) comprising a positive electrode (2), the positive electrode (2) comprising a positive electrode active material particle (222) comprising lithium cobaltate (see LiCoO_2 , [0018]), wherein the positive electrode active material particle (222) comprising a first region (222a) and a second region (222a, [0061]), wherein the first region (222a) comprises a layered rock-salt crystal structure (Fig. 3, [0061]), wherein the second region (222a) comprises a rock-salt crystal structure (Fig. 3, [0061]), wherein the second region (222a) covers at least a first part of the first region (222a, [0061]), wherein a crystal orientation of at least a second part of the first region (222a) and a crystal orientation of at least a part of the second region (222a) are substantially aligned with each other (Fig. 3, [0062]).

Yura does not disclose, teach, or suggest the following distinguishing feature(s):

A lithium-ion secondary battery comprising a positive electrode, the positive electrode comprising a positive active material comprising lithium cobaltate in a first region and titanium, magnesium, fluorine, and oxygen in a second region.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue

fee. Such submissions should be clearly labeled “Comments on Statement of Reasons for Allowance.”

Conclusion

10. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Sean P Cullen, Ph.D. whose telephone number is (571)270-1251. The examiner can normally be reached on Monday to Thursday 6:00 am to 4:00 pm CT, Friday 6:00 am to 12:00 pm CT.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at <http://www.uspto.gov/interviewpractice>.

If attempts to reach the examiner by telephone are unsuccessful, the examiner’s supervisor, Basia A Ridley can be reached on (571)272-1453. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <https://ppair-my.uspto.gov/pair/PrivatePair>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to

the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Sean P Cullen, Ph.D./
Primary Examiner, Art Unit 1725

Issue Classification 	Application/Control No. 16/923,494	Applicant(s)/Patent Under Reexamination OCHIAI et al.
	Examiner Sean P Cullen, Ph.D.	Art Unit 1725

CPC						
Symbol					Type	Version
H01M	/	4	/	131	F	2013-01-01
H01M	/	4	/	1315	I	2013-01-01
H01M	/	4	/	1391	I	2013-01-01
H01M	/	4	/	625	I	2013-01-01
H01M	/	4	/	13915	I	2013-01-01
H01M	/	4	/	134	I	2013-01-01
H01M	/	4	/	366	I	2013-01-01
H01M	/	4	/	525	I	2013-01-01
H01M	/	4	/	8657	I	2013-01-01
H01M	/	2004	/	021	A	2013-01-01
H01M	/	2004	/	028	A	2013-01-01
H01M	/	10	/	0525	A	2013-01-01

CPC Combination Sets							
Symbol				Type	Set	Ranking	Version
	/		/				

NONE (Assistant Examiner) _____ (Date) _____		Total Claims Allowed: 10	
/Sean P Cullen, Ph.D./ Primary Examiner, Art Unit 1725 (Primary Examiner) _____ (Date) _____		12 February 2021 O.G. Print Claim(s) 1	O.G. Print Figure 3

Issue Classification 	Application/Control No. 16/923,494	Applicant(s)/Patent Under Reexamination OCHIAI et al.
	Examiner Sean P Cullen, Ph.D.	Art Unit 1725

INTERNATIONAL CLASSIFICATION				
CLAIMED				
H01M4/131	/	4	/	131
H01M4/1315	/	4	/	1315
H01M4/1391	/	4	/	1391
H01M4/62	/	4	/	62
H01M4/13915	/	4	/	13915
H01M4/134	/	4	/	134
H01M4/36	/	4	/	36
H01M4/525	/	4	/	525
H01M4/86	/	4	/	86
H01M4/02	/	4	/	02
H01M10/0525	/	10	/	0525
NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	SUBCLASS
429	231.3

CROSS REFERENCES(S)					
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)				
429	231.5	231.6	231.95		

NONE (Assistant Examiner) _____ (Date) _____		Total Claims Allowed: 10	
/Sean P Cullen, Ph.D./ Primary Examiner, Art Unit 1725 (Primary Examiner) _____ (Date) _____		12 February 2021 O.G. Print Claim(s) 1	O.G. Print Figure 3

Issue Classification 	Application/Control No. 16/923,494	Applicant(s)/Patent Under Reexamination OCHIAI et al.
	Examiner Sean P Cullen, Ph.D.	Art Unit 1725

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47															
CLAIMS															
Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	13	10	4												
2	17														
3	18														
4	15														
5	16														
6	1														
7	5														
8	6														
9	3														

NONE (Assistant Examiner) _____ (Date) _____		Total Claims Allowed: 10	
/Sean P Cullen, Ph.D./ Primary Examiner, Art Unit 1725 (Primary Examiner) _____ (Date) _____		12 February 2021 O.G. Print Claim(s) 1	O.G. Print Figure 3

<i>Search Notes</i> 	Application/Control No. 16/923,494	Applicant(s)/Patent Under Reexamination OCHIAI et al.
	Examiner Sean P Cullen, Ph.D.	Art Unit 1725

CPC - Searched*		
Symbol	Date	Examiner
H01M4/131, 1315, 1391, 13915, 625, 8657	09/14/2020	SPC
Updated CPC search	01/05/2021	SPC
Updated CPC search	02/12/2021	SPC

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner
429	231.3, 231.5, 231.6, 231.95	09/14/2020	SPC
	Updated USPC search	01/05/2021	SPC
	Updated USPC search	02/12/2021	SPC

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

--	--

<i>Search Notes</i> 	Application/Control No. 16/923,494	Applicant(s)/Patent Under Reexamination OCHIAI et al.
	Examiner Sean P Cullen, Ph.D.	Art Unit 1725

Search Notes		
Search Notes	Date	Examiner
H01M4/131, 1315, 1391, 13915, 625, 8657	09/14/2020	SPC
429/231.3, 231.5, 231.6, 231.95	09/14/2020	SPC
Inventor/applicant search, PALM	09/14/2020	SPC
PE2E SEARCH text search, see search history	09/14/2020	SPC
Updated inventor/applicant search, PALM	01/05/2021	SPC
Updated PE2E SEARCH text search, see search history	01/05/2021	SPC
Updated inventor/applicant search, PALM	02/12/2021	SPC
Updated PE2E SEARCH text search, see search history	02/12/2021	SPC

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner
H01M4	131, 1315, 1391, 13915, 625, 8657	02/12/2021	SPC
429	231.3, 231.5, 231.6, 231.95	02/12/2021	SPC

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PE2E SEARCH - Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	British Equivalents	Time Stamp
L203	3196	((429/231.3,231.5,231.6,231.95).ccls. (H01M4/131,1315,1391,13915,625,8657).cpc.) AND (shell coating layer) WITH (LiTiO.sub.2 LiTiO2 lithium ADJ (titanate titanium ADJ oxide) Li\$Ti\$O{d1} Li\$Ti\$O.sub.{d1} Li\$Ti\$O{d2} Li\$Ti\$O.sub.{d2}))	US-PGPUB; USPAT; USOCR; FIT (AU, AP, AT, CA, CH, CN, DD, DE, EA, EP, ES, FR, GB, JP, KR, OA, RU, SU, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/02/12 11:22 AM
L204	1	L203 AND (shell coating layer) WITH Mg\$F\$	US-PGPUB; USPAT; USOCR; FIT (AU, AP, AT, CA, CH, CN, DD, DE, EA, EP, ES, FR, GB, JP, KR, OA, RU, SU, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/02/12 11:23 AM
L205	3	L203 AND (shell coating layer) WITH magnesium near2 fluoride	US-PGPUB; USPAT; USOCR; FIT (AU, AP, AT, CA, CH, CN, DD, DE, EA, EP, ES, FR, GB, JP, KR, OA, RU, SU, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/02/12 11:23 AM
L206	3	L203 AND (shell coating layer) WITH magnesium near2 fluoride	US-PGPUB; USPAT; USOCR; FIT (AU, AP, AT, CA, CH, CN, DD, DE, EA, EP, ES, FR, GB, JP, KR, OA, RU, SU, WO); FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	ON	2021/02/12 11:25 AM

PE2E SEARCH - Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	British Equivalents	Time Stamp
N170	690	((429/231.3,231.5,231.6,231.95).ccls. (H01M4/131,1315,1391,13915,625,8657).cpc.)	US-PGPUB; USPAT	OR	ON	ON	2021/02/12 11:23 AM

		AND (shell coating layer) WITH (LiTiO.sub.2 LiTiO2 lithium ADJ (titanate titanium ADJ oxide) Li\$Ti\$O{d1} Li\$Ti\$"O.sub.{d1} Li\$Ti\$O{d2} Li\$Ti\$"O.sub.{d2})					
N171	2370	L199 AND (shell coating layer) WITH (magnesium near2 fluoride Mg\$F\$)	US-PGPUB; USPAT	OR	ON	ON	2021/02/12 11:24 AM
N172	1	N170 AND (shell coating layer) WITH (magnesium near2 fluoride Mg\$F\$)	US-PGPUB; USPAT	OR	ON	ON	2021/02/12 11:25 AM

Bibliographic Data

Application No: 16/923,494

Foreign Priority claimed: ☒ Yes ☐ No

35 USC 119 (a-d) conditions met: ☒ Yes ☐ No ☐ Met After Allowance

Verified and Acknowledged: /Sean P Cullen, Ph.D./

Examiner's Signature

Initials

Title:

POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING
LITHIUM COBALTATE COATED WITH LITHIUM TITANATE
AND MAGNESIUM OXIDE

FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
07/08/2020	429	1725	12732-2003004
RULE			

APPLICANTS

SEMICONDUCTOR ENERGY LABORATORY CO., LTD., ATSUGI-SHI, JAPAN

INVENTORS

Teruaki OCHIAI, Atsugi, JAPAN

Takahiro KAWAKAMI, Atsugi, JAPAN

Mayumi MIKAMI, Atsugi, JAPAN

Yohei MOMMA, Isehara, JAPAN

Masahiro TAKAHASHI, Atsugi, JAPAN

Ayae TSURUTA, Atsugi, JAPAN

CONTINUING DATA

This application is a CON of 15638449 06/30/2017 PAT 10741828

FOREIGN APPLICATIONS

JAPAN JP2016-133143 07/05/2016

JAPAN JP2016-133997 07/06/2016

JAPAN JP2017-002831 01/11/2017

JAPAN JP2017-030693 02/22/2017

JAPAN JP2017-084321 04/21/2017

JAPAN JP2017-119272 06/19/2017

IF REQUIRED, FOREIGN LICENSE GRANTED**

07/17/2020

STATE OR COUNTRY

JAPAN

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P.O. BOX 1022
MINNEAPOLIS, MN 55440-1022
UNITED STATES

FILING FEE RECEIVED

\$7,120

02/12/2021

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

First Named Inventor :	Teruaki OCHIAI	Art Unit :	1725
Application No. :	16/923,494	Examiner :	Sean P. Cullen
Filed :	July 8, 2020	Conf. No. :	3273
Title :	POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING POSITIVE ELECTRODE ACTIVE MATERIAL, AND SECONDARY BATTERY		

MAIL STOP AF
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

INTERVIEW SUMMARY AND REPLY TO ACTION OF JANUARY 11, 2021

Please consider the following reply.

To: PATDOCTC@fr.com,,
From: PAIR_eOfficeAction@uspto.gov
Cc: PAIR_eOfficeAction@uspto.gov
Subject: Private PAIR Correspondence Notification for Customer Number 26171

Feb 22, 2021 03:46:52 AM

Dear PAIR Customer:

FISH & RICHARDSON P.C. (DC)
P.O. BOX 1022
MINNEAPOLIS, MN 55440-1022
UNITED STATES

The following USPTO patent application(s) associated with your Customer Number, 26171 , have new outgoing correspondence. This correspondence is now available for viewing in Private PAIR.

The official date of notification of the outgoing correspondence will be indicated on the form PTOL-90 accompanying the correspondence.

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Application	Document	Mailroom Date	Attorney Docket No.
16923494	NOA	02/22/2021	12732-2003004

To view your correspondence online or update your email addresses, please visit us anytime at <https://portal.uspto.gov/secure/myportal/privatepair>.

If you have any questions, please email the Electronic Business Center (EBC) at EBC@uspto.gov with 'e-Office Action' on the subject line or call 1-866-217-9197 during the following hours:

Monday - Friday 6:00 a.m. to 12:00 a.m.

Thank you for prompt attention to this notice,

UNITED STATES PATENT AND TRADEMARK OFFICE
PATENT APPLICATION INFORMATION RETRIEVAL SYSTEM

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

First Named Inventor : Teruaki OCHIAI Art Unit : 1725
Application No. : 16/923,494 Examiner : Sean P. Cullen
Filed : July 8, 2020 Confirmation No. : 3273
Notice of Allowance Date: February 22, 2021
Title : POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING
LITHIUM COBALTATE COATED WITH LITHIUM TITANATE
AND MAGNESIUM OXIDE

MAIL STOP ISSUE FEE

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

REPLY TO NOTICE OF ALLOWANCE

In response to the Notice of Allowance mailed February 22, 2021, enclosed is a completed issue fee transmittal form PTOL 85b. A fee in the amount of \$1200 for the issue fee is being paid concurrently herewith on the Electronic Filing System (EFS) by way of Deposit Account authorization.

Please apply any other charges or credits to Deposit Account No. 06-1050, referencing attorney docket number 12732-2003004.

Respectfully submitted,

Date: March 1, 2021

/John F. Hayden/
John F. Hayden
Reg. No. 37640

Customer Number 26171
Fish & Richardson P.C.
Telephone: (202) 783-5070
Facsimile: (877) 769-7945

41509947.doc

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web

By mail, send to: Mail Stop ISSUE FEE
 Commissioner for Patents
 P.O. Box 1450
 Alexandria, Virginia 22314-1450

By fax, send to: (571) 273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

26171 7590 02/22/2021

FISH & RICHARDSON P.C.
 P.O. BOX 1022
 MINNEAPOLIS, MN 55440-1022

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)

(Signature)

(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/923,494	07/08/2020	Teruaki OCHIAI	12732-2003004	3273

TITLE OF INVENTION: POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING LITHIUM COBALTATE COATED WITH LITHIUM TITANATE AND MAGNESIUM OXIDE

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	LARGE	\$1200	\$0		\$1200	05/24/2021
EXAMINER		ART UNIT	CLASS-SUBCLASS			
CULLEN, SEAN P.		1725	429-488000			

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

- ☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
- ☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list

- (1) The names of up to 3 registered patent attorneys or agents OR, alternatively, 1 Fish & Richardson P.C.
- (2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed. 2 _____
- 3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE
 Semiconductor Energy Laboratory Co., Ltd.

(B) RESIDENCE: (CITY and STATE OR COUNTRY)
 Atsugi-shi, Kanagawa-ken, JAPAN

Please check the appropriate assignee category or categories (will not be printed on the patent): ☐ Individual ☒ Corporation or other private group entity ☐ Government4a. Fees Submitted: ☒ Issue Fee ☐ Publication Fee (if required) ☐ Advance Order - # of Copies

4b. Method of Payment (Please first reapply any previously paid fee shown above):

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5. Change of Entity Status (from status indicated above)

- ☐ Applicant certifying micro entity status. See 37 CFR 1.29
- ☐ Applicant asserting small entity status. See 37 CFR 1.27.
- ☐ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid Certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.

NOTE: If the application was previously under micro entity status, checking this box will be taken as a notification of loss of entitlement to micro entity status.

NOTE: Checking this box will be taken as a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature /John F. Hayden/Date March 1, 2021Typed or printed name John F. HaydenRegistration No. 37640

PTOL-85 Part B (08-18). Approved for use through 1/31/2020

OMB 0851-0033

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

41509950.doc

Electronic Patent Application Fee Transmittal

Application Number:	16923494			
Filing Date:	08-Jul-2020			
Title of Invention:	POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING LITHIUM COBALTATE COATED WITH LITHIUM TITANATE AND MAGNESIUM OXIDE			
First Named Inventor/Applicant Name:	Teruaki OCHIAI			
Filer:	John F. Hayden/April Saunders-Fuller			
Attorney Docket Number:	12732-2003004			
Filed as Large Entity				
Filing Fees for Utility under 35 USC 111(a)				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
UTILITY APPL ISSUE FEE	1501	1	1200	1200

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Extension-of-Time:				
Miscellaneous:				
Total in USD (\$)				1200

Electronic Acknowledgement Receipt

EFS ID:	42053917
Application Number:	16923494
International Application Number:	
Confirmation Number:	3273
Title of Invention:	POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING LITHIUM COBALTATE COATED WITH LITHIUM TITANATE AND MAGNESIUM OXIDE
First Named Inventor/Applicant Name:	Teruaki OCHIAI
Customer Number:	26171
Filer:	John F. Hayden/April Saunders-Fuller
Filer Authorized By:	John F. Hayden
Attorney Docket Number:	12732-2003004
Receipt Date:	01-MAR-2021
Filing Date:	08-JUL-2020
Time Stamp:	15:39:57
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	\$ 1200
RAM confirmation Number	E202131F40160665
Deposit Account	061050
Authorized User	April Saunders-Fuller

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

37 CFR 1.17 (Patent application and reexamination processing fees)

37 CFR 1.19 (Document supply fees)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	12732-2003004-REPLY.pdf	56910	no	1
			18799dae50c9011d432eb190a1b07dbc5feab9af		

Warnings:**Information:**

2	Issue Fee Payment (PTO-85B)	12732-2003004-IF.pdf	122879	no	1
			173657f95d52e3d9646b54b411b2603f1eac4336		

Warnings:**Information:**

3	Fee Worksheet (SB06)	fee-info.pdf	30782	no	2
			6eb5bf28efedd009c28a9c203b358c218be09e4a		

Warnings:**Information:**

Total Files Size (in bytes):			210571
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This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

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National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.



APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/923,494	04/27/2021	10991934	12732-2003004	3273

26171 7590 04/07/2021

FISH & RICHARDSON P.C. (DC)
P.O. BOX 1022
MINNEAPOLIS, MN 55440-1022

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b) (application filed on or after May 29, 2000)

The Patent Term Adjustment is 0 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (<http://pair.uspto.gov>).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site <http://pair.uspto.gov> for additional applicants):

Teruaki OCHIAI, Atsugi, JAPAN;
SEMICONDUCTOR ENERGY LABORATORY CO., LTD., ATSUGI-SHI, JAPAN;
Takahiro KAWAKAMI, Atsugi, JAPAN;
Mayumi MIKAMI, Atsugi, JAPAN;
Yohei MOMMA, Isehara, JAPAN;
Masahiro TAKAHASHI, Atsugi, JAPAN;
Ayae TSURUTA, Atsugi, JAPAN;

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To: PATDOCTC@fr.com,,
From: PAIR_eOfficeAction@uspto.gov
Cc: PAIR_eOfficeAction@uspto.gov
Subject: Private PAIR Correspondence Notification for Customer Number 26171

Apr 08, 2021 10:15:28 AM

Dear PAIR Customer:

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P.O. BOX 1022
MINNEAPOLIS, MN 55440-1022
UNITED STATES

The following USPTO patent application(s) associated with your Customer Number, 26171 , have new outgoing correspondence. This correspondence is now available for viewing in Private PAIR.

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Application	Document	Mailroom Date	Attorney Docket No.
16923494	ISSUE.NTF	04/07/2021	12732-2003004

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UNITED STATES PATENT AND TRADEMARK OFFICE
PATENT APPLICATION INFORMATION RETRIEVAL SYSTEM

REQUEST FOR CONTINUED EXAMINATION(RCE)TRANSMITTAL (Submitted Only via EFS-Web)

Application Number	16/923,494	Filing Date	2020-07-08	Docket Number (if applicable)	12732-2003004	Art Unit	1725
First Named Inventor	Teruaki OCHIAI			Examiner Name	Sean P. Cullen		

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application.

Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application. The Instruction Sheet for this form is located at WWW.USPTO.GOV

SUBMISSION REQUIRED UNDER 37 CFR 1.114

Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on _____

☐ Other _____

☒ Enclosed

☐ Amendment/Reply

☒ Information Disclosure Statement (IDS)

☐ Affidavit(s)/ Declaration(s)

☒ Other

e-Petition to Withdraw from Issue; QPIDS (Form PTO/SB/09)

MISCELLANEOUS

☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of months _____
(Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(i) required)

☐ Other _____

FEES

The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.

☒ The Director is hereby authorized to charge any underpayment of fees, or credit any overpayments, to Deposit Account No 061050

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED

☒ Patent Practitioner Signature

Applicant Signature

Signature of Registered U.S. Patent Practitioner			
Signature	John F. Hayden/	Date (YYYY-MM-DD)	2021-04-09
Name	John F. Hayden	Registration Number	37640

This collection of information is required by 37 CFR 1.114. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450.

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The information provided by you in this form will be subject to the following routine uses:

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
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**CERTIFICATION AND REQUEST FOR CONSIDERATION OF AN INFORMATION DISCLOSURE
STATEMENT FILED AFTER PAYMENT OF THE ISSUE FEE UNDER THE QPIDS PROGRAM**

Non-Provisional Application Number:
16/923,494

Filing Date:
July 8, 2020

First Named Inventor:
Teruaki OCHIAI

Title of Invention:
POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING
LITHIUM COBALTATE WITH LITHIUM TITANATE AND
MAGNESIUM OXIDE

**THE UNDERSIGNED HEREBY CERTIFIES AND REQUESTS THE FOLLOWING FOR THE ABOVE-
IDENTIFIED APPLICATION.**

1. Consideration is requested of the information disclosure statement (IDS) submitted herewith, which is being filed after payment of the issue fee.
2. Check the box next to the appropriate selection:
☒ Each item of information contained in the IDS was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the IDS. See 37 CFR 1.97(e)(1).
OR
☐ No item of information contained in the IDS was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the IDS was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the IDS. See 37 CFR 1.97(e)(2).
OR
☐ See attached certification statement in compliance with 37 CFR 1.97(e).
3. Please charge the IDS fee set forth in 37 CFR 1.17(p) to Deposit Account No. **06-1050**.
4. A Petition to Withdraw from Issue After Payment of the Issue Fee (37 CFR 1.313(c)(2)), including the petition fee set forth in 37 CFR 1.17(h), is submitted herewith as a **Web-based ePetition**.
WARNING: Do not submit the petition as a follow-on paper via EFS-Web. Submit the petition as a Web-based ePetition by signing on to EFS-Web as a registered user, selecting the radio button next to "Existing application/patent," and then selecting the radio button next to "ePetition (for automatic processing and immediate grant, if all petitions requirements are met)." Failure to use the Web-based ePetition interface will result in automatic entry of the RCE.
5. A request for continued examination (RCE) under 37 CFR 1.114 and the RCE fee under 37 CFR 1.17(e) are submitted herewith.
6. The RCE will be treated as a "conditional" RCE. In the event the examiner determines that any item of information contained in the IDS necessitates the reopening of prosecution in the application, the undersigned understands that (i) the RCE will be processed and treated as an RCE under 37 CFR 1.114 and therefore (ii) the IDS fee under 37 CFR 1.17(p) will be returned in accordance with 37 CFR 1.97(b)(4). In the event that no item of information in the IDS necessitates reopening prosecution, the undersigned understands that the RCE will not be processed and the RCE fee under 37 CFR 1.17(e) will be returned.
7. This certification and request is being filed as a **Web-based ePetition** and is not accompanied by an amendment to the application. Inclusion of an amendment will result in automatic entry of the RCE.

Signature /John F. Hayden/

Date April 9, 2021

Name
(Print/Typed) John F. Hayden

Practitioner
Registration Number
(If applicable) 37640

Note: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required in accordance with 37 CFR 1.33 and 11.18. Please see 37 CFR 1.4(d) for the form of the signature. If necessary, submit multiple forms for more than one signature, see below.*

☒ *Total of 1 forms are submitted.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

First Named Inventor : Teruaki OCHIAI Art Unit : 1725
Application No. : 16/923,494 Examiner : Sean P. Cullen
Filed : July 8, 2020
Title : POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING
LITHIUM COBALTATE WITH LITHIUM TITANATE AND
MAGNESIUM OXIDE

MAIL STOP ISSUE FEE

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

INFORMATION DISCLOSURE STATEMENT

Please consider the documents listed on the disclosure form submitted with this statement. Copies of the documents are being submitted with this statement to the extent required under 37 C.F.R. § 1.98(a)(2). This statement is being filed after payment of the issue fee under the Quick Path Information Disclosure Statement (QPIDS) Program.

Certification under 37 C.F.R. § 1.97(e)(1)

Each item of information in this information disclosure statement was first cited in a communication from a foreign patent office in a counterpart foreign application dated February 26, 2021, which is not more than three months prior to the filing of this information disclosure statement. See 37 CFR 1.97(e)(1). The communication was an Office Action from the Korea Patent Office in counterpart Korean Application No. 2019-7034933.

A late submission fee in the amount of \$260, specified by 37 C.F.R. §1.17(p) is being authorized with this statement. Apply any additional necessary charges or credits to deposit account 06-1050, referencing Attorney Docket No. 06-1050.

Respectfully submitted,

Date: April 9, 2021

/John F. Hayden/
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SUBSTITUTE FOR FORM 1449/PTO INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Use as many sheets as necessary)				Complete if Known	
				Application Number	16/923,494
				Filing Date	July 8, 2020
				First Named Inventor	Teruaki OCHIAI
				Art Unit	1725
				Examiner Name	S. CULLEN
Sheet	1	of	1	Attorney Docket Number	12732-2003004

[illegible]

FOREIGN PATENT DOCUMENTS						
Examiner Initials*	Cite No. ¹	Foreign Patent Document	Publication Date	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	T ⁶
		Country Code ³ -Number ⁴ -Kind Code ⁵ (if known)	MM-DD-YYYY			
		KR-2015-0062724A	06-08-2015			Full
		KR-2014-0125856A	10-29-2014			Full

Examiner Signature		Date Considered	
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*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. 1 Applicant's unique citation designation number (optional). 2 See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. 3 Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). 4 For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. 5 Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. 6 Applicant is to place a check mark here if English language Translation is attached.

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450. **DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Espacenet

Family list: KR20150062724 (A) — 2015-06-08

2 application(s) for: KR20150062724 (A)

1. POSITIVE ACTIVE MATERIAL FOR RECHARGEABLE LITHIUM BATTERY, METHOD FOR MANUFACTURING THE SAME, AND RECHARGEABLE LITHIUM BATTERY INCLUDING THE SAME					
Inventor: CHO JAE PHIL [KR] OH PIL GUN [KR]	Applicant: UNIST ACADEMY IND RES CORP [KR]	CPC: <u>H01M10/052</u> <u>H01M2004/028</u> <u>H01M4/0419</u> (+5)	IPC: H01M10/052 H01M4/505	Publication info: KR20150062724 (A) 2015-06-08 KR101646994 (B1) 2016-08-10 <u>Global Dossier</u>	Priority date: 2013-11-29
2. CATHODE ACTIVE MATERIAL FOR LITHIUM RECHARGEABLE BATTERY, METHOD OF MANUFACTURING THE SAME, AND LITHIUM RECHARGEABLE BATTERY INCLUDING THE SAME					
Inventor: CHO JAEPHIL [KR] OH PILGUN [KR]	Applicant: UNIST ACADEMY IND RES CORP [KR]	CPC: <u>H01M10/052</u> <u>H01M2004/028</u> <u>H01M4/0419</u> (+5)	IPC: H01M4/04 H01M4/36 H01M4/48	Publication info: US2015155553 (A1) 2015-06-04 US9954221 (B2) 2018-04-24 <u>Global Dossier</u>	Priority date: 2013-11-29

(19) Korea Patent Office (KR)

(12) Patent Application Gazette (A)

(11) Publication No. 10-2015-0062724

(43) Date of Publication: June 8, 2015

(51) Int. Cl.

H01M 4/505 (2010.01) *H01M 10/052* (2010.01)

(21) Application Number: 10-2013-0147677

(22) Date of Filing: November 29, 2013

Date of Request for Examination: November 29, 2013

(71) Applicant: UNIST Academy-Industry Research Corporation

50, UNIST-gil, Eonyang-eup, Ulju-gun, Ulsan

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Pilgun Oh

50, UNIST-gil, Eonyang-eup, Ulju-gun, Ulsan

(74) Agent:

YOU ME Patent & Law Firm

Number of all claims: 19 claims in total

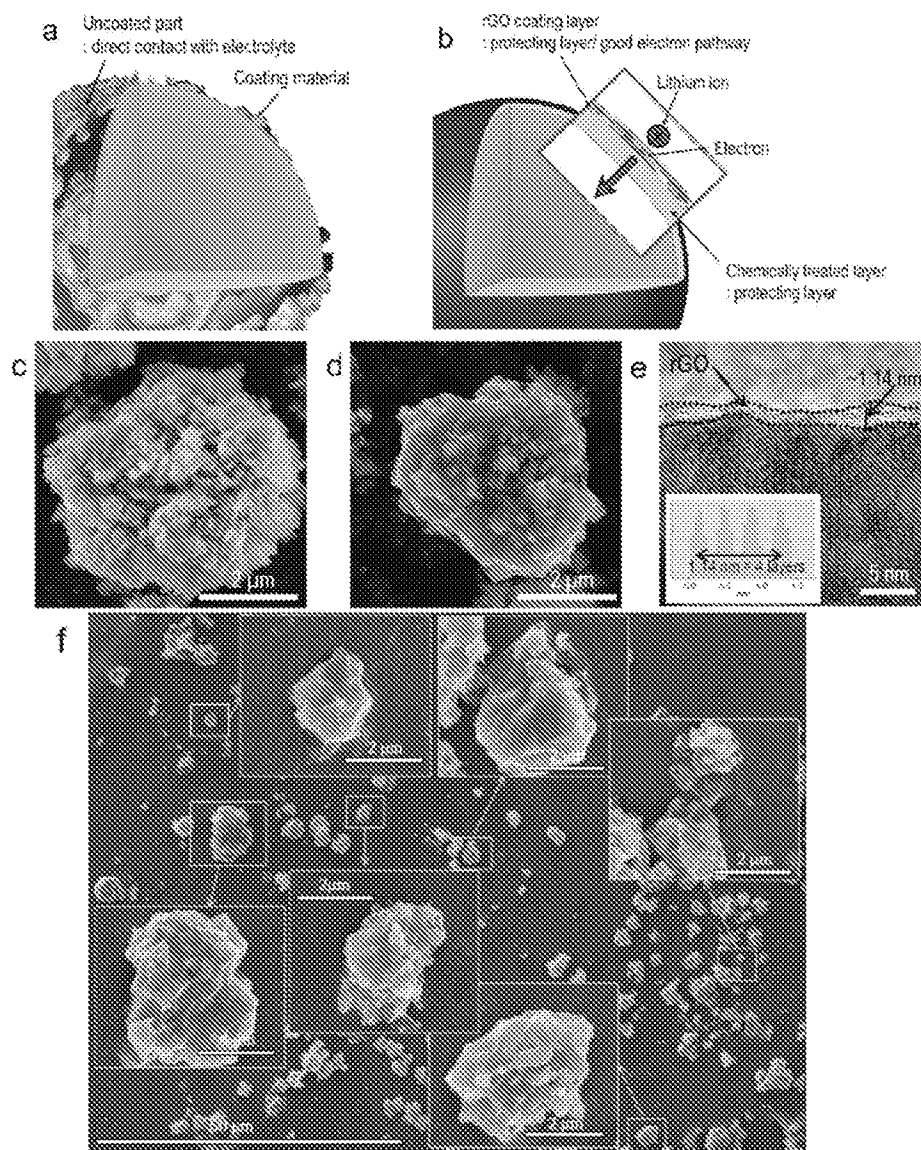
(54) Title of the Invention: CATHODE ACTIVE MATERIAL FOR LITHIUM RECHARGEABLE BATTERY, METHOD OF MANUFACTURING THE SAME, AND LITHIUM RECHARGEABLE BATTERY INCLUDING THE SAME

(57) Abstract

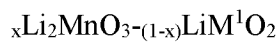
The prevent invention relates to a cathode active material for a lithium rechargeable battery, a method of manufacturing the same, and a lithium rechargeable battery including the same, and provides the cathode active material for the lithium rechargeable battery, including a core including a compound represented by the following Chemical Formula 1; and a coating layer positioned on the core and including a compound represented by the following Chemical Formula 2.

(Continued on the next page)

Typical Drawing - Fig. 2

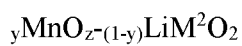


[Chemical Formula 1]



In Chemical Formula 1, $0 < x < 1$ and M^1 is a transition metal.

[Chemical Formula 2]



In Chemical Formula 2, $0 < y < 1$, $1 < z < 4$, and M^2 is a transition metal.

The National R&D Project applying the Present Invention

Subject Identification Number: 10046309

Ministry Name: Ministry of Trade, Industry and Energy

Special Agency of National R&D Management: Korea Evaluation Institute of Industrial Technology

Research Project Name: Construction Project of Green Energy Material Technology Development Center

Research Subject Name: Technology Development of LI-RICH cathode material for high-capacity/high-power lithium rechargeable battery (>240 MAH/G)

Contribution Rate: 1/1

Managing Department: UNIST Academy-Industry Research Corporation

Research Period: June 1, 2013 to May 31, 2014

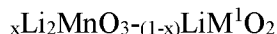
SPECIFICATION

Scope of Claims

[Claim 1]

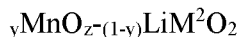
A cathode active material for a lithium rechargeable battery, comprising:
a core including a compound represented by the following Chemical Formula 1;
and
a coating layer positioned on the core and including a compound represented by the following Chemical Formula 2:

[Chemical Formula 1]



wherein, in Chemical Formula 1, $0 < x < 1$ and M^1 is a transition metal;

[Chemical Formula 2]



wherein, in Chemical Formula 2, $0 < y < 1$, $1 < z < 4$, and M^2 is a transition metal.

[Claim 2]

The cathode active material for a lithium rechargeable battery of claim 1, further comprising:
a reduced graphene oxide layer positioned on the coating layer.

[Claim 3]

The cathode active material for a lithium rechargeable battery of claim 2, wherein
a thickness of the reduced graphene oxide layer is 1 to 5 nm.

[Claim 4]

The cathode active material for a lithium rechargeable battery of claim 1, wherein
a Li/M molar ratio of the entire cathode active material including the core and the coating layer is 1.05 to 1.6.

[Claim 5]

The cathode active material for a lithium rechargeable battery of claim 1, wherein
a thickness of the coating layer is 1 to 13 nm.

[Claim 6]

The cathode active material for a lithium rechargeable battery of claim 1, wherein

M¹ of Chemical Formula 1 and M² of Chemical Formula 2 include Ni, Co, and Mn.

[Claim 7]

A method of manufacturing a cathode active material for a lithium rechargeable battery, comprising:

preparing a lithium complex oxide and a basic solution;

activating a surface of the lithium complex oxide by adding the lithium complex oxide to the basic solution, and performing mixing and heating; and

firing the lithium complex oxide with the activated surface.

[Claim 8]

The method of claim 7, wherein

the activating of the surface of the lithium complex oxide by adding the lithium complex oxide to the basic solution and performing mixing and heating includes:

heating the basic solution to 30 to 120 °C; and

performing agitation after adding the lithium complex oxide to the heated basic solution.

[Claim 9]

The method of claim 8, wherein

the performing of agitation after adding the lithium complex oxide to the heated basic solution is performed for 1 to 240 hours.

[Claim 10]

The method of claim 7, further comprising,

before the firing of the lithium complex oxide with the activated surface,

drying the lithium complex oxide with the activated surface.

[Claim 11]

The method of claim 10, wherein

the drying of the lithium complex oxide with the activated surface is performed at 80 to 160 °C.

[Claim 12]

The method of claim 10, wherein
the firing of the lithium complex oxide with the activated surface is performed
at 150 to 900 °C.

[Claim 13]

The method of claim 7, wherein
the basic solution is a solution having hydrogen ions that are exchanged with
lithium ions.

[Claim 14]

The method of claim 7, wherein
the basic solution is a hydrazine solution, an ammonia solution, or a combination
thereof.

[Claim 15]

The method of claim 7, wherein
in the preparing of the lithium complex oxide and the basic solution,
the lithium complex oxide is a lithium complex oxide in which a graphene oxide
layer is formed.

[Claim 16]

The method of claim 15, wherein
the lithium complex oxide in which the graphene oxide layer is formed is
prepared by:
preparing a solution in which a graphene oxide is dispersed;
performing agitation after adding the lithium complex oxide to the solution; and
obtaining the lithium complex oxide in which the reduced graphene oxide layer
is formed by using the solution where the graphene oxide and the lithium complex oxide
are agitated by a spray drying method.

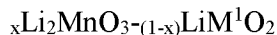
[Claim 17]

The method of claim 16,
wherein the cathode active material formed by the manufacturing method
includes:

a core including a compound represented by the following Chemical Formula 1;
a coating layer positioned on the core and including a compound represented by the following Chemical Formula 2; and

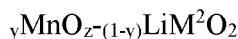
the reduced graphene oxide layer positioned on the coating layer:

[Chemical Formula 1]



wherein, in Chemical Formula 1, $0 < x < 1$ and M^1 is a transition metal;

[Chemical Formula 2]



wherein, in Chemical Formula 2, $0 < y < 1$, $1 < z < 4$, and M^2 is a transition metal.

[Claim 18]

The method of claim 7, wherein

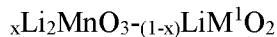
the cathode active material formed by the manufacturing method includes:

a core including a compound represented by the following Chemical Formula 1;

and

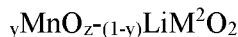
a coating layer positioned on the core and including a compound represented by the following Chemical Formula 2:

[Chemical Formula 1]



wherein, in Chemical Formula 1, $0 < x < 1$ and M^1 is a transition metal;

[Chemical Formula 2]



wherein, in Chemical Formula 2, $0 < y < 1$, $1 < z < 4$, and M^2 is a transition metal.

[Claim 19]

A lithium rechargeable battery comprising:

a cathode including the cathode active material for the lithium rechargeable battery according to any one of claim 1 to claim 6;

an anode including an anode active material; and

an electrolyte.

Description of the Invention

Technical Field

[0001]

The present invention relates to a cathode active material for a lithium

rechargeable battery, a method of manufacturing the same, and a lithium rechargeable battery including the same.

Background Art

[0002]

With respect to the recent trend of a reduction in size and weight of portable electronic devices, demand for an increase in performance and capacity of a battery used as a power source for the devices has increased.

[0003]

The battery generates electric power by using a material which can electrochemically react with a cathode and an anode. A representative example of the batteries includes a lithium rechargeable battery generating electrical energy by a change in chemical potential when lithium ions are subjected to intercalation/deintercalation in the cathode and the anode.

[0004]

The lithium rechargeable battery is manufactured by using a material where reversible intercalation/deintercalation of the lithium ions is feasible as cathode and anode active materials, and charging an organic electrolyte solution or a polymer electrolyte solution between the cathode and the anode.

[0005]

A lithium complex metal compound is used as the cathode active material of the lithium rechargeable battery, and complex metal oxides such as LiCoO_2 , LiMn_2O_4 , LiNiO_2 , $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($0 < x < 1$), and LiMnO_2 have been researched as an example thereof.

[0006]

Among the cathode active materials, a Mn-based cathode active material such as LiMn_2O_4 and LiMnO_2 can be easily synthesized and is relatively inexpensive, and has the highest thermal stability during over-charging as compared to other active materials, and a low degree of pollution to the environment, and thus is attractive, but has a drawback in that capacity thereof is small.

[0007]

Further, LiNiO_2 has a battery characteristic of the highest discharging capacity among the aforementioned cathode active materials, but has a drawback in that it is difficult to synthesize LiNiO_2 . Further, a high oxidation state of nickel becomes a cause of deterioration of the life-span of both a battery and an electrode, and there are problems in that self-discharging is severe and reversibility is poor. Moreover, since stability is not completely secured, there is difficulty in commercialization.

[0008]

Currently, LiCoO_2 is generalized as an active material having a particle diameter of about 10 μm , but does not ensure sufficient energy density.

Summary of the Invention

Objects to be Achieved

[0009]

The present invention has been made in an effort to provide a cathode active material having an improved characteristic. To be more specific, the present invention relates to a cathode active material for a lithium rechargeable battery having high initial coulombic efficiency and excellent lifespan and output characteristics, a method of manufacturing the same, and a lithium rechargeable battery manufactured using the same.

Means for Achieving the Objects

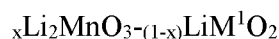
[0010]

An exemplary embodiment of the present invention provides a cathode active material for a lithium rechargeable battery, including: a core including a compound represented by the following Chemical Formula 1; and a coating layer positioned on the core and including a compound represented by the following Chemical Formula 2.

[0011]

[Chemical Formula 1]

[0012]



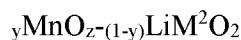
[0013]

In Chemical Formula 1, $0 < x < 1$ and M^1 is a transition metal.

[0014]

[Chemical Formula 2]

[0015]



[0016]

In Chemical Formula 2, $0 < y < 1$, $1 < z < 4$, and M^2 is a transition metal.

[0017]

The cathode active material may further include a reduced graphene oxide layer positioned on the coating layer.

[0018]

A thickness of the reduced graphene oxide layer may be 1 to 5 nm.

[0019]

A Li/M molar ratio of the entire cathode active material including the core and the coating layer may be 1.05 to 1.6.

[0020]

A thickness of the coating layer may be 1 to 13 nm.

[0021]

M¹ of Chemical Formula 1 and M² of Chemical Formula 2 may include Ni, Co, and Mn.

[0022]

Another exemplary embodiment of the present invention provides a method of manufacturing a cathode active material for a lithium rechargeable battery, including: preparing a lithium complex oxide and a basic solution; activating a surface of the lithium complex oxide by adding the lithium complex oxide to the basic solution, and performing mixing and heating; and firing the lithium complex oxide with the activated surface.

[0023]

The activating of the surface of the lithium complex oxide by adding the lithium complex oxide to the basic solution and performing mixing and heating may include: heating the basic solution to 30 to 120 °C; and performing agitation after adding the lithium complex oxide to the heated basic solution.

[0024]

The performing of agitation after adding the lithium complex oxide to the heated basic solution may take place for 1 to 240 hours.

[0025]

The method may further include, before the firing of the lithium complex oxide with the activated surface, drying the lithium complex oxide with the activated surface.

[0026]

The drying of the lithium complex oxide with the activated surface may be performed at 80 to 160 °C.

[0027]

The firing of the lithium complex oxide with the activated surface may be performed at 150 to 900 °C.

[0028]

The basic solution may be a solution having hydrogen ions that are exchanged with lithium ions.

[0029]

The basic solution may be a hydrazine solution, an ammonia solution, or a combination thereof.

[0030]

In the preparing of the lithium complex oxide and the basic solution, the lithium

complex oxide may be a lithium complex oxide in which a graphene oxide layer is formed.
[0031]

The lithium complex oxide in which the graphene oxide layer is formed may be prepared by: preparing a solution in which a graphene oxide is dispersed; performing agitation after adding the lithium complex oxide to the solution; and obtaining the lithium complex oxide in which the reduced graphene oxide layer is formed by using the solution where the graphene oxide and the lithium complex oxide are agitated by a spray drying method.

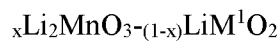
[0032]

The cathode active material formed by the manufacturing method may include: a core including a compound represented by the following Chemical Formula 1; a coating layer positioned on the core and including a compound represented by the following Chemical Formula 2; and the reduced graphene oxide layer positioned on the coating layer.

[0033]

[Chemical Formula 1]

[0034]



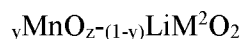
[0035]

In Chemical Formula 1, $0 < x < 1$ and M^1 is a transition metal.

[0036]

[Chemical Formula 2]

[0037]



[0038]

In Chemical Formula 2, $0 < y < 1$, $1 < z < 4$, and M^2 is a transition metal.

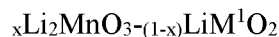
[0039]

The cathode active material formed by the manufacturing method may include: a core including a compound represented by the following Chemical Formula 1; and a coating layer positioned on the core and including a compound represented by the following Chemical Formula 2.

[0040]

[Chemical Formula 1]

[0041]



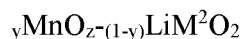
[0042]

In Chemical Formula 1, $0 < x < 1$ and M^1 is a transition metal.

[0043]

[Chemical Formula 2]

[0044]



[0045]

In Chemical Formula 2, $0 < y < 1$, $1 < z < 4$, and M^2 is a transition metal.

[0046]

Yet another exemplary embodiment of the present invention provides a lithium rechargeable battery including: a cathode including the cathode active material for the lithium rechargeable battery according to the aforementioned exemplary embodiments of the present invention; an anode including an anode active material; and an electrolyte.

Effect of the Invention

[0047]

According to the exemplary embodiments of the present invention, it is possible to provide a cathode active material for a lithium rechargeable battery having high initial coulombic efficiency and excellent life-span and output characteristics, a method of manufacturing the same, and a lithium rechargeable battery manufactured using the same.

Brief Description of the Drawings

[0048]

FIG. 1 shows XRD analysis results of Examples 1 and 2 and Comparative Example 1.

FIG. 2 shows SEM photographs of active materials according to the examples and the comparative examples.

FIG. 3 shows TEM photographs of the active material according to Example 1.

FIG. 4 shows TEM photographs of the active material according to Example 2.

FIG. 5 is a graph illustrating life-span characteristics of batteries according to Example 5 and Comparative Example 2.

FIG. 6 is a graph illustrating initial efficiency characteristics of batteries according to Example 7 and Comparative Example 2.

FIG. 7 is a graph illustrating output characteristics of batteries according to Examples 5, 6, and 7 and Comparative Example 2.

FIG. 8 is a graph illustrating life-span and operation voltage characteristics of batteries according to Example 7 and Comparative Example 2.

FIG. 9 is a graph illustrating the life-span characteristics according to Example 7 and Comparative Example 2 after initial charging/discharging at 2.0 to 4.8 V.

Mode for Carrying Out the Invention

[0049]

Exemplary embodiments of the present invention will hereinafter be described in detail. However, the exemplary embodiments are illustrative only, and are not to be construed to limit the present invention, and the present invention is just defined by the scope of the claims as will be described below.

[0050]

An exemplary embodiment of the present invention may provide a cathode active material for a lithium rechargeable battery having high initial coulombic efficiency and excellent life-span and output characteristics, a method of manufacturing the same, and a lithium rechargeable battery manufactured using the same.

[0051]

In the cathode active material according to the exemplary embodiment of the present invention, a structurally and electrochemically stable coating layer (or surface layer) may be formed on a surface of the active material by chemically activating a Li_2MnO_3 phase of the surface of the active material by using an aqueous solution (e.g., a basic solution) including hydrogen ions, and then performing heat treatment.

[0052]

Further, optionally, the cathode active material for the lithium rechargeable battery according to the exemplary embodiment of the present invention may further include a reduced graphene oxide layer having excellent electrical conductivity as the coating layer.

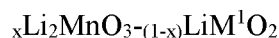
[0053]

To be more specific, the exemplary embodiment of the present invention provides the cathode active material for the lithium rechargeable battery including a core including a compound represented by the following Chemical Formula 1, and a coating layer positioned on the core and including a compound represented by the following Chemical Formula 2.

[0054]

[Chemical Formula 1]

[0055]



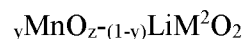
[0056]

In Chemical Formula 1, $0 < x < 1$ and M^1 is a transition metal.

[0057]

[Chemical Formula 2]

[0058]



[0059]

In Chemical Formula 2, $0 < y < 1$, $1 < z < 4$, and M^2 is a transition metal.

[0060]

A structure of the compound represented by Chemical Formula 2 is a structure in which lithium which is generated by a manufacturing method using a basic solution as will be described below is eliminated. This structure is structurally and electrochemically stable, and may improve the lifespan and output characteristics of the battery. A thickness of the coating layer may be 1 to 13 nm, and more specifically 1 to 10 nm. The life-span and output characteristics may be slightly changed according to a thickness range, and an agitation time as will be described below may be controlled according to a target thickness.

[0061]

Further, the cathode active material may further include a reduced graphene oxide layer positioned on the coating layer. A thickness of the reduced graphene oxide layer may be 1 to 5 nm. The thickness range can be optionally adjusted according to the characteristic of the active material, but is not limited thereto.

[0062]

A Li/M molar ratio of the entire cathode active material including the core and the coating layer may be 1.05 to 1.6, and more specifically 1.1 to 1.35. This ratio is a ratio of elimination of Li as compared to an initially added raw material, and may be changed according to the thickness of the coating layer.

[0063]

M^1 of Chemical Formula 1 and M^2 of Chemical Formula 2 may be Ni, Co, and Mn. All transition metals already known in the art can be used, so M^1 and M^2 are not limited thereto.

[0064]

Another exemplary embodiment of the present invention provides a method of manufacturing a cathode active material for a lithium rechargeable battery, including: preparing a lithium complex oxide and a basic solution; activating a surface of the lithium complex oxide by adding the lithium complex oxide to the basic solution, and performing mixing and heating; and firing the lithium complex oxide with the activated surface.

[0065]

The activating of the surface of the lithium complex oxide by adding the lithium complex oxide to the basic solution and performing mixing and heating may include:

heating the basic solution to 30 to 120 °C; and performing agitation after adding the lithium complex oxide to the heated basic solution.

[0066]

The performing of agitation after adding the lithium complex oxide to the heated basic solution may take place for 1 to 240 hours, and more specifically 1 to 20 hours. The thickness of the aforementioned coating layer may be controlled according to the agitation time.

[0067]

The method may further include, before the firing of the lithium complex oxide with the activated surface, drying the lithium complex oxide with the activated surface.

[0068]

The drying of the lithium complex oxide with the activated surface may be performed at 80 to 160 °C. However, the drying is not limited thereto.

[0069]

The firing of the lithium complex oxide with the activated surface may be performed at 150 to 900 °C, more specifically 180 to 220 °C. However, the firing is not limited thereto.

[0070]

The basic solution may be a solution having hydrogen ions exchanged with lithium ions.

[0071]

To be more specific, the basic solution may be a hydrazine solution, an ammonia solution, or a combination thereof. However, the basic solution is not limited thereto.

[0072]

In the preparing of the lithium complex oxide and the basic solution, the lithium complex oxide may be a lithium complex oxide in which a graphene oxide layer is formed.

[0073]

The lithium complex oxide in which a graphene oxide layer is formed may be prepared by: preparing a solution in which a graphene oxide is dispersed; performing agitation after adding the lithium complex oxide to the solution; and obtaining the lithium complex oxide in which the graphene oxide layer is formed by using the solution where the graphene oxide and the lithium complex oxide are agitated by a spray drying method. Since the spray drying method is well known in the art, a detailed description thereof will be omitted.

[0074]

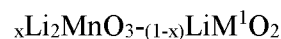
The cathode active material prepared by the manufacturing method may include

the core including the compound represented by the following Chemical Formula 1; the coating layer positioned on the core and including the compound represented by the following Chemical Formula 2; and the reduced graphene oxide layer positioned on the coating layer.

[0075]

[Chemical Formula 1]

[0076]



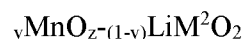
[0077]

In Chemical Formula 1, $0 < x < 1$ and M^1 is a transition metal.

[0078]

[Chemical Formula 2]

[0079]



[0080]

In Chemical Formula 2, $0 < y < 1$, $1 < z < 4$, and M^2 is a transition metal.

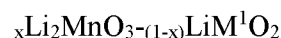
[0081]

The cathode active material prepared by the manufacturing method may include the core including the compound represented by the following Chemical Formula 1; and the coating layer positioned on the core and including the compound represented by the following Chemical Formula 2.

[0082]

[Chemical Formula 1]

[0083]



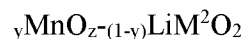
[0084]

In Chemical Formula 1, $0 < x < 1$ and M^1 is a transition metal.

[0085]

[Chemical Formula 2]

[0086]



[0087]

In Chemical Formula 2, $0 < y < 1$, $1 < z < 4$, and M^2 is a transition metal.

[0088]

Since a detailed description of the structure of the cathode active material is the same as that of the aforementioned exemplary embodiment of the present invention, the

description will be omitted.

[0089]

The cathode active material according to the exemplary embodiment of the present invention may be effectively used in a cathode of the lithium rechargeable battery. The lithium rechargeable battery includes an anode including an anode active material and an electrolyte together with the cathode.

[0090]

The cathode is manufactured by mixing the cathode active material according to the exemplary embodiment of the present invention, a conductive material, a binder, and a solvent to manufacture a cathode active material composition, and then directly applying and drying the cathode active material composition on an aluminum current collector. Alternatively, the cathode can be manufactured by casting the cathode active material composition on a separate support, and then laminating a film obtained by stripping the cathode active material from the support on an aluminum current collector.

[0091]

In this case, carbon black, graphite, or a metal powder is used as the conductive material, and a vinylidene fluoride/hexafluoropropylene copolymer, polyvinylidene fluoride, polyacrylonitrile, polymethyl methacrylate, polytetrafluoroethylene, and a mixture thereof are feasible as the binder. Further, N-methylpyrrolidone, acetone, tetrahydrofuran, decane, and the like are used as the solvent. In this case, the cathode active material, the conductive material, the binder, and the solvent are used in a content at a level typically used in the lithium rechargeable battery.

[0092]

Like the cathode, the anode is manufactured by mixing an anode active material, a binder, and a solvent to manufacture an anode active material composition, directly applying the anode active material composition on a copper current collector or casting the anode active material composition on a separate support, and laminating an anode active material film stripped from the support on the copper current collector. In this case, if necessary, the anode active material composition may further contain a conductive material.

[0093]

A material where intercalation/deintercalation of lithium is feasible is used as the anode active material, and for example, a lithium metal or a lithium alloy, cokes, artificial graphite, natural graphite, organic polymer compound combustion bodies, carbon fibers, and the like are used. Further, the conductive material, the binder, and the solvent are used identically to those of the aforementioned cathode.

[0094]

All separators typically used in the lithium rechargeable battery can be used, and for example, polyethylene, polypropylene, polyvinylidene fluoride, or a multilayer of two or more layers thereof may be used, and needless to say, a mixed multilayer such as a polyethylene/polypropylene two-layered separator, a polyethylene/polypropylene/polyethylene three-layered separator, and a polypropylene/polyethylene/polypropylene three-layered separator may be used.

[0095]

A non-aqueous electrolyte, a known solid electrolyte, or the like can be used as the electrolyte charged in the lithium rechargeable battery, and an electrolyte where a lithium salt is dissolved is used.

[0096]

The solvent of the non-aqueous electrolyte is not particularly limited, but cyclic carbonates such as ethylene carbonate, propylene carbonate, butylene carbonate, and vinylene carbonate; chained carbonates such as dimethyl carbonate, methylethyl carbonate, and diethyl carbonate; esters such as methyl acetate, ethyl acetate, propyl acetate, methyl propionate, ethyl propionate, and γ -butyrolactone; ethers such as 1,2-dimethoxyethane, 1,2-diethoxyethane, tetrahydrofuran, 1,2-dioxane, and 2-methyltetrahydrofuran; nitriles such as acetonitrile; amides such as dimethylformamide; and the like may be used. The aforementioned examples may be used either alone or in a combination of a plurality of examples. Particularly, a mixed solvent of a cyclic carbonate and a chained carbonate may be preferably used.

[0097]

Further, a gel-shaped polymer electrolyte where an electrolyte solution is impregnated in a polymer electrolyte such as polyethylene oxide and polyacrylonitrile, or an inorganic solid electrolyte such as LiI and Li_3N , is feasible as the electrolyte.

[0098]

In this case, one kind selected from the group consisting of LiPF_6 , LiBF_4 , LiSbF_6 , LiAsF_6 , LiClO_4 , LiCF_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, $\text{LiC}_4\text{F}_9\text{SO}_3$, LiSbF_6 , LiAlO_4 , LiAlCl_4 , LiCl , and LiI is feasible as the lithium salt.

[0099]

Hereinafter, preferred examples and comparative examples of the present invention will be described. However, the following examples are only the preferred examples of the present invention, and the present invention is not limited thereto.

[0100]

Examples

[0101]

Example 1: Manufacturing of Cathode Active Material

[0102]

After 40 µg of hydrazine monohydrate was added to 10 mg of deionized water, the aqueous solution was heated to 90 °C, and the temperature was maintained.

[0103]

Subsequently, after 2 g of $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ was added and mixed, agitation was performed for 3 hours.

[0104]

Drying was then performed at a temperature of 120 °C for 12 hours, and heat treatment was performed at a temperature of 200 °C for 3 hours.

[0105]

Thereby, the cathode active material for the lithium rechargeable battery was manufactured. The composition of the manufactured cathode active material for the lithium rechargeable battery was $0.33\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$.

[0106]

Example 2: Manufacturing of Cathode Active Material

[0107]

After 40 µg of hydrazine monohydrate was added to 10 mg of deionized water, the aqueous solution was heated to 90 °C, and the temperature was maintained.

[0108]

Subsequently, after 2 g of $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ was added and mixed, agitation was performed for 10 hours.

[0109]

Drying was then performed at a temperature of 120 °C for 12 hours, and heat treatment was performed at a temperature of 200 °C for 3 hours.

[0110]

Thereby, the cathode active material for the lithium rechargeable battery was manufactured. The composition of the manufactured cathode active material for the lithium rechargeable battery was $0.18\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$.

[0111]

Example 3: Manufacturing of Cathode Active Material

[0112]

200 ml of a 4 mg/ml graphene oxide solution was added to 10 mg of deionized water, and then agitated.

[0113]

Subsequently, after 16 g of $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ was added and mixed, agitation was performed for 1 hour.

[0114]

Spraying was then performed into the cylinder at 190 °C by using a spray drier.

[0115]

Subsequently, drying was performed at a temperature of 120 °C for 12 hours.

[0116]

Thereby, the cathode active material for the lithium rechargeable battery was manufactured. The composition of the manufactured cathode active material for the lithium rechargeable battery was $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, the surface of which was coated with graphene oxide.

[0117]

Example 4: Manufacturing of Cathode Active Material for Lithium Rechargeable Battery

[0118]

After 40 µg of hydrazine monohydrate was added to 10 mg of deionized water, the aqueous solution was heated to 90 °C, and the temperature was maintained.

[0119]

Subsequently, after 2 g of $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ that was the resulting material of Example 3, the surface of which was coated with graphene oxide, was added and mixed, agitation was performed for 3 hours.

[0120]

Drying was then performed at a temperature of 120 °C for 12 hours, and heat treatment was performed at a temperature of 200 °C for 3 hours.

[0121]

Thereby, the cathode active material for the lithium rechargeable battery was manufactured. The composition of the manufactured cathode active material for the lithium rechargeable battery was $0.33\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, the surface of which was coated with reduced graphene oxide.

[0122]

[0123]

Example 5: Manufacturing of Lithium Rechargeable Battery

[0124]

The cathode active material for the lithium rechargeable battery manufactured in Example 1, Super-P as a conductive material, and polyvinylidene fluoride (PVdF) as a binder were mixed at the weight ratio of 8:1:1 to manufacture a slurry. The slurry was

uniformly applied on an aluminum foil having a thickness of 15 μm , and vacuum-dried at a temperature of 120 °C to manufacture a cathode.

[0125]

A half cell was manufactured by using the manufactured cathode and a lithium foil as the counter electrode, and using the liquid electrolyte solution in which LiPF_6 was dissolved in a concentration of 1.0 M in the solvent where porous polyethylene carbonate, ethylmethyl carbonate, and dimethyl carbonate were mixed at a volume ratio of 3:4:3, according to the typically known manufacturing process.

[0126]

Example 6: Manufacturing of Lithium Rechargeable Battery

[0127]

The same procedure as Example 5 was performed to manufacture a coin half cell, except that the cathode active material for the lithium rechargeable battery manufactured in Example 2 was used.

[0128]

Example 7: Manufacturing of Lithium Rechargeable Battery

[0129]

The same procedure as Example 5 was performed to manufacture a coin half cell, except that the cathode active material for the lithium rechargeable battery manufactured in Example 4 was used.

[0130]

Comparative Example 1: Cathode Active Material for Lithium Rechargeable Battery

[0131]

The compound represented by $0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ was used as the cathode active material for the lithium rechargeable battery.

[0132]

Comparative Example 2: Manufacturing of Lithium Rechargeable Battery

[0133]

The same procedure as Example 5 was performed to manufacture a coin half cell, except that the cathode active material for the lithium rechargeable battery of Comparative Example 1 was used.

[0134]

Experimental Example

[0135]

Experimental Example 1: IPC Analysis

[0136]

The following Table 1 shows component analysis results of Example 1 and Comparative Example 1.

[0137]

Table 1

	Li	Mn	Co	Ni	L/M ratio (molar ratio)
Comparative Example 1	7.01	3.01	0.98	1.00	1.41
Example 1	6.46	2.99	0.98	1.00	1.3

[0138]

As a result of the analysis, it can be confirmed that the Li/M ratio is changed by hydrazine treatment of Example 1. This is judged to be caused by chemical elimination of Li.

[0139]

Experimental Example 2: XRD Analysis

[0140]

FIG. 1 shows XRD analysis results of Examples 1 and 2 and Comparative Example 1.

[0141]

It can be seen that an XRD peak is formed around 19° according to an increase in hydrazine treatment time. Accordingly, it can be seen that Li⁺/H⁺ ions are exchanged.

[0142]

Experimental Example 3: SEM analysis

[0143]

FIG. 2 shows SEM photographs of the active materials according to the examples and the comparative examples. After the cathode active materials for the lithium rechargeable batteries of Example 1 and Comparative Example 1 were sampled on a carbon tape, platinum (Pt) plasma coating was performed to take SEM photographs. To be more specific, a description of each picture in FIG. 2 is as follows.

[0144]

a. Conceptual diagram of the cathode active material, the surface of which is coated by a general sol-gel method

[0145]

b. Conceptual diagram of the cathode active material according to Example 4

[0146]

c. $0.4\text{Li}_2\text{MnO}_3$ - $0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ bare material used

[0147]

d. $0.4\text{Li}_2\text{MnO}_3$ - $0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, the surface of which is coated with graphene oxide formed by Example 3

[0148]

e. Active material according to Example 4

[0149]

f. Active material according to Example 3

[0150]

It can be confirmed that surface treatment and graphene oxide treatment according to the examples of the present invention are uniformly performed well.

[0151]

Experimental Example 4: TEM Analysis

[0152]

FIG. 3 shows TEM photographs of the active material according to Example 1. It can be confirmed that a 2 to 3 nm coating layer is formed on the surface.

[0153]

FIG. 4 shows TEM photographs of the active material according to Example 2. It can be confirmed that the coating layer of around 13 nm is formed on the surface. That is, it can be seen that the thickness of the coating layer can be adjusted according to the treatment time.

[0154]

Experimental Example 5: Battery Characteristic Data

[0155]

FIG. 5 is a graph illustrating life-span characteristics of the batteries according to Example 5 and Comparative Example 2. In FIG. 5, the number of the used active material was used for identification. More specifically, the life-span characteristic was measured at 2.0 to 4.6 V after the first cycle at room temperature/2.0 to 4.7 V (1 C-rate).

[0156]

It can be seen that the life-span characteristic of the coin-cell using the active material according to Example 1 is better.

[0157]

FIG. 6 is a graph illustrating initial efficiency characteristics of the batteries according to Example 7 and Comparative Example 2.

[0158]

It can be seen that the coin-cell using the active material according to Example

4 has high initial efficiency.

[0159]

FIG. 7 is a graph illustrating output characteristics of the batteries according to Examples 5, 6, and 7 and Comparative Example 2.

[0160]

It can be seen that the coin-cells using the active materials of Examples 1 and 4 have the better output characteristic as compared to the coin-cell using Comparative Example 1, but in the case of Example 2, the output characteristic is inferior to that of Comparative Example 1. That is, it can be seen that the output characteristic of the battery is partially affected by the thickness of the coating layer according to the hydrazine treatment time.

[0161]

FIG. 8 is a graph illustrating the life-span and operation voltage characteristics of the batteries according to Example 7 and Comparative Example 2.

[0162]

It can be seen that even though Example 7 and Comparative Example 2 have the similar life-span characteristics, in the case of Example 7, an operation voltage reduction is small.

[0163]

FIG. 9 is a graph illustrating the life-span characteristics according to Example 7 and Comparative Example 2 after initial charging/discharging at 2.0 to 4.8 V.

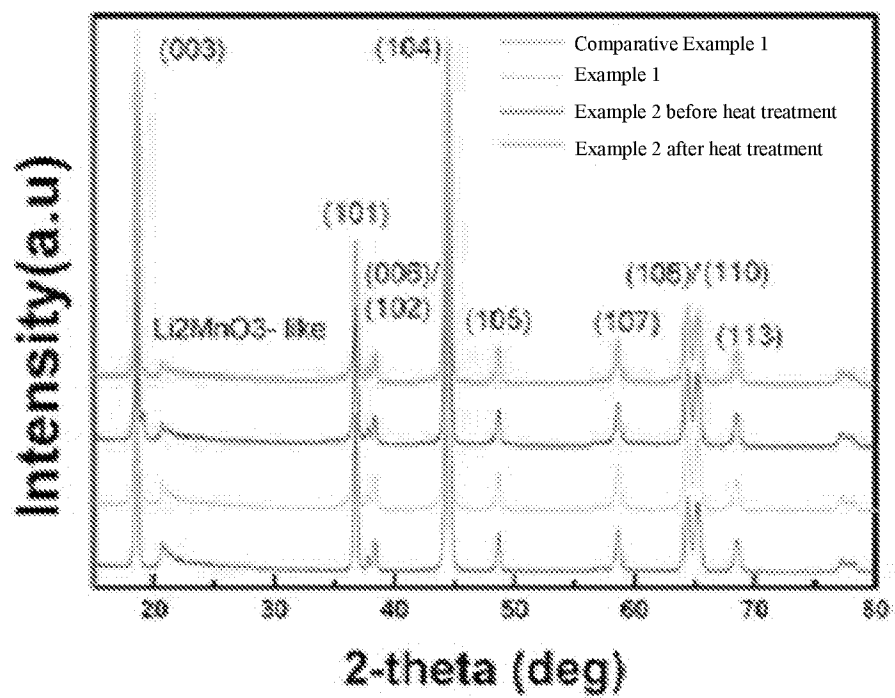
[0164]

It can be seen that the coin-cell according to Example 7 has the improved life-span characteristic as compared to the coin-cell according to Comparative Example 2.

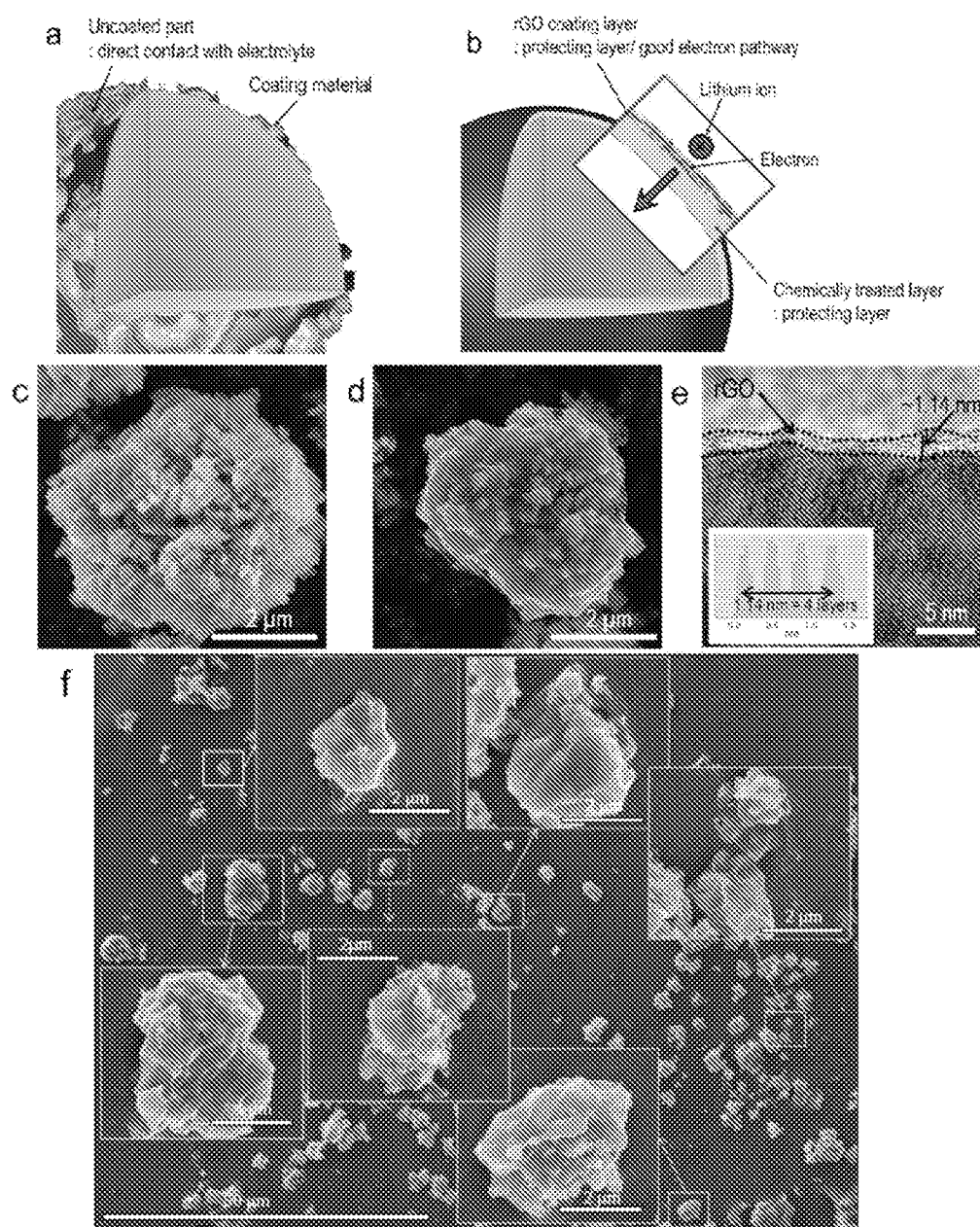
[0165]

The present invention is not limited to the above Examples, but may be manufactured in a variety of different modes, and it will be appreciated by those skilled in the art that the present invention can be implemented in different specific modes without changing the technical idea or essential features of the present invention. Therefore, the aforementioned embodiments should be understood to be exemplary but not limiting in any way.

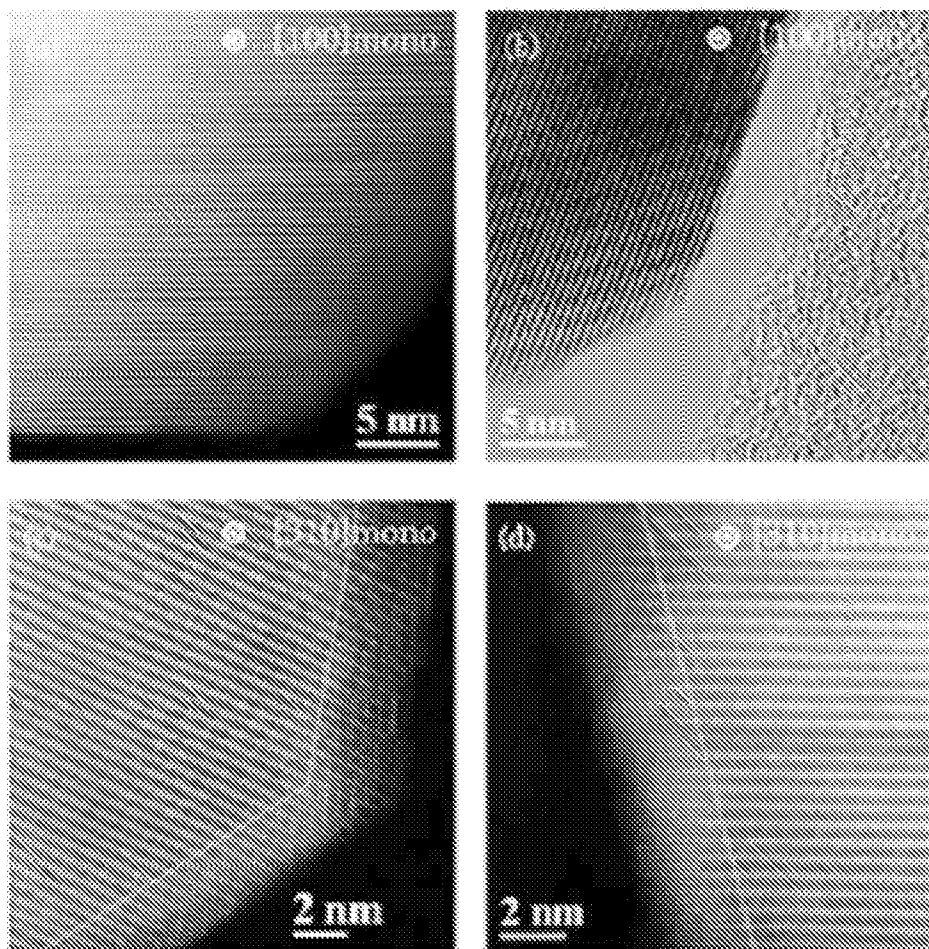
[FIG. 1]



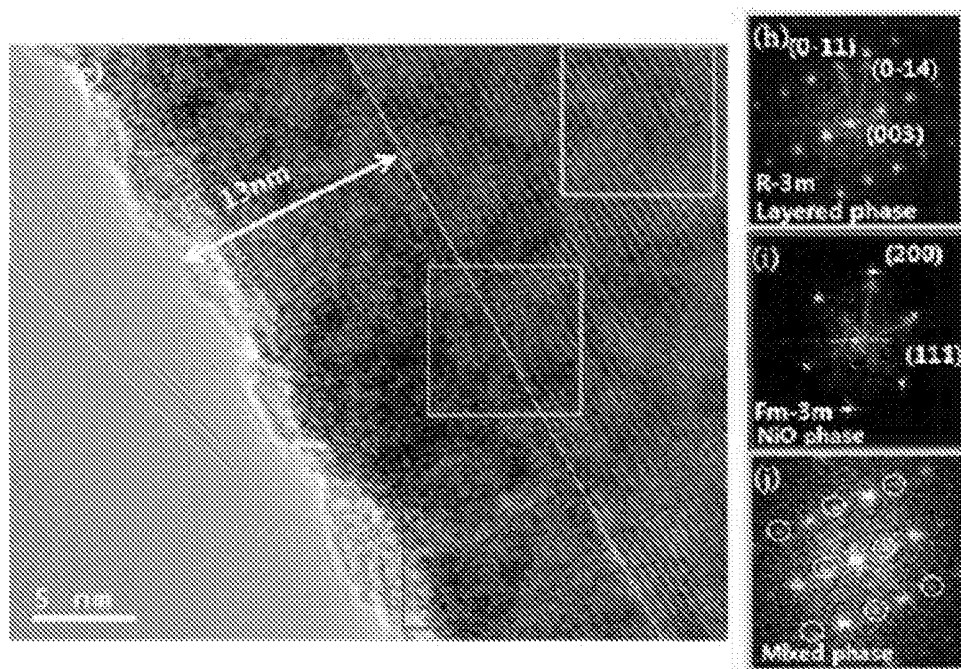
[FIG. 2]



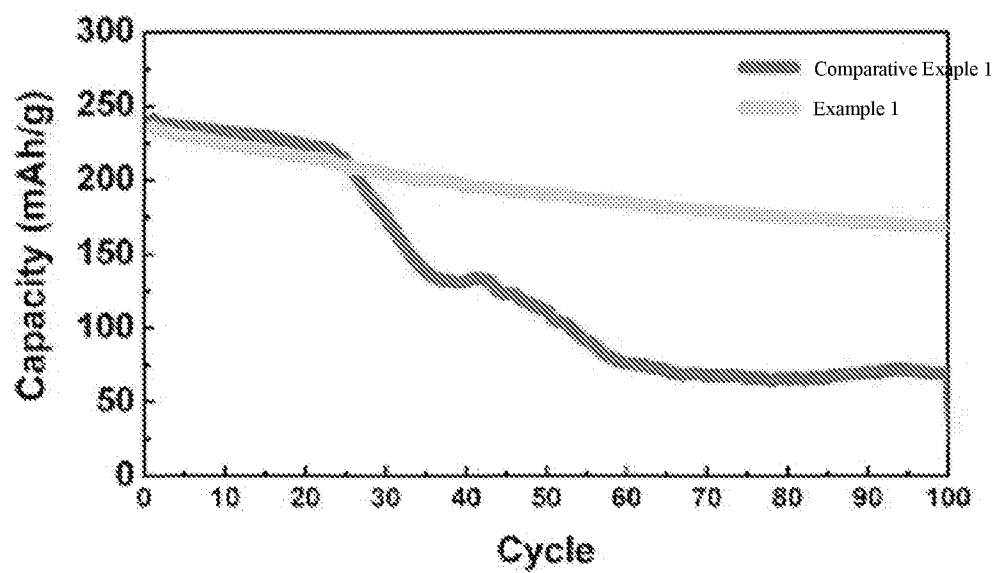
[FIG. 3]



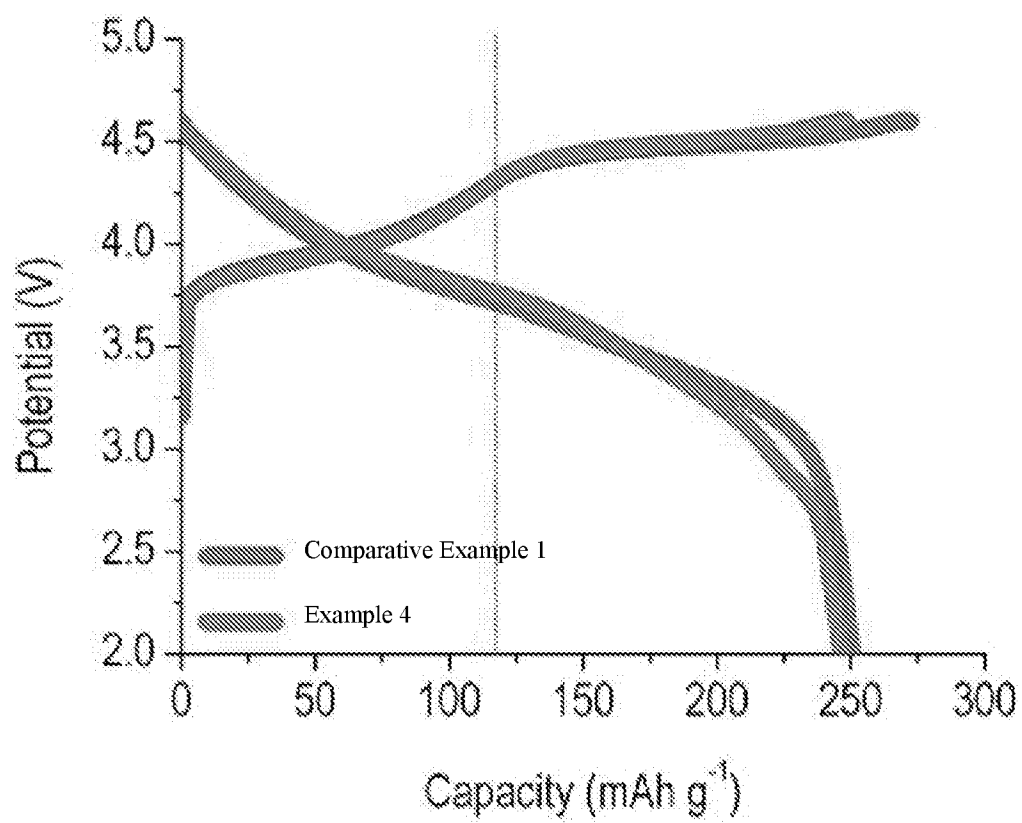
[FIG. 4]



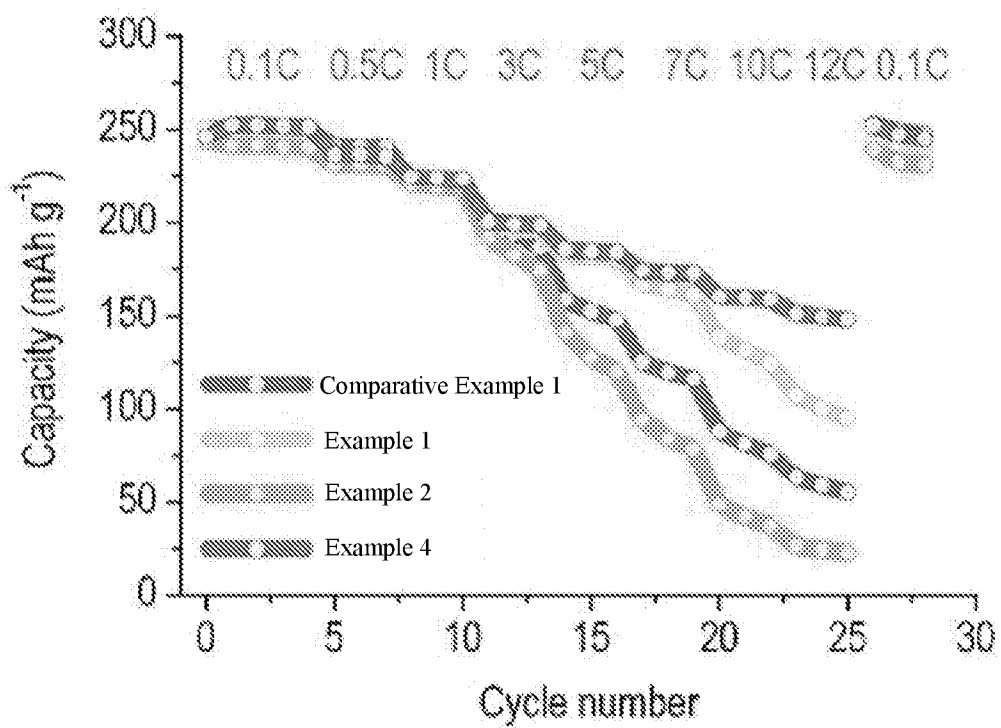
[FIG. 5]



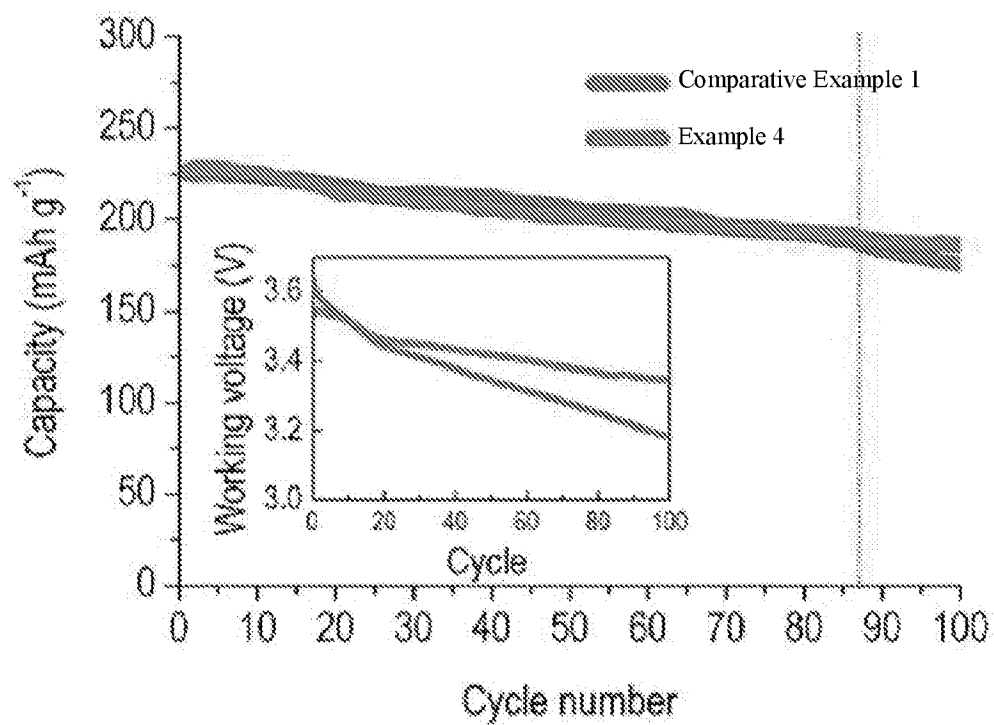
[FIG. 6]



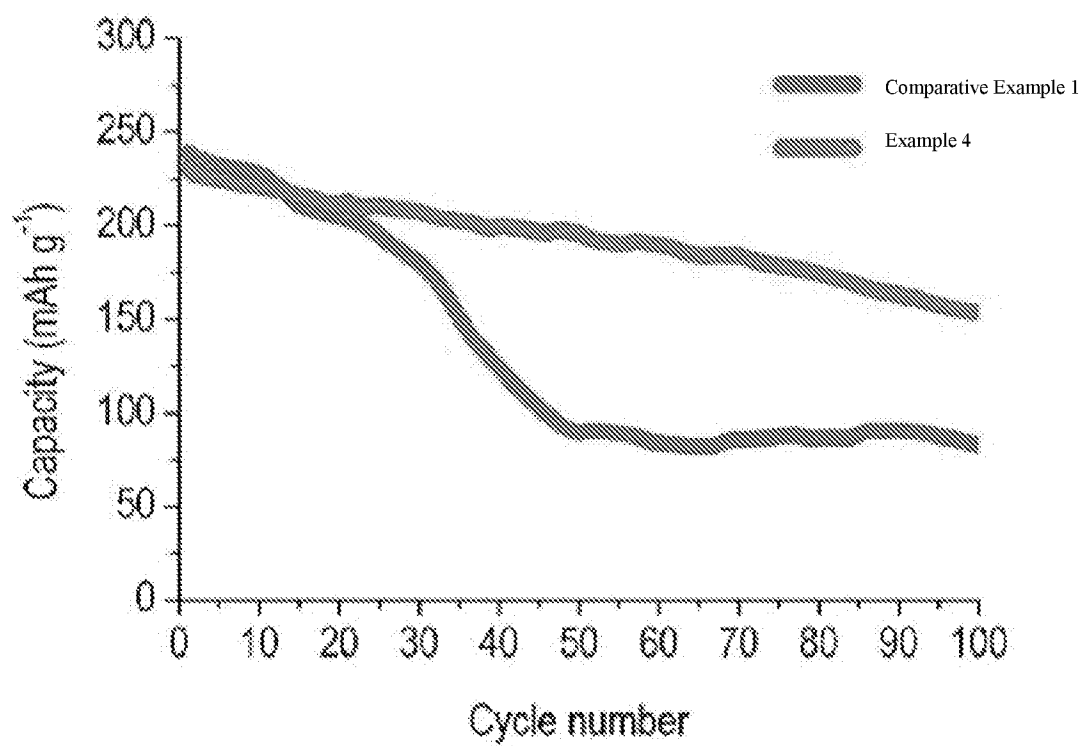
[FIG. 7]



[FIG. 8]



[FIG. 9]



	(19) 대한민국특허청(KR) (12) 공개특허공보(A)	(11) 공개번호 10-2015-0062724 (43) 공개일자 2015년06월08일
<hr/>		
(51) 국제특허분류(Int. Cl.) H01M 4/505 (2010.01) H01M 10/052 (2010.01)	(71) 출원인 국립대학법인 울산과학기술대학교 산학협력단 울산광역시 울주군 언양읍 유니스트길 50	
(21) 출원번호 10-2013-0147677 (22) 출원일자 2013년11월29일 심사청구일자 2013년11월29일	(72) 발명자 조재필 울산광역시 남구 문수로 409번길 20 현대아이파크1차 아파트 105동 1701호 오필건 울산 울주군 언양읍 유니스트길 50,	
	(74) 대리인 유미특허법인	

전체 청구항 수 : 총 19 항

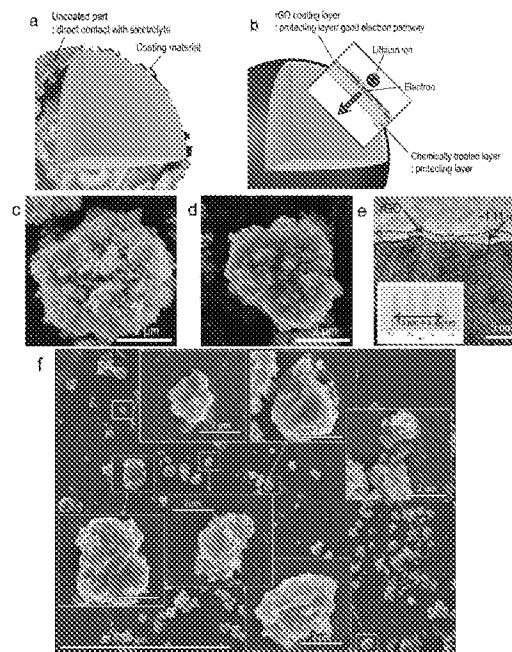
(54) 발명의 명칭 리튬 이차전지용 양극 활물질, 이들의 제조방법, 및 이를 포함하는 리튬 이차전지

(57) 요약

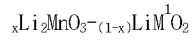
리튬 이차전지용 양극 활물질, 이들의 제조방법, 및 이를 포함하는 리튬 이차전지에 관한 것으로, 하기 화학식 1로 표시되는 화합물을 포함하는 코어; 및 상기 코어 상에 위치하며, 하기 화학식 2로 표시되는 화합물을 포함하는 코팅층;을 포함하는 리튬 이차전지용 양극 활물질을 제공한다.

(뒷면에 계속)

도면 - 도2

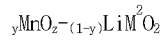


[화학식 1]



(상기 화학식 1에서, $0 < x < 1$ 이고, M^1 은 전이금속이다.)

[화학식 2]



(상기 화학식 2에서, $0 < y < 1$ 이고, $1 \leq z \leq 4$ 이고, M^2 은 전이금속이다.)

이 발명을 지원한 국가연구개발사업

과제고유번호 10046309

부처명 산업통상자원부

연구관리전문기관 한국산업기술평가관리원

연구사업명 그린에너지 소재기술 개발센터 구축사업

연구과제명 고용량/고출력 리튬이차전지용 LI-RICH계 양극소재(≥ 240 MAH/G) 기술개발

기 여 율 1/1

주관기관 국립대학법인 울산과학기술대학교 산학협력단

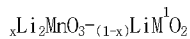
연구기간 2013.06.01~2014.05.31

형성

청구항 1

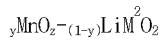
하기 화학식 1로 표시되는 화합물을 포함하는 코어; 및
상기 코어 상에 위치하며, 하기 화학식 2로 표시되는 화합물을 포함하는 코팅층;
을 포함하는 리튬 이차전지용 양극 활물질.

[화학식 1]



(상기 화학식 1에서, $0 < x < 1$ 이고, M^1 은 전이금속이다.)

[화학식 2]



(상기 화학식 2에서, $0 < y < 1$ 이고, $1 \leq z \leq 4$ 이고, M^2 은 전이금속이다.)

청구항 2

제1항에 있어서,
상기 코팅층 상에 위치하는 환원된 산화 그래펜(reduced graphene oxide)층을 더 포함하는 리튬 이차전지용 양극 활물질.

청구항 3

제2항에 있어서,
상기 환원된 산화 그래펜층의 두께는 1 내지 5nm인 것인 리튬 이차전지용 양극 활물질.

청구항 4

제1항에 있어서,
상기 코어 및 코팅층을 포함하는 전체 양극 활물질 내 Li/M 몰비율은 1.05 내지 1.6인 것인 리튬 이차전지용 양극 활물질.

청구항 5

제1항에 있어서,
상기 코팅층의 두께는 1 내지 13nm 인 것인 리튬 이차전지용 양극 활물질.

청구항 6

공개특허 10-2015-0062724

제1항에 있어서,

상기 화학식 1의 M^1 및 화학식 2의 M^2 는 Ni, Co, 및 Mn를 포함하는 것인 리튬 이차전지용 양극 활물질.

청구항 7

리튬 복합 산화물, 및 양극 용액을 준비하는 단계;

상기 양극 용액에 상기 리튬 복합 산화물을 투입, 혼합, 및 가열하여 상기 리튬 복합 산화물의 표면을 활성화시키는 단계; 및

상기 표면이 활성화된 리튬 복합 산화물을 소성시키는 단계;

를 포함하는 리튬 이차전지용 양극 활물질의 제조 방법.

청구항 8

제7항에 있어서,

상기 양극 용액에 상기 리튬 복합 산화물을 투입, 혼합, 및 가열하여 상기 리튬 복합 산화물의 표면을 활성화시키는 단계;는,

상기 양극 용액을 30 내지 120℃로 가열하는 단계; 및

상기 가열된 양극 용액에 상기 리튬 복합 산화물을 투입 후 교반하는 단계;

를 포함하는 것인 리튬 이차전지용 양극 활물질의 제조 방법.

청구항 9

제8항에 있어서,

상기 가열된 양극 용액에 상기 리튬 복합 산화물을 투입 후 교반하는 단계;는, 1 내지 240 시간 동안 수행되는 것인 리튬 이차전지용 양극 활물질의 제조 방법.

청구항 10

제7항에 있어서,

상기 표면이 활성화된 리튬 복합 산화물을 소성시키는 단계; 이전에,

상기 표면이 활성화된 리튬 복합 산화물을 건조시키는 단계를 더 포함하는 것인 리튬 이차전지용 양극 활물질의 제조 방법.

청구항 11

제10항에 있어서,

상기 표면이 활성화된 리튬 복합 산화물을 건조시키는 단계는, 80 내지 160℃에서 수행되는 것인 리튬 이차전지용 양극 활물질의 제조 방법.

청구항 12

제10항에 있어서,

공개특허 10-2015-0062724

상기 표면이 활성화된 리튬 복합 산화물을 조성시키는 단계;는, 150 내지 900℃에서 수행되는 것인 리튬 이차전지용 양극 활물질의 제조 방법.

청구항 13

제7항에 있어서,
상기 염기성 용액은 수소 이온을 가지고 있어 리튬 이온과 교환을 일으킬 수 있는 용액인 것인 리튬 이차전지용 양극 활물질의 제조 방법.

청구항 14

제7항에 있어서,
상기 염기성 용액은 하이드라진 용액, 암모니아 용액, 또는 이들의 조합인 것인 리튬 이차전지용 양극 활물질의 제조 방법.

청구항 15

제7항에 있어서,
상기 리튬 복합 산화물, 및 염기성 용액을 준비하는 단계;에서,
상기 리튬 복합 산화물은 산화 그래핀층이 형성된 리튬 복합 산화물인 것인 리튬 이차전지용 양극 활물질의 제조 방법.

청구항 16

제15항에 있어서,
상기 산화 그래핀층이 형성된 리튬 복합 산화물은,
산화 그래핀이 분산된 용액을 준비하는 단계;
상기 용액에 상기 리튬 복합 산화물을 투입 후 교반하는 단계; 및

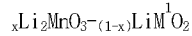
상기 산화 그래핀 및 리튬 복합 산화물이 교반된 용액을 분무 건조법을 이용하여 환원된 산화 그래핀층이 형성된 리튬 복합 산화물을 수득하는 단계;

를 통해 준비되는 것인 리튬 이차전지용 양극 활물질의 제조 방법.

청구항 17

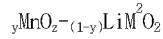
제16항에 있어서,
상기 제조 방법에 의한 양극 활물질은,
하기 화학식 1로 표시되는 화합물을 포함하는 코어; 및
하기 화학식 2로 표시되는 화합물을 포함하는 코어;를 포함하고,
상기 코어 상에 위치하며, 하기 화학식 2로 표시되는 화합물을 포함하는 코팅층;을 포함하는 것인 리튬 이차전지용 양극 활물질의 제조 방법.

[화학식 1]



(상기 화학식 1에서, $0 < x < 1$ 이고, M^1 은 전이금속이다.)

[화학식 2]



(상기 화학식 2에서, $0 < y < 1$ 이고, $1 \leq z \leq 4$ 이고, M^2 은 전이금속이다.)

청구항 18

제7항에 있어서,

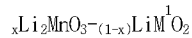
상기 제조 방법에 의한 양극 활물질은,

하기 화학식 1로 표시되는 화합물을 포함하는 코어; 및

상기 코어 상에 위치하며, 하기 화학식 2로 표시되는 화합물을 포함하는 코팅층;

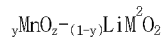
을 포함하는 구조인 것인 리튬 이차전지용 양극 활물질의 제조 방법.

[화학식 1]



(상기 화학식 1에서, $0 < x < 1$ 이고, M^1 은 전이금속이다.)

[화학식 2]



(상기 화학식 2에서, $0 < y < 1$ 이고, $1 \leq z \leq 4$ 이고, M^2 은 전이금속이다.)

청구항 19

제1항 내지 제6항 중 어느 하나의 항에 따른 리튬 이차전지용 양극 활물질을 포함하는 양극;

음극 활물질을 포함하는 음극; 및

전해질;

을 포함하는 리튬 이차전지.

발명의 설명

기술 분야

{0001} 리튬 이차전지용 양극 활물질, 이들의 제조방법, 및 이를 포함하는 리튬 이차전지에 관한 것이다.

배경 기술

{0002} 최근 휴대용 전자기기의 소형화 및 경량화 추세와 관련하여 이들 기기의 전원으로 사용되는 전지의 고성능화 및 대용량화에 대한 필요성이 높아지고 있다.

- [0003] 전지는 양극과 음극에 전기 화학 반응이 가능한 물질을 사용함으로써 전력을 발생시키는 것이다. 이러한 전지 중 대표적인 예로는 양극 및 음극에서 리튬 이온이 인터칼레이션/디인터칼레이션될 때의 화학전위(chemical potential)의 변화에 의하여 전기 에너지를 생성하는 리튬 이차 전지가 있다.
- [0004] 상기 리튬 이차 전지는 리튬 이온의 가역적인 인터칼레이션/디인터칼레이션이 가능한 물질을 양극과 음극 활물질로 사용하고, 상기 양극과 음극 사이에 유기 전해액 또는 폴리머 전해액을 충전시켜 제조한다.
- [0005] 리튬 이차 전지의 양극 활물질로는 리튬 복합금속 화합물이 사용되고 있으며, 그 예로 LiCoO_2 , LiMn_2O_4 , LiNiO_2 , $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($0 < x < 1$), LiMnO_2 등의 복합금속 산화물들이 연구되고 있다.
- [0006] 상기 양극 활물질 중 LiMn_2O_4 , LiMnO_2 등의 Mn계 양극 활물질은 합성하기도 쉽고, 값이 비교적 싸며, 과충전시 다른 활물질에 비하여 열적 안정성이 가장 우수하고, 환경에 대한 오염이 낮아 매력이 있는 물질이기는 하나, 용량이 적다는 단점을 가지고 있다.
- [0007] 또한 LiNiO_2 는 위에서 언급한 양극 활물질 중 가장 높은 방전 용량의 전지 특성을 나타내고 있으나, 합성하기 어려운 단점이 있다. 또한 니켈의 높은 산화상태는 전지 및 전극 수명 저하의 원인이 되며, 자기 방전이 심하고 가역성이 떨어지는 문제가 있다. 아울러, 안정성 확보가 완전하지 않아서 상용화에 어려움을 겪고 있다.
- [0008] LiCoO_2 는 현재 약 $10\mu\text{m}$ 입径의 활물질이 보편화 되어 있으나, 이는 충분한 에너지 밀도를 보장하지 않는다.

발명의 내용

해결하려는 과제

- [0009] 개선된 특성의 양극 활물질을 제공할 수 있다. 보다 구체적으로, 높은 초기 쿨롱효율과 함께, 수명 특성이 우수하고, 출력 특성이 우수한 리튬 이차전지용 양극 활물질, 이의 제조방법 및 이를 이용하여 제조된 리튬 이차전지에 관한 것이다.

과제의 해결 수단

- [0010] 본 발명의 일 구현예에서는, 하기 화학식 1로 표시되는 화합물을 포함하는 코어; 및 상기 코어 상에 위치하며, 하기 화학식 2로 표시되는 화합물을 포함하는 코팅층;을 포함하는 리튬 이차전지용 양극 활물질을 제공한다.
- [0011] [화학식 1]
- [0012] $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiM}^1\text{O}_2$
- [0013] (상기 화학식 1에서, $0 < x < 1$ 이고, M^1 은 전이금속이다.)
- [0014] [화학식 2]
- [0015] $y\text{MnO}_z-(1-y)\text{LiM}^2\text{O}_2$
- [0016] (상기 화학식 2에서, $0 < y < 1$ 이고, $1 \leq z \leq 4$ 이고, M^2 은 전이금속이다.)
- [0017] 상기 코팅층 상에 위치하는 환원된 산화 그래펜(reduced graphene oxide)층을 더 포함할 수 있다.
- [0018] 상기 환원된 산화 그래펜층의 두께는 1 내지 5nm일 수 있다.
- [0019] 상기 코어 및 코팅층을 포함하는 전체 양극 활물질 내 Li/M 몰비율은 1.05 내지 1.6일 수 있다.
- [0020] 상기 코팅층의 두께는 1 내지 13nm일 수 있다.
- [0021] 상기 화학식 1의 M^1 및 화학식 2의 M^2 는 Ni, Co, 및 Mn을 포함할 수 있다.
- [0022] 본 발명의 다른 일 구현예에서는, 리튬 복합 산화물, 및 염기성 용액을 준비하는 단계; 상기 염기성 용액에 상

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기 리튬 복합 산화물을 투입, 혼합, 및 가열하여 상기 리튬 복합 산화물의 표면을 활성화시키는 단계; 및 상기 표면에 활성화된 리튬 복합 산화물을 조성시키는 단계;를 포함하는 리튬 이차전지용 양극 활물질의 제조 방법을 제공한다.

상기 염기성 용액에 상기 리튬 복합 산화물을 투입, 혼합, 및 가열하여 상기 리튬 복합 산화물의 표면을 활성화시키는 단계;는, 상기 염기성 용액은 30 내지 120℃로 가열하는 단계; 및 상기 가열된 염기성 용액에 상기 리튬 복합 산화물을 투입 후 교반하는 단계;를 포함할 수 있다.

상기 가열된 염기성 용액에 상기 리튬 복합 산화물을 투입 후 교반하는 단계;는, 1 내지 240 시간 동안 수행될 수 있다.

상기 표면에 활성화된 리튬 복합 산화물을 조성시키는 단계; 이전에, 상기 표면에 활성화된 리튬 복합 산화물을 건조시키는 단계를 더 포함할 수 있다.

상기 표면에 활성화된 리튬 복합 산화물을 건조시키는 단계는, 80 내지 160℃에서 수행될 수 있다.

상기 표면에 활성화된 리튬 복합 산화물을 조성시키는 단계;는, 150 내지 900℃에서 수행될 수 있다.

상기 염기성 용액은 수소 이온을 가지고 있어 리튬 이온과 교환을 일으킬 수 있는 용액일 수 있다.

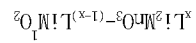
상기 염기성 용액은 하이드라진 용액, 암모니아 용액, 또는 이들의 조합일 수 있다.

상기 리튬 복합 산화물, 및 염기성 용액을 준비하는 단계;에서, 상기 리튬 복합 산화물은 산화 그래페닉이 형성된 리튬 복합 산화물일 수 있다.

상기 산화 그래페닉이 형성된 리튬 복합 산화물은, 산화 그래페닉 분산된 용액을 준비하는 단계; 상기 용액에 상기 리튬 복합 산화물을 투입 후 교반하는 단계; 및 상기 산화 그래페닉 및 리튬 복합 산화물이 교반된 용액을 분무 건조법을 이용하여 환원된 산화 그래페닉이 형성된 리튬 복합 산화물을 수득하는 단계;를 통해 준비될 수 있다.

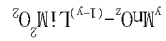
상기 제조 방법에 의한 양극 활물질은, 하기 화학식 1로 표시되는 화합물을 포함하는 코어; 및 상기 코어 상에 위치하며, 하기 화학식 2로 표시되는 화합물을 포함하는 코팅층;을 포함하는 구조일 수 있다.

[화학식 1]



(상기 화학식 1에서, $0 < x < 1$ 이고, M_1 은 전이금속이다.)

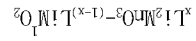
[화학식 2]



(상기 화학식 2에서, $0 < y < 1$ 이고, $1 \leq z \leq 4$ 이고, M_2 은 전이금속이다.)

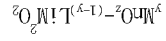
상기 제조 방법에 의한 양극 활물질은, 하기 화학식 1로 표시되는 화합물을 포함하는 코어; 및 상기 코어 상에 위치하며, 하기 화학식 2로 표시되는 화합물을 포함하는 코팅층;을 포함하는 구조일 수 있다.

[화학식 1]



(상기 화학식 1에서, $0 < x < 1$ 이고, M_1 은 전이금속이다.)

[화학식 2]



(상기 화학식 2에서, $0 < y < 1$ 이고, $1 \leq z \leq 4$ 이고, M_2 은 전이금속이다.)

{0046} 본 발명의 또 다른 일 구현예에서는, 전술한 본 발명의 일 구현예에 따른 리튬 이차전지용 양극 활물질을 포함하는 양극; 음극 활물질을 포함하는 음극; 및 전해질;을 포함하는 리튬 이차전지를 제공한다.

활명의 효과

{0047} 높은 초기 쿨롱효율과 함께, 수명 특성이 우수하고, 출력 특성이 우수한 리튬 이차전지용 양극 활물질, 이의 제조방법 및 이를 이용하여 제조된 리튬 이차전지를 제공할 수 있다.

도면의 간단한 설명

{0048} 도 1은 실시예 1, 2 및 비교예 1의 XRD 분석 결과이다.
 도 2는 실시예 및 비교예에 따른 활물질의 SEM 사진이다.
 도 3은 실시예 1에 따른 활물질의 TEM 사진이다.
 도 4은 실시예 2에 따른 활물질의 TEM 사진이다.
 도 5는 실시예 5 및 비교예 2에 따른 전지의 수명 특성을 나타낸 그래프이다.
 도 6은 실시예 7 및 비교예 2에 따른 전지의 초기 효율 특성을 나타낸 그래프이다.
 도 7은 실시예 5, 6, 7 및 비교예 2에 따른 전지의 출력 특성을 나타낸 그래프이다.
 도 8은 실시예 7 및 비교예 2에 따른 전지의 수명 특성 및 작동 전압 특성을 나타낸 그래프이다.
 도 9는 실시예 7 및 비교예 2에 따른 초기 2.0 내지 4.8V 의 충/방전 후 수명 특성을 나타낸 그래프이다.

활명을 실시하기 위한 구체적인 내용

{0049} 이하, 본 발명의 구현예를 상세히 설명하기로 한다. 다만, 이는 예시로서 제시되는 것으로, 이에 의해 본 발명이 제한되지는 않으며 본 발명은 후술할 청구범위의 범주에 의해 정의될 뿐이다.

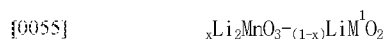
{0050} 본 발명의 일 구현예에서는, 높은 초기 쿨롱효율과 함께, 수명특성이 우수하고, 출력 특성이 우수한 리튬 이차전지용 양극 활물질, 이의 제조방법 및 이를 이용하여 제조된 리튬 이차 전지를 제공할 수 있다.

{0051} 본 발명의 일 구현예에 따른 양극 활물질은 수소 이온을 포함하는 수용액(예를 들어, 염기성 용액)을 이용하여 활물질 표면의 Li_2MnO_3 상을 화학적으로 활성화 시킨 후 열처리하여 활물질 표면에 구조적, 및 전기화학적 안정한 코팅층(또는 표면층)을 형성할 수 있다.

{0052} 또한, 선택적으로, 본 발명의 일 구현예에 따른 리튬 이차전지용 양극 활물질은 전기 전도성이 우수한 환원된 산화 그라펜층을 코팅층으로 더 포함할 수 있다.

{0053} 보다 구체적으로, 본 발명의 일 구현예에서는, 하기 화학식 1로 표시되는 화합물을 포함하는 코어; 및 상기 코어 상에 위치하며, 하기 화학식 2로 표시되는 화합물을 포함하는 코팅층;을 포함하는 리튬 이차전지용 양극 활물질을 제공한다.

{0054} [화학식 1]



{0056} (상기 화학식 1에서, $0 < x < 1$ 이고, M^1 은 전이금속이다.)

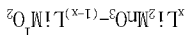
{0057} [화학식 2]



- {0059} (상기 화학식 2에서, $0 < y < 1$ 이고, $1 \leq z \leq 4$ 이고, M^2 은 전이금속이다.)
- {0060} 상기 화학식 2로 표시되는 화합물의 구조는 후술하는 염기성 용액을 이용한 제조 방법에 의해 생성되는 리튬이 탈리된 구조이다. 이러한 구조는 구조적, 및 전기화학적으로 안정한 구조로 전지의 수명 특성, 출력 특성을 개선시킬 수 있다. 상기 코팅층의 두께는 1 내지 13nm일 수 있으며, 보다 구체적으로 1 내지 10nm일 수 있다. 두께 범위에 따라 수명 특성과 출력 특성이 다소 변화될 수 있으며, 목적하는 두께에 따라 후술하는 교반 시간을 제어할 수 있다.
- {0061} 또한, 상기 코팅층 상에 위치하는 환원된 산화 그래펜(reduced graphene oxide)층을 더 포함할 수 있다. 상기 환원된 산화 그래펜층의 두께는 1 내지 5nm일 수 있다. 상기 두께 범위는 활물질의 특성에 따라 선택적으로 조절 가능하며 이에 제한되는 것은 아니다.
- {0062} 상기 코어 및 코팅층을 포함하는 전체 양극 활물질 내 Li/M 몰비율은 1.05 내지 1.6일 수 있으며, 보다 구체적으로 1.1 내지 1.35일 수 있다. 이는 최초 투입되는 원재료보다 Li이 탈리된 비율이며, 코팅층의 두께에 따라 변화될 수 있다.
- {0063} 상기 화학식 1의 M^1 및 화학식 2의 M^2 는 Ni, Co, 및 Mn을 포함할 수 있다. 이미 당업계에 알려진 전이금속이면 모두 사용 가능하며, 이에 제한되는 것은 아니다.
- {0064} 본 발명의 다른 일 구현예에서는, 리튬 복합 산화물, 및 염기성 용액을 준비하는 단계; 상기 염기성 용액에 상기 리튬 복합 산화물을 투입, 혼합, 및 가열하여 상기 리튬 복합 산화물의 표면을 활성화시키는 단계; 및 상기 표면이 활성화된 리튬 복합 산화물을 소성시키는 단계;를 포함하는 리튬 이차전지용 양극 활물질의 제조 방법을 제공한다.
- {0065} 상기 염기성 용액에 상기 리튬 복합 산화물을 투입, 혼합, 및 가열하여 상기 리튬 복합 산화물의 표면을 활성화시키는 단계;는, 상기 염기성 용액을 30 내지 120℃로 가열하는 단계; 및 상기 가열된 염기성 용액에 상기 리튬 복합 산화물을 투입 후 교반하는 단계;를 포함할 수 있다.
- {0066} 상기 가열된 염기성 용액에 상기 리튬 복합 산화물을 투입 후 교반하는 단계;는, 1 내지 240시간 동안 수행될 수 있으며, 보다 구체적으로 1 내지 20 시간 동안 수행될 수 있다. 상기 교반 시간에 따라 전술한 코팅층의 두께를 제어할 수 있다.
- {0067} 상기 표면이 활성화된 리튬 복합 산화물을 소성시키는 단계; 이전에, 상기 표면이 활성화된 리튬 복합 산화물을 건조시키는 단계를 더 포함할 수 있다.
- {0068} 상기 표면이 활성화된 리튬 복합 산화물을 건조시키는 단계는, 80 내지 160℃에서 수행될 수 있다. 다만, 이에 제한되는 것은 아니다.
- {0069} 상기 표면이 활성화된 리튬 복합 산화물을 소성시키는 단계;는, 150 내지 900℃에서 수행될 수 있으며, 보다 구체적으로 180 내지 220℃에서 수행될 수 있다. 다만, 이에 제한되는 것은 아니다.
- {0070} 상기 염기성 용액은 수소 이온을 가지고 있어 리튬 이온과 교환을 일으킬 수 있는 용액일 수 있다.
- {0071} 보다 구체적으로, 상기 염기성 용액은 하이드라진 용액, 암모니아 용액, 또는 이들의 조합일 수 있다. 다만, 이에 제한되는 것은 아니다.
- {0072} 상기 리튬 복합 산화물, 및 염기성 용액을 준비하는 단계;에서, 상기 리튬 복합 산화물은 산화 그래펜층이 형성된 리튬 복합 산화물일 수 있다.
- {0073} 상기 산화 그래펜층이 형성된 리튬 복합 산화물은, 산화 그래펜이 분산된 용액을 준비하는 단계; 상기 용액에 상기 리튬 복합 산화물을 투입 후 교반하는 단계; 및 상기 산화 그래펜 및 리튬 복합 산화물이 교반된 용액을 분무 건조법을 이용하여 산화 그래펜층이 형성된 리튬 복합 산화물을 수득하는 단계;를 통해 준비될 수 있다. 이러한 분무 건조법은 당업계에 잘 알려져 있기에 구체적인 설명은 생략하도록 한다.
- {0074} 상기 제조 방법에 의한 양극 활물질은, 하기 화학식 1로 표시되는 화합물을 포함하는 코어; 및 상기 코어 상에 위치하며, 하기 화학식 2로 표시되는 화합물을 포함하는 코팅층;을 포함하고, 상기 코팅층 상에 위치하는 환원된 산화 그래펜(reduced graphene oxide)층을 더 포함하는 구조일 수 있다.

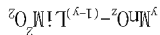
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[0075] [화학식 1]



(상기 화학식 1에서, $0 < x < 1$ 이고, M' 은 전이금속이다.)

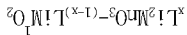
[화학식 2]



(상기 화학식 2에서, $0 < y < 1$ 이고, $1 \leq z \leq 4$ 이고, M'' 은 전이금속이다.)

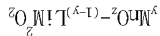
[0081] 제조 방법에 의한 양극 활물질을, 하기 화학식 1로 표시되는 화합물을 포함하는 코어; 및 상기 코어 상에 위치하며, 하기 화학식 2로 표시되는 화합물을 포함하는 코팅층;을 포함하는 구조일 수 있다.

[화학식 1]



(상기 화학식 1에서, $0 < x < 1$ 이고, M' 은 전이금속이다.)

[화학식 2]



(상기 화학식 2에서, $0 < y < 1$ 이고, $1 \leq z \leq 4$ 이고, M'' 은 전이금속이다.)

[0088] 이러한 양극 활물질의 구조에 대한 구체적인 설명은 전술한 본 발명의 일 구현예와 동일하기 때문에 그 설명은 생략하도록 한다.

[0089] 본 발명의 일 구현예에 따른 양극 활물질은 리튬 이차 전지의 양극에 유용하게 사용될 수 있다. 상기 리튬 이차 전지는 양극과 함께 양극 활물질을 포함하는 양극 및 전해질을 포함한다.

[0090] 상기 양극은 본 발명의 일 구현예에 따른 양극 활물질과, 도전제, 결합제 및 용매를 혼합하여 양극 활물질 조성물을 제조한 다음, 알루미늄 전진체 상에 직접 코팅 및 건조하여 제조한다. 또는 상기 양극 활물질 조성물을 제조한 다음, 알루미늄 전진체 상에 케스팅한 다음, 이 지지체로부터 박리하여 얻은 필름을 알루미늄 전진체 상에 라미네이션하여 제조가 가능하다.

[0091] 이때 도전제는 카본 블랙, 흑연, 금속 분말을 사용하며, 결합제는 비틸리덴플루오라이드/헥사플루오로프로필렌 포플리머, 폴리비닐리덴플루오라이드, 폴리아크릴로니트릴, 폴리메틸메타크릴레이트, 폴리테트라플루오로에틸렌 및 그 혼합물이 가능하다. 또한 용매는 N-메틸피롤리돈, 아세톤, 테트라하이드로퓨란, 테칸 등을 사용한다. 이때 양극 활물질, 도전제, 결합제 및 용매의 함량은 리튬 이차 전지에서 통상적으로 사용하는 수준으로 사용된다.

[0092] 상기 양극은 양극과 마관가지로 양극 활물질, 결합제 및 용매를 혼합하여 애노드 활물질 조성물을 제조하며, 이를 구리 전진체에 직접 코팅하거나 별도의 지지체 상에 케스팅하고 이 지지체로부터 박리시킨 양극 활물질 필름을 구리 전진체에 라미네이션하여 제조한다. 이때 양극 활물질 조성물에는 필요한 경우에는 도전제를 더욱 함유하기도 한다.

[0093] 상기 양극 활물질로는 리튬을 인터칼레이션/디인터칼레이션할 수 있는 재료가 사용되고, 예컨대, 리튬 금속이나 리튬 합금, 코크스, 인조 흑연, 천연 흑연, 유기 고분자 화합물 연소재, 탄소 섬유 등을 사용한다. 또한 도전제, 결합제 및 용매는 전술한 양극의 경우와 동일하게 사용된다.

[0094] 상기 세퍼레이터는 리튬 이차 전지에서 통상적으로 사용되는 것이라면 모두 다 사용가능하며, 인에르 폴리에틸렌, 폴리프로필렌, 폴리비닐리덴 플루오라이드 또는 이들의 2층 이상의 다층막이 사용될 수 있으며, 폴리에틸렌

/폴리프로필렌 2층 설퍼레이터, 폴리에틸렌/폴리프로필렌/폴리에틸렌 3층 설퍼레이터, 폴리프로필렌/폴리에틸렌/폴리프로필렌 3층 설퍼레이터 등과 같은 혼합 다층막이 사용될 수 있음은 물론이다.

[0095] 상기 리튬 이차 전지에 충전되는 전해질로는 비수성 전해질 또는 공지된 고체 전해질 등이 사용 가능하며, 리튬염이 용해된 것을 사용한다.

[0096] 상기 비수성 전해질의 용매는 특별히 한정되는 것은 아니지만, 에틸렌카보네이트, 프로필렌카보네이트, 부틸렌카보네이트, 비닐렌카보네이트 등의 환상 카보네이트; 디메틸카보네이트, 메틸에틸카보네이트, 디에틸카보네이트 등의 쇠상 카보네이트; 아세트산메틸, 아세트산에틸, 아세트산프로필, 프로피온산메틸, 프로피온산에틸, γ -부티로락톤 등의 에스테르류; 1,2-디메톡시에탄, 1,2-디에톡시에탄, 테트라히드로푸란, 1,2-디옥산, 2-메틸테트라히드로푸란 등의 에테르류; 아세토니트릴 등의 니트릴류; 디메틸포름아미드 등의 아미드류 등을 사용할 수 있다. 이들을 단독또는 복수개 조합하여 사용할 수 있다. 특히, 환상 카보네이트와 쇠상 카보네이트와의 혼합 용매를 바람직하게 사용할 수 있다.

[0097] 또한 전해질로서, 폴리에틸렌옥사이드, 폴리아크릴로니트릴 등의 중합체 전해질에 전해액을 함침한 겔상 중합체 전해질이나, LiI, Li₃N 등의 무기 고체 전해질이 가능하다.

[0098] 이때 리튬염은 LiPF₆, LiBF₄, LiSbF₆, LiAsF₆, LiClO₄, LiCF₃SO₃, Li(CF₃SO₂)₂N, LiC₄F₉SO₃, LiSbF₆, LiAlO₄, LiAlCl₄, LiCl, 및 LiI로 이루어진 군에서 선택된 1종이 가능하다.

[0099] 이하 본 발명의 바람직한 실시예 및 비교예를 기재한다. 그러나 하기 실시예는 본 발명의 바람직한 일 실시예일 뿐 본 발명이 하기 실시예에 한정되는 것은 아니다.

[0100] 실시예

[0101] 실시예1: 양극 활물질의 제조

[0102] 탈이온수(deionized water) 10mg에 하이드라진 모노하이드레이트(hydrazine monohydrate) 40 μ g를 첨가한 후, 수용액을 90℃으로 가열한 후 온도 유지하였다.

[0103] 이어서, 0.4Li₂MnO₃-0.6LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ 2g을 넣고 혼합한 후, 3시간동안 교반하였다.

[0104] 이어서, 120℃의 온도에서 12시간 동안 건조하고, 200℃의 온도에서 3시간 열처리 하였다.

[0105] 이로써, 리튬 이차 전지용 양극 활물질을 제조하였다. 상기 제조한 리튬 이차전지용 양극 활물질의 조성은 0.33Li₂MnO₃-0.6LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂이다.

[0106] 실시예2: 양극 활물질의 제조

[0107] 탈이온수(deionized water) 10mg에 하이드라진 모노하이드레이트(hydrazine monohydrate) 40 μ g를 첨가한 후, 수용액을 90℃으로 가열한 후 온도 유지하였다.

[0108] 이어서, 0.4Li₂MnO₃-0.6LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ 2g을 넣고 혼합한 후, 10시간동안 교반하였다.

[0109] 이어서, 120℃의 온도에서 12시간 동안 건조하고, 200℃의 온도에서 3시간 열처리 하였다.

[0110] 이로써, 리튬 이차 전지용 양극 활물질을 제조하였다. 상기 제조한 리튬 이차전지용 양극 활물질의 조성은 0.18Li₂MnO₃-0.6LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂이다.

[0111] 실시예3: 양극 활물질의 제조

[0112] 탈이온수(deionized water) 10mg에 4mg/ml의 산화 그래펜 용액(graphene oxid solution)을 200ml를 첨가한 후, 교반하였다.

{0113} 이어서, $0.4\text{Li}_2\text{MnO}_3-0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ 16g을 넣고 혼합한 후, 1시간동안 교반하였다.

{0114} 이어서, 스프레이 드라이어를 이용하여 190°C 의 실린더 내부로 스프레이 분사하였다.

{0115} 이어서, 120°C 의 온도로 12시간 동안 건조 하였다.

{0116} 이로써, 리튬 이차 전지용 양극 활물질을 제조하였다. 상기 제조한 리튬 이차전지용 양극 활물질은 산화 그래핀(graphene oxide)이 표면 도포된 $0.4\text{Li}_2\text{MnO}_3-0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ 이다.

{0117} 실시예4: 리튬 이차 전지용 양극 활물질의 제조

{0118} 탈이온수(deionized water) 10mg에 하이드라진 모노하이드레이트(hydrazine monohydrate) $40\mu\text{g}$ 을 첨가한 후, 수용액을 90°C 으로 가열한 후 온도 유지하였다.

{0119} 이어서, 상기 실시예 3의 결과 물질인, 산화 그래핀이 표면 도포된 $0.4\text{Li}_2\text{MnO}_3-0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ 2g을 넣고 혼합한 후, 3시간동안 교반하였다.

{0120} 이어서, 120°C 의 온도에서 12시간 동안 건조하고, 200°C 의 온도에서 3시간 열처리 하였다.

{0121} 이로써, 리튬 이차 전지용 양극 활물질을 제조하였다. 상기 제조한 리튬 이차전지용 양극 활물질의 조성은 표면에 환원된 산화 그래핀이 도포된 $0.33\text{Li}_2\text{MnO}_3-0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ 이다.

{0122} 실시예 5: 리튬 이차 전지의 제조

{0124} 상기 실시예 1에서 제조한 리튬 이차 전지용 양극 활물질과 도전제로 슈퍼-P, 바인더로 폴리비닐리덴 플루오라이드(PVdF)를 각각 8:1:1의 중량비로 혼합하여 슬러리를 제조하였다. 상기 슬러리를 $15\mu\text{m}$ 두께의 알루미늄박에 균일하게 도포하고, 120°C 의 온도에서 진공 건조하여 양극을 제조하였다.

{0125} 상기 제조된 양극과 리튬 호일을 상대 전극으로 하며, 다공성 폴리에틸렌막 카보네이트, 에틸메틸 카보네이트 그리고 디메틸카보네이트를 3:4:3의 부피비로 혼합한 용매에 LiPF_6 가 1.0M 농도로 녹아 있는 액체 전해액을 사용하여 통상적으로 알려져 있는 제조 공정에 따라 반쪽 셀을 제조 하였다.

{0126} 실시예6: 리튬 이차 전지의 제조

{0127} 상기 실시예 2에서 제조한 리튬 이차 전지용 양극 활물질을 사용한 것을 제외하고는 상기 실시예 5와 동일하게 실시하여 코인 반쪽 셀을 제조 하였다.

{0128} 실시예7: 리튬 이차 전지의 제조

{0129} 상기 실시예 4에서 제조한 리튬 이차 전지용 양극 활물질을 사용한 것을 제외하고는 상기 실시예 5와 동일하게 실시하여 코인 반쪽 셀을 제조 하였다.

{0130} 비교예 1: 리튬 이차 전지용 양극 활물질

{0131} $0.4\text{Li}_2\text{MnO}_3-0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ 로 표시되는 화합물을 리튬 이차 전지용 양극 활물질로 사용하였다.

{0132} 비교예 2. 리튬 이차 전지의 제조

{0133} 상기 비교예 1의 리튬 이차 전지용 양극 활물질을 사용한 것을 제외하고는 상기 실시예 5와 동일하게 실시하여 코인 반쪽 셀을 제조 하였다.

실험예**실험예 1: IPC 분석**

하기 표 1은 실시예 1 및 비교예 1의 성분 분석 결과이다.

표 1

	Li	Mn	Co	Ni	L/M ratio(몰비)
비교예 1	7.01	3.01	0.98	1.00	1.41
실시예 1	6.46	2.99	0.98	1.00	1.3

분석 결과, 실시예 1의 하이드라진 처리에 의해 Li/M의 비율이 변한 것을 확인할 수 있다. 이는 Li의 화학적 탈리로 인한 것으로 판단된다.

실험예 2: XRD 분석

도 1은 실시예 1, 2 및 비교예 1의 XRD 분석 결과이다.

하이드라진 처리 시간이 증가함에 따라 19도 부근에 XRD 피크가 발생하는 것을 알 수 있다. 이로부터 Li^+/H^+ 의 이온 교환이 이루어짐을 알 수 있다.

실험예 3: SEM 분석

도 2는 실시예 및 비교예에 따른 활물질의 SEM 사진이다. 상기 실시예 1, 비교예 1의 리튬 이차 전지용 양극 활물질을 각각 탄소 테이프 위에 샘플링한 후, 플래티늄(Pt) 플라즈마 코팅하여 SEM 사진을 촬영하였다. 보다 구체적으로, 도 2 내의 각각의 사진에 대한 설명은 다음과 같다.

a. 일반적인 sol-gel 방법으로 표면코팅된 양극활물질 개념도

b. 실시예 4에 따른 양극 활물질 개념도

c. 사용된 $0.4\text{Li}_2\text{MnO}_5-0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ bare 물질

d. 실시예 3에 의해 형성된 산화 그래펜이 표면 도포된 $0.4\text{Li}_2\text{MnO}_5-0.6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$

e. 실시예 4에 따른 활물질

f. 실시예 3에 따른 활물질

본 발명의 실시예에 따른 표면 처리, 및 산화 그래펜 처리가 균일하게 잘 이루어진 것을 확인할 수 있다.

실험예 4: TEM 분석

도 3은 실시예 1에 따른 활물질의 TEM 사진이다. 표면에 2 내지 3nm의 코팅층이 형성된 것을 확인할 수 있다.

도 4은 실시예 2에 따른 활물질의 TEM 사진이다. 표면에 ~13nm의 코팅층이 형성된 것을 확인할 수 있다. 즉, 처리 시간에 따라 코팅층의 두께를 조절할 수 있음을 알 수 있다.

실험예 5: 전지 특성 데이터

도 5는 실시예 5 및 비교예 2에 따른 전지의 수명 특성을 나타낸 그래프이다. 도 5 내의 식별은 사용한 활물질

공개특허 10-2015-0062724

의 변호를 이용하였다. 보다 구체적으로, 상온/ 2.0-4.7V로 첫 사이클 후 2.0-4.6V로 수명 특성을 측정(IC-rate)하였다.

[0156] 실시예 1에 따른 활물질을 이용한 코인-셀의 수명 특성이 개선된 점을 알 수 있다.

[0157] 도 6은 실시예 7 및 비교예 2에 따른 전지의 초기 효율 특성을 나타낸 그래프이다.

[0158] 실시예 4에 따른 활물질을 이용한 코인-셀이 높은 초기 효율을 가지는 것을 알 수 있다.

[0159] 도 7은 실시예 5, 6, 7 및 비교예 2에 따른 전지의 출력 특성을 나타낸 그래프이다.

[0160] 실시예 1, 및 4의 활물질을 이용한 코인-셀은 비교예 1을 이용한 코인-셀보다 좋은 출력 특성을 보이나, 실시예 2의 경우 출력 특성이 비교예 1에도 못 미치는 것을 알 수 있다. 즉, 하이드라진 처리 시간에 따른 코팅층의 두께에 따라 전지의 출력 특성에 일부 영향이 있는 것을 알 수 있다.

[0161] 도 8은 실시예 7 및 비교예 2에 따른 전지의 수명 특성 및 작동 전압 특성을 나타낸 그래프이다.

[0162] 실시예 7 및 비교예 2는 비슷한 수명 특성을 보임에도, 실시예 7의 경우가 작동 전압 감소가 적음을 알 수 있다.

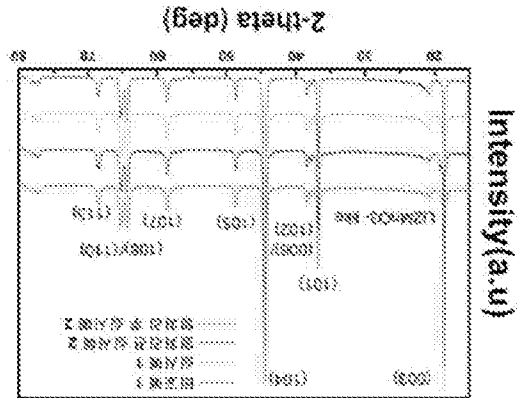
[0163] 도 9는 실시예 7 및 비교예 2에 따른 초기 4.8V의 충/방전 후 수명 특성을 나타낸 그래프이다.

[0164] 실시예 7에 따른 코인-셀이 비교예 2에 따른 코인-셀보다 수명 특성이 개선된 것을 알 수 있다.

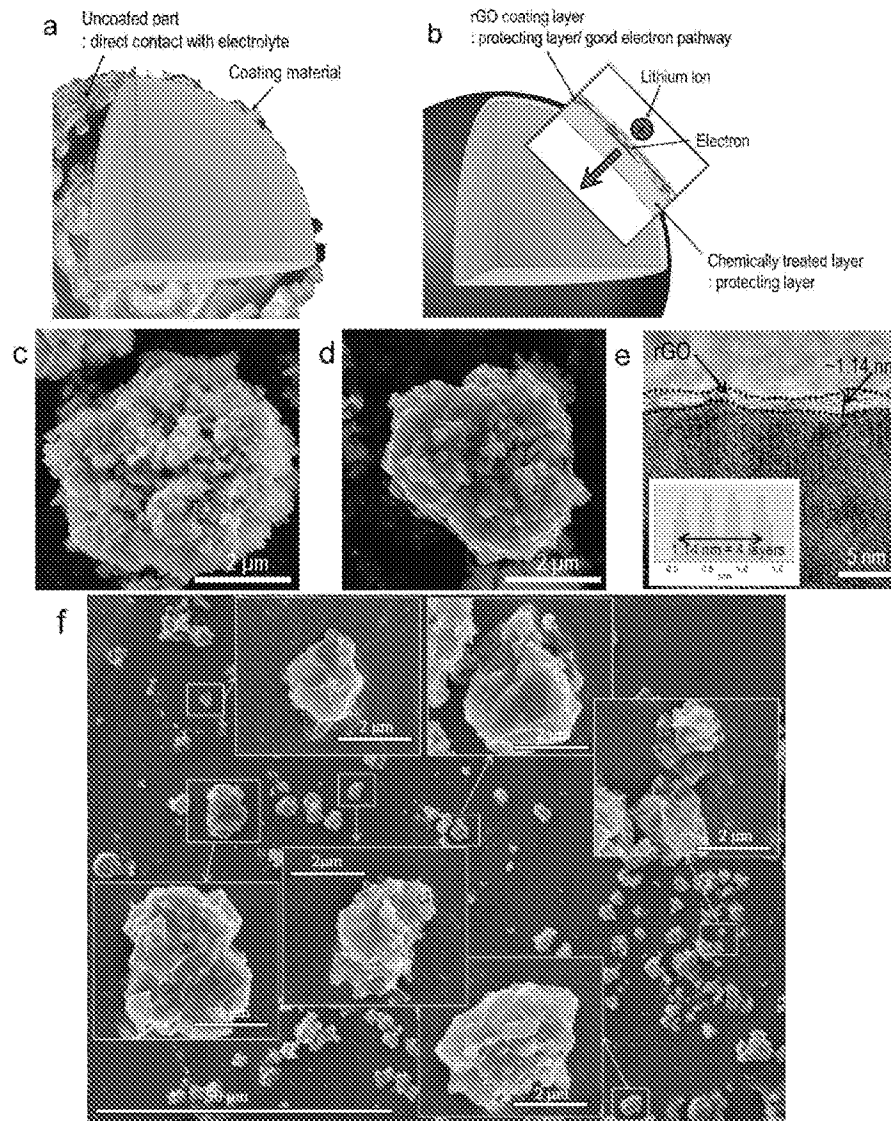
[0165] 본 발명은 상기 실시예들에 한정되는 것이 아니라 서로 다른 다양한 형태로 제조될 수 있으며, 본 발명이 속하는 기술분야에서 통상의 지식을 가진 자는 본 발명의 기술적 사상이나 필수적인 특징을 변경하지 않고서 다른 구체적인 형태로 실시될 수 있다는 것을 이해할 수 있을 것이다. 그러므로 이상에서 기술한 실시예들은 모든 면에서 예시적인 것이며 한정적이 아닌 것으로 이해해야만 한다.

도 1

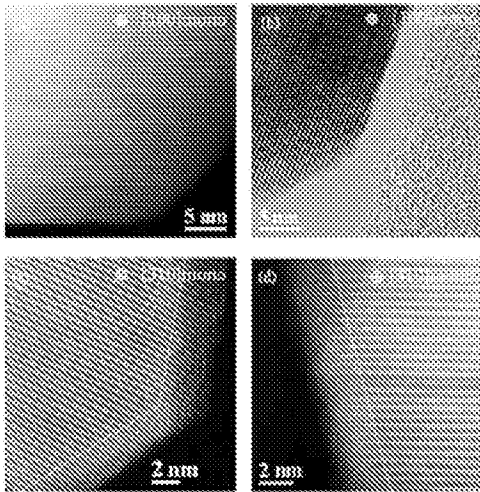
도 2



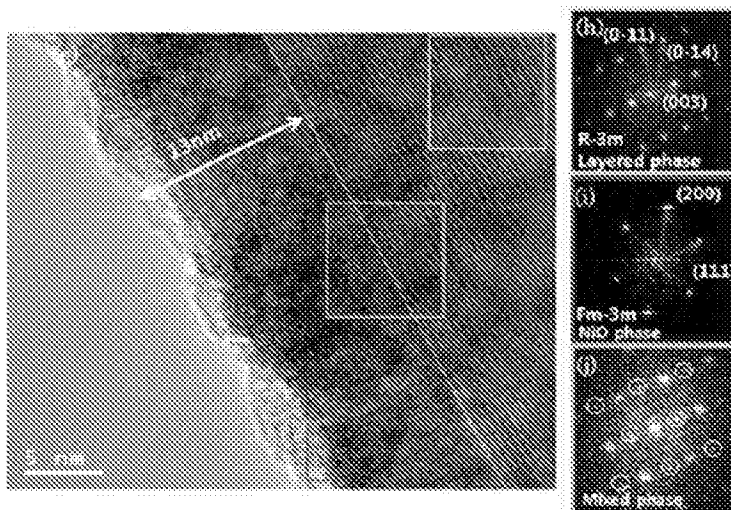
도면2



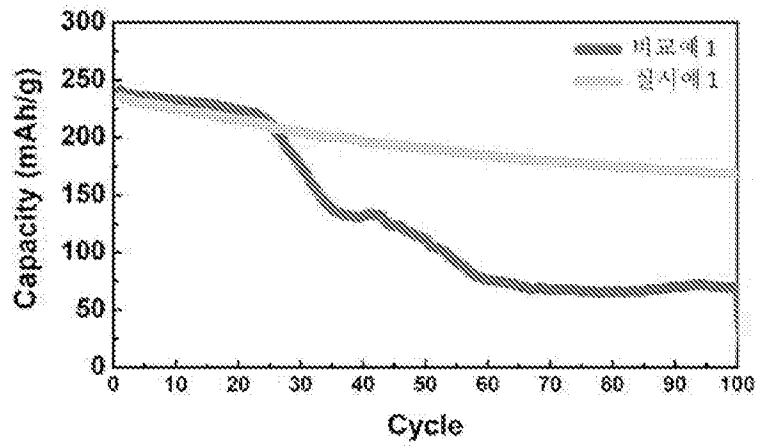
도면3



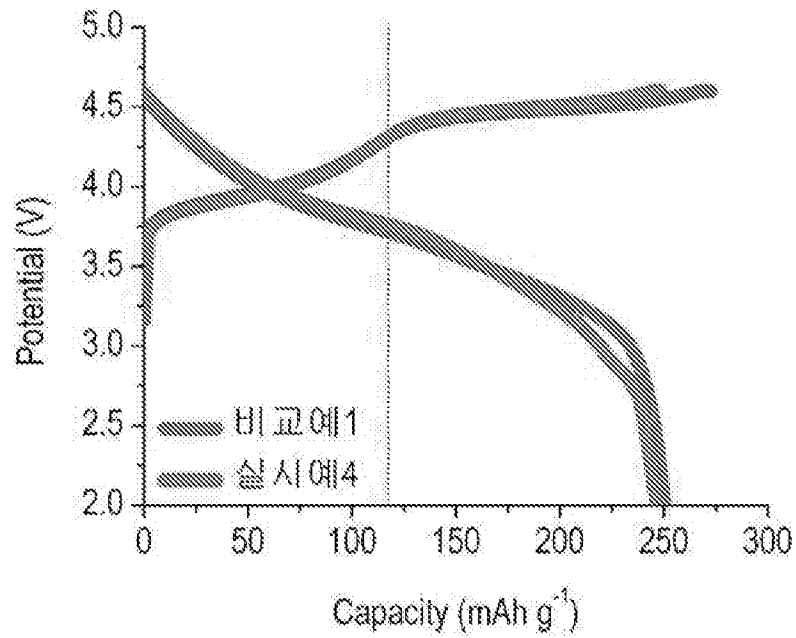
도면4



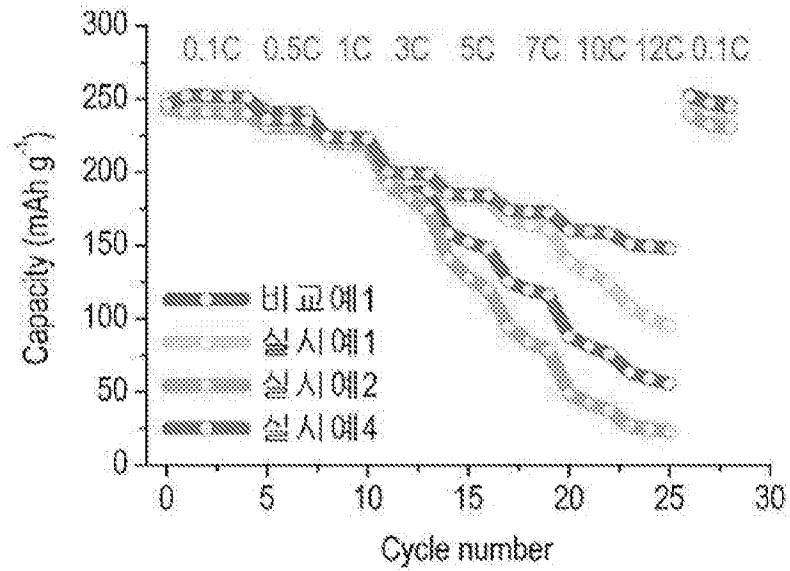
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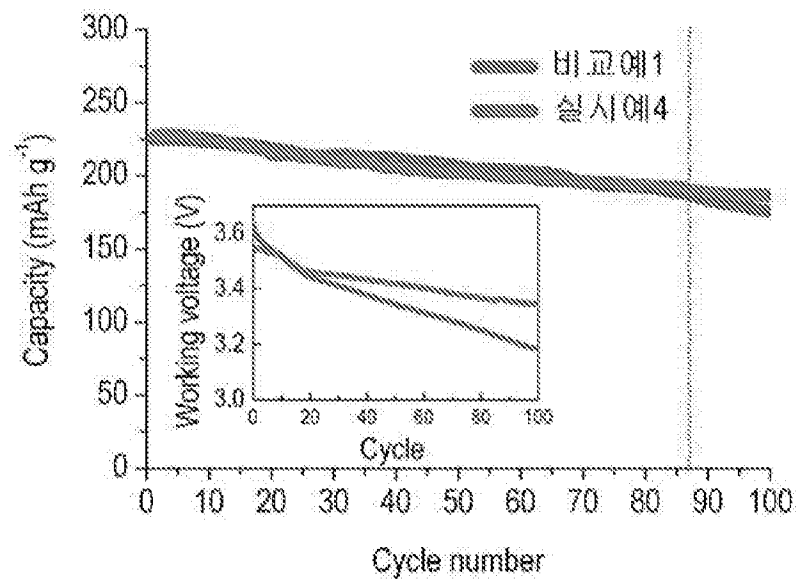
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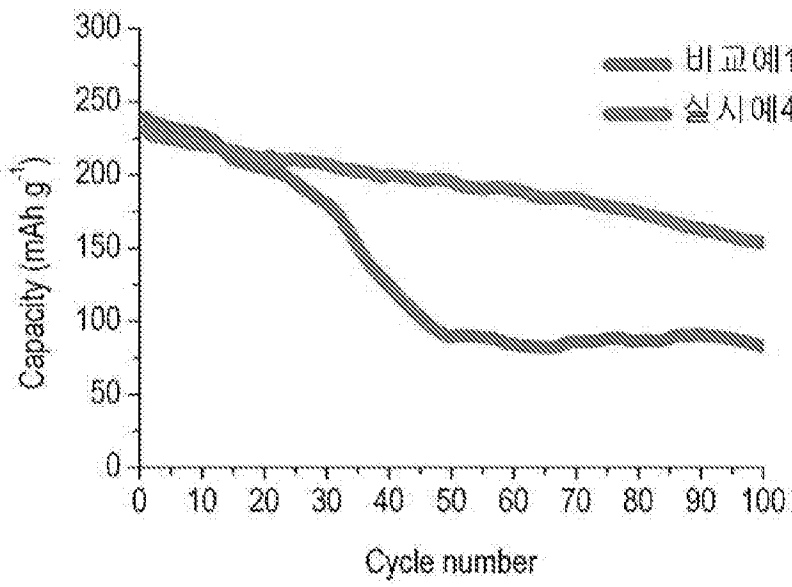
도면7



도면8



도면9





Espacenet

[RSS family dossier](#)

Family list: KR20140125856 (A) — 2014-10-29

5 application(s) for: KR20140125856 (A)

1. PARTICLES, METHOD FOR THE PRODUCTION THEREOF, AND USE THEREOF					
Inventor: VOLKOV ALEKSEI [EE] LEITNER KLAUS [AT] (+2)	Applicant: BASF SE [DE]	CPC: C01G53/006 C01G53/50 C01P2002/52 (+6)	IPC: C01D15/00 C01G53/00 H01M10/052 (+4)	Publication info: KR20140125856 (A) 2014-10-29 Global Dossier	Priority date: 2012-02-15
2. Particles, method for the production thereof, and use thereof					
Inventor: VOLKOV ALEKSEI LEITNER KLAUS (+2)	Applicant: BASF SE	CPC: C01G53/006 C01G53/50 C01P2002/52 (+6)	IPC: C01G51/00 C01G53/00 H01M4/1315 (+4)	Publication info: CN104540783 (A) 2015-04-22 Global Dossier	Priority date: 2012-02-15
3. PARTICLES, METHOD FOR THE PRODUCTION THEREOF, AND USE THEREOF					
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4. PARTICLES, METHOD FOR THE PRODUCTION THEREOF, AND USE THEREOF					
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5. PARTICLES, METHOD FOR THE PRODUCTION THEREOF, AND USE THEREOF					
Inventor: VOLKOV ALEKSEI [DE] LEITNER KLAUS [DE] (+2)	Applicant: BASF SE [DE]	CPC: C01G53/006 C01G53/50 C01P2002/52 (+6)	IPC: C01G51/00 C01G53/00 H01M4/1315 (+4)	Publication info: WO2013120724 (A1) 2013-08-22 Global Dossier	Priority date: 2012-02-15

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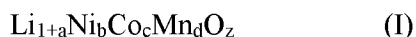
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(54) Title of the Invention: Particle, Formation Method of the Particle, and Use of the Particle

(57) Overview:

25 The present invention relates to a particle including a mixed oxide of General Formula (I) below and the particle is completely or partially coated with one or more fluorides.



30 (In the Formula (I), variables are each defined as follows: b is a number in the range of 0.25 to 0.45; c is a number in the range of 0.15 to 0.25; d = 1-b-c; (1+a) is in the range of 1.05 to 1.20; and $1.8+a \leq z \leq 2.2+a$). The present invention also relates to a formation method and a use of the particle of the invention.

[Scope of Claim]

[Claim 1]

A particle including a mixed oxide of General Formula (I) below that is completely or partially coated with one or more fluorides:



(In the Formula (I), variables are each defined as follows: b is a number in the range of 0.25 to 0.45; c is a number in the range of 0.15 to 0.25; $1.8 + a \leq z \leq 2.2 + a$; $d = 1 - b - c$; and $(1 + a)$ is in the range of 1.05 to 1.20).

[Claim 2]

10 The particle according to claim 1, wherein a molar ratio of fluoride to the sum of transition metals in the mixed oxide of General Formula (I) is in the range of 0.02 to 0.15.

[Claim 3]

15 The particle according to claim 1 or 2, wherein 5 % or more of an external surface of the particle is covered with fluoride.

[Claim 4]

The particle according to any one of claims 1 to 3, wherein fluoride is selected from LiF, NiF₂, CoF₂, MnF₂, and oxyfluoride of one or more metals selected from Ni, Mn, and Co.

20 [Claim 5]

The particle according to any one of claims 1 to 4, wherein an average diameter (D50) is in the range of 1 μm to 30 μm.

[Claim 6]

25 The particle according to any one of claims 1 to 5, wherein the particle is substantially spherical.

[Claim 7]

The particle according to any one of claims 1 to 6, wherein the particle includes Li₂MnO₃.

[Claim 8]

30 A use of the particle according to any one of claims 1 to 7 for manufacturing of an electrode.

[Claim 9]

An electrode comprising;

the particle according to claims 1 to 8, one or more carbon-containing materials having electric conductivity, and one or more binders.

[Claim 10]

5 The electrode according to claim 9, wherein the carbon-containing materials having electric conductivity are selected from graphite, carbon black, carbon nanotube, graphene, and a mixture of at least two of the above materials.

[Claim 11]

10 A use of the particle according to claims 1 to 7 and the electrode according to claim 9 or 10 in a battery.

[Claim 12]

 A manufacturing method of a battery using the particle according to claims 1 to 7 and the electrode according to claim 9 or 10.

[Claim 13]

15 A manufacturing method of an electrode using the particle according to claims 1 to 7 and the electrode according to claim 9 or 10.

[Claim 14]

A battery comprising;

20 an electrode material according to claims 1 to 7 and one or more electrodes according to claim 9 or 10.

[Claim 15]

A use of the battery according to claim 14, as a power source in a mobile device.

[Claim 16]

A use of the battery according to claim 14 or 15,

25 wherein the mobile device is an automobile, a motorcycle, an aircraft, a computer, a telephone, or a power tool.

[Claim 17]

A formation method of the particle according to claims 1 to 7 comprising a step of;

30 calcining of hydroxide, carbonate, oxyhydroxide, or basic carbonate of nickel, manganese, and cobalt in the presence of fluoride and one or more lithium salts.

[Claim 18]

The method according to claim 17,
 wherein the selected fluoride is ammonium fluoride or ammonium hydrogen difluoride.

[Description]

5 [Technical Field]

[0001]

The present invention relates to a particle including a mixed oxide of General Formula (I) below:

[0002]

10 $\text{Li}_{1+a}\text{Ni}_b\text{Co}_c\text{Mn}_d\text{O}_z$ (I)

[0003]

(In the Formula (I),

[0004]

variables are each defined as follows:

15 [0005]

b is a number in the range of 0.25 to 0.45;

[0006]

c is a number in the range of 0.15 to 0.25;

[0007]

20 $d = 1 - b - c$;

[0008]

$1.8 + a \leq z \leq 2.2 + a$;

[0009]

and $(1 + a)$ is in the range of 1.05 to 1.20),

25 [0010]

wherein the particle is completely or partially coated with one or more fluorides.

[0011]

The present invention also relates to a formation method of the particle of the invention. The present invention also relates to a use of the particle of the invention.

30 [Background of the Invention]

[0012]

Batteries with high storage capacitance at maximum working voltage are becoming increasingly important. In general, with batteries that operate on the basis of aqueous systems, it is difficult to obtain the desired capacitance.

[0013]

5 In lithium-ion batteries, charge transfer is ensured by non-aqueous solvents or by lithium ion in non-aqueous solvent systems, not by protons in hydrated form. Electrode materials have a specific role to play. The demands for cathode materials are particularly high.

[0014]

10 In many cases, these cathodes that operate at high voltages become problematic at high voltages—that is, at 4.3 V or higher, for example. Under these circumstances, oxidation of the electrolyte may occur, sometimes accompanied by its polymerization. In the most unfavorable cases, however, the polymer layer on the cathode functions as an insulator, leading to a drastic reduction in battery efficiency. Furthermore, many
15 cathode materials have been found to lack cycling stability at such voltages. This is because too much lithium is removed from the structure during the discharge (delithiation) process, which can lead to a collapse of the corresponding cathode material structure.

[0015]

20 Therefore, the object of the present invention is to provide material suitable for manufacturing a cathode having a long lifetime even at a high voltage—that is, at 4.3 V or higher, for example—and even after several significant delithiation processes in particular. An additional object of the present invention is to provide a formation method of a material that can be further processed into a corresponding cathode.
25 Another object of the present invention is to provide an electrode and a battery having a long lifetime even at a high voltage and even after several significant delithiation processes in particular.

[0016]

30 Therefore, we have found the particle defined at the beginning. In the present invention, the particle is referred to as “the particle of the invention”.

[0017]

In the present invention, the term “cycling” refers to the charging and the discharging of a battery or a cell.

[Content of the Invention]

[0018]

5 The present invention relates to one or more mixed oxides in General Formula (I) below:

[0019]



[0020]

10 (In the Formula (I),

[0021]

variables are each defined as follows:

[0022]

b is a number in the range of 0.25 to 0.45, preferably 0.37 to 0.42;

15 [0023]

c is a number in the range of 0.15 to 0.25, preferably 0.17 to 0.22;

[0024]

d = 1 - b - c;

[0025]

20 (1 + a) is in the range of 1.05 to 1.20, preferably 1.10 to 1.15;

[0026]

and $1.8 + a \leq z \leq 2.2 + a$,

[0027]

25 wherein the particle is completely or preferably partially coated with one or more fluorides.

[0028]

30 In one embodiment of the present invention, the particle of the invention includes two or more mixed oxides of General Formula (I). In another embodiment of the present invention, the particle of the invention includes exactly one mixed oxide of General Formula (I).

[0029]

In one embodiment of the present invention, the particle of the invention does not include any additional Mn-, Co- or Ni-containing oxide compound other than the mixed oxide of General Formula (I). In another embodiment of the present invention, the particle of the invention includes, for example, Li_2MnO_3 in the range of 5 mol% to 22 mol%, based on the compound of General Formula (I).

[0030]

In one embodiment of the present invention, the particle of the invention has a molar ratio of fluorine to the sum of the transition materials in the mixed oxide of General formula (I) in the range of 0.02 to 0.15.

[0031]

In one embodiment of the present invention, the material of the present invention substantially has a layered structure, which is an oxide formed of layers in other words. The structure of each crystal lattice can be measured by known methods—for example X-ray diffraction or electron diffraction—in particular X-ray powder diffraction.

[0032]

In one embodiment of the present invention, the particle of the invention, for example, may have a BET surface area in the range of $0.1 \text{ m}^2/\text{g}$ to $5 \text{ m}^2/\text{g}$, measured by nitrogen adsorption according to DIN ISO 9277:2003-05.

[0033]

In one embodiment of the present invention, the material of the invention may be doped with metal ions selected from Na, K, Rb, Cs, alkali earth metal, Ti, V, Cr, Fe, Cu, Ag, Zn, B, Al, Zr, Mo, W, Nb, Si, Ga, and Ge cations, with a total of 2 wt% or lower, preferably with a total of 1 wt% or lower, based on the overall compounds (I). In a favorable embodiment of the present invention, the material of the invention is not doped with any other metal ions.

[0034]

The term “doping” should be understood to signify an addition of one or more compounds having one or more cations selected from Na, K, Rb, Cs, alkali earth metal, Ti, V, Cr, Fe, Cu, Ag, Zn, B, Al, Zr, Mo, W, Nb, Si, Ga, and Ge cations in one or more steps during the formation of the material of the invention. Impurities introduced by minor contaminants of the starting material, like a sodium ion in the range of 0.1 ppm to

100 ppm based on the material of the invention, are not referred to as doping in the present invention.

[0035]

5 In one embodiment of the present invention, the particle of the invention includes sulfate or carbonate up to 1 wt% or lower. In another embodiment of the present invention, the material of the invention does not include a given detectable ratio of sulfate and/or carbonate.

[0036]

10 In one embodiment of the present invention, the compound of General Formula (I) is in the form of a crystalline powder.

[0037]

In one embodiment of the present invention, the particle of the invention is substantially spherical. In one embodiment of the present invention, the particle of the invention is a secondary aggregate of primary particles, which is substantially spherical.
15 The particle diameter (D50) of the secondary aggregate can be in the range of 1 μm to 30 μm , preferably 2 μm to 25 μm , more preferably 4 μm to 20 μm . In the present invention, the particle diameter (D50), for example, refers to the average particle diameter (weight average) that is measurable by evaluation with light scattering or an electron microscope.

[0038]

20 It should be understood that the term “substantially spherical” signifies that the particle of the invention is exactly spherical or has a circular shape, in which case the difference between the diameter at the largest point and the diameter at the smallest point does not exceed 10 %.

[0039]

25 The particle of the invention is completely or partially coated with one or more fluorides, which means that the particle of the invention includes coating material including one or more fluorides. The coating material is considered to be a part of the particle of the invention.

[0040]

30 In one embodiment of the present invention, 5 % or more of an external surface of the particle of the invention is coated with fluoride, indicating an average value. In a favorable embodiment, 10 % to 90 % of the external surface of the particle of the

invention is covered with fluoride. The coverage, for example, can be measured by photoelectron spectroscopy (XPS) or electron microscopy (SEM, TEM).

[0041]

5 Fluoride that coats the particle of the invention may be either crystalline or amorphous.

[0042]

In one embodiment of the present invention, fluoride is selected from LiF, NiF₂, CoF₂, MnF₂, possibly mixed fluoride of two or more metals selected from Mn, Ni, and Co, and oxyfluoride of one or more metals selected from Ni, Mn, and Co. Fluoride
10 selected from LiF, NiF₂, CoF₂, and MnF₂ is preferred.

[0043]

In one embodiment of the present invention, the particle of the invention is completely or partially coated with fluoride compounds, such as LiF, NiF₂, CoF₂, MnF₂, and two or more fluorides selected from oxyfluoride of one or more metals selected from
15 Ni, Mn, and Co.

[0044]

In one embodiment of the present invention, fluoride(s) is(are) arranged in the form of a single crystal, or amorphous or crystalline layer on the external surface of the particle of the invention.

20 [0045]

In one embodiment of the present invention, fluoride exists on the external surface, but it does not exist in pores of the particle of the invention. In another embodiment of the present invention, fluoride exists not only on the external surface, but also in pores of the particle of the invention, especially in pores derived from the
25 aggregation of the primary particles.

[0046]

A battery with a favorable property can be manufactured by using the particle of the invention. More particularly, a battery manufactured with the compound of General Formula (I) has a high discharge capacitance when cycled against lithium elements at 3.0
30 V to 4.6 V. It is observed that the battery of the invention shows only a very small drop (if it exists) in potential during the cycling. During the cycling against the lithium

elements at 3.0 V to 4.6 V, the average discharge potential should exceed 3.5 V in 25 mA/g of a current rate in the material of the invention.

[0047]

5 The present invention also provides an electrode including the particle of the invention.

[0048]

In the present invention, the particle of the invention may be referred to as material (A).

[0049]

10 In one embodiment of the present invention, the particle of the invention is used as a composite including carbon-containing materials having electric conductivity in the electrode of the invention. For example, the particle of the invention can be treated, or coated, with the carbon-containing materials having electric conductivity, for example. Such a composite is also a part of the main subject of the present invention.

15 [0050]

The carbon-containing material having electric conductivity, for example, can be selected from graphite, carbon black, carbon nanotube, graphene and a mixture of at least two of the aforementioned materials. In the present invention, the carbon-containing material having electric conductivity may be referred to as carbon (B), for short.

20

[0051]

In one embodiment of the present invention, the carbon-containing material having electric conductivity is carbon black. Carbon black, for example, can be selected from lamp black, furnace black, flame black, thermal black, acetylene black, and industrial black. Carbon black may include impurities, such as hydrocarbon (especially aromatic hydrocarbon), oxygen-containing compounds, or oxygen-containing groups (e.g., OH group). In addition, sulfur- or iron-containing impurities may exist in the carbon black.

25

[0052]

30 In a variation, the carbon-containing material having electric conductivity is a partially oxidized carbon black.

[0053]

In one embodiment of the present invention, the carbon-containing material having electric conductivity includes carbon nanotubes. Carbon nanotubes (CNTs, for short), for example, single-walled carbon nanotubes (SWCNTs) and preferably multi-walled carbon nanotubes (MWCNTs) are known. The formation method and some
5 properties thereof, for example, are described in the study conducted by A. Jess et al. (Chemie Ingenieur Technik 2006, 78, 94–100).

[0054]

In one embodiment of the present invention, a diameter of carbon nanotubes is in the range of 0.4 nm to 50 nm, preferably 1 nm to 25 nm.

10 [0055]

In one embodiment of the present invention, a length of carbon nanotubes is in the range of 10 nm to 1 μ m, preferably 100 nm to 500 nm.

[0056]

Carbon nanotubes can be formed with known methods. For example, a volatile
15 carbon compound (e.g., methane or carbon monoxide), acetylene or ethylene, or a mixture of volatile carbon compounds (e.g., a combined gas) can be decomposed in the presence of one or more reductants (e.g., hydrogen and/or additional gas like nitrogen). Another suitable gaseous mixture is a mixture of carbon monoxide and ethylene. A suitable temperature for decomposition, for example, is in the range of 400 °C to 1000 °C,
20 preferably 500 °C to 800 °C. A suitable pressure condition for decomposition, for example, is in the range of standard pressure to 100 bar, preferably up to 10 bar.

[0057]

For example, single- or multi-walled carbon nanotubes can be obtained by the decomposition of carbon compounds during light arc discharge, specifically in the
25 presence or absence of a decomposing catalyst.

[0058]

In one embodiment, the decomposition of volatile carbon-containing compound(s) is(are) performed in the presence of a decomposing catalyst (e.g., Fe, Co or preferably Ni).

30 [0059]

In the present invention, a graphene is understood to signify the same or almost the same two-dimensional hexagonal carbon crystal having a structural similarity to a single graphene layer.

[0060]

5 In one embodiment of the present invention, the weight ratio of the particle of the invention to the carbon-containing material having electric conductivity in the electrode of the invention is in the range of 200:1 to 5:1, preferably 100:1 to 10:1.

[0061]

10 An additional embodiment of the present invention is an electrode, specifically a cathode (including the particle of the invention, one or more carbon-containing materials having electric conductivity, and one or more binders). The particle of the invention, one or more carbon-containing materials having electric conductivity, and one or more binders are combined to form an electrode material, which also is a part of the subject matter of the present invention.

15 [0062]

The particle of the invention and the carbon-containing material having electric conductivity are as described above.

[0063]

20 A suitable binder is preferably selected from organic (co)polymers. A suitable (co)polymer (i.e. homopolymer or copolymer), for example, can be selected from the (co)polymer obtained by anionic, catalytic or free-radical (co)polymerization, specifically polyethylene, polyacrylonitrile, polybutadiene, polystyrene, as well as the (co)polymer of two or more comonomers selected from ethylene, propylene, styrene, (meta)acrylonitrile, and 1,3-butadiene. Polypropylene is also suitable. Polyisoprene and polyacrylate are
25 additionally suitable. Polyacrylonitrile is preferable.

[0064]

In the present invention, polyacrylonitrile is understood to signify not only polyacrylonitrile homopolymer, but also copolymer of acrylonitrile and 1,3-butadiene or styrene. Polyacrylonitrile homopolymer is preferred.

30 [0065]

In the present invention, polyethylene not only signifies homopolyethylene, but also 50 mol% or more of co-polymerized ethylene and copolymer of ethylene including

50 mol% or less of one or more additional comonomers like α -olefin (e.g., propylene, butylene (1-butene), 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-pentene; isobutene and aromatic vinyl like styrene; as well as (methyl) acrylic acid, vinyl acetate, vinyl propionate, C₁-C₁₀-alkyl ester of (methyl) acrylic acid, especially methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, 2-ethylhexyl acrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, and also maleic acid, maleic anhydride and itaconic anhydride). Polyethylene can be HDPE or LDPPE.

[0066]

In the present invention, polypropylene not only signifies homopolypropylene, but also 50 mol% or more of co-polymerized polypropylene and copolymer of polypropylene including 50 mol% or less of one or more additional comonomers(e.g., ethylene and α -olefin like butylene, 1-hexene, 1-decene, 1-dodecene and 1-pentene). Polypropylene is preferably isotactic or substantially isotactic polypropylene.

[0067]

In the present invention, polystyrene signifies not only the homopolymer of styrene, but also a copolymer of acrylonitrile, 1,3-butadiene, (methyl) acrylic acid, C₁-C₁₀-alkyl ester of (methyl) acrylic acid, divinylbenzene, especially 1,3-divinylbenzene, 1,2-diphenyl ethylene and α -methylstyrene.

[0068]

Another favorable binder is polybutadiene.

[0069]

Other suitable binders are selected from polyethylene oxide (PEO), cellulose, carboxymethyl cellulose, polyimide, and polyvinyl alcohol.

[0070]

In one embodiment of the present invention, the binder is selected from these (co)polymers having an average molecular weight M_w in the range of 50,000 g/mol to 1,000,000 g/mol, preferably up to 500,000 g/mol.

[0071]

The binder may be a crosslinked or non-crosslinked (co)polymer.

[0072]

In a particularly favorable embodiment of the present invention, the binder is selected from halogenated (co)polymers, especially from fluorinated (co)polymers. Halogenated or fluorinated (co)polymers are understood to signify these (co)polymers containing one or more co-polymerized comonomers having one or more halogen elements or one or more fluorine elements per molecule, preferably having two or more halogen elements or two or more fluorine elements per molecule.

[0073]

Examples of the binders include polyvinyl chloride, polyvinylidene chloride, polytetrafluoroethylene, polyvinylidene fluoride (Pvdf), tetrafluoroethylene-hexafluoropropylene copolymer, vinylidene fluoride-tetrafluoroethylene copolymer (PVdF-HFP), vinylidene fluoride-tetrafluoroethylene copolymer, perfluoroalkyl vinyl ether copolymer, ethylene-tetrafluoroethylene copolymer, vinylidene fluoride-chlorotrifluoroethylene copolymer, and ethylene-chlorofluoroethylene copolymer.

[0074]

Suitable binders are, in particular, polyvinyl alcohol and halogenated (co)polymer (e.g., polychlorinated vinyl or polychlorinated vinylidene), fluorinated (co)polymers (e.g., polyfluorinated vinyl), and polyfluorinated vinylidene and polytetrafluoroethylene.

[0075]

In one embodiment, the carbon-containing material having electric conductivity in the electrode of the invention is selected from graphite, carbon black, carbon nanotube, graphene, and a mixture of at least two of the above materials.

[0076]

In one embodiment of the present invention, the electrode material of the invention includes:

[0077]

(A) the particle of the invention in the range of 60 wt% to 98 wt%, preferably 70 wt% to 96 wt%,

[0078]

(B) carbon-containing material having electric conductivity in the range of 1 wt% to 25 wt%, preferably 2 wt% to 20 wt%, and

[0079]

(C) binder in the range of 1 wt% to 20 wt%, preferably 2 wt% to 15 wt%.

[0080]

[0081]

5 The geometry of the electrode of the invention can be selected from wide ranges. The electrode of the invention, for example, is preferably formed in a thin layer with a thickness in the range of 10 μm to 250 μm , preferably 20 μm to 130 μm .

[0082]

10 In one embodiment of the present invention, the electrode of the invention includes foil (e.g., metal foil, especially aluminum foil, or polymer film such as polyester film, which can be untreated or siliconized).

[0083]

15 The present invention further provides for the use of the electrode material or the electrode of the invention in a battery. The present invention also provides a manufacturing method of a battery using the electrode material or the electrode of the invention. The present invention provides a battery including one or more electrode materials or electrodes of the invention as well.

[0084]

20 By definition, the electrode in the battery of the invention functions as a cathode. The battery of the invention includes a counter electrode, defined as an anode in the present invention, which can be, for example, a carbon anode, specifically a graphite anode, a lithium anode, a silicon anode or a lithium titanate anode.

[0085]

The battery of the invention, for example, can be a battery or an accumulator.

25 [0086]

The battery of the invention can further include additional components (e.g., a conductive salt, a non-aqueous solvent, a separator, and/or an output conductor such as those manufactured with metal or alloy) as well as cable connection part and housing in addition to the anode or the electrode of the invention.

30 [0087]

In one embodiment of the invention, the battery of the invention includes one or more non-aqueous solvents selected from preferably polymer, cyclic or acyclic ether,

cyclic and acyclic acetal, and cyclic or acyclic organic carbonate, which can be in liquid or solid form at room temperature.

[0088]

5 Examples of suitable polymers are specifically polyalkylene glycol, preferably poly-C₁-C₄-alkylene glycol, and polyethylene glycol in particular. These polyethylene glycols can include 20 mol% or less of one or more C₁-C₄-alkylene glycols in a co-polymerized form. Polyalkylene glycols are preferably polyalkylene glycols that are double-capped with methyl or ethyl.

[0089]

10 A molecular weight M_w of suitable polyalkylene glycol and especially suitable polyethylene glycol can be 400 g/mol or more.

[0090]

A molecular weight M_w of suitable polyalkylene glycol and especially suitable polyethylene glycol can be 5,000,000 g/mol or less, preferably 2,000,000 g/mol or less.

15 [0091]

Examples of suitable acyclic ethers are diisopropyl ether, di-n-butyl ether, 1,2-dimethoxyethane, 1,2-diethoxyethane, and in those, 1,2-dimethoxyethane is preferable.

[0092]

Examples of suitable cyclic ethers are tetrahydrofuran and 1,4-dioxane.

20 [0093]

Examples of suitable acyclic acetals are dimethoxymethane, diethoxymethane, 1,1-dimethoxymethane and 1,1-diethoxymethane.

[0094]

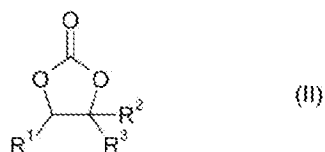
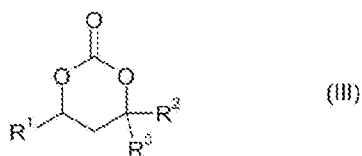
Example of suitable cyclic acetals are 1,3-dioxane and specifically 1,3-dioxolane.

25 [0095]

Examples of suitable acyclic organic carbonates are dimethyl carbonate, ethyl methyl carbonate, and diethyl carbonate.

[0096]

30 Examples of suitable cyclic organic carbonates are compounds of General Formulas (II) and (III) below:



[0097]

[0098]

(In the formula,

5 [0099]

R^1 , R^2 , and R^3 may be the same or different, and are selected from hydrogen and C_1 - C_4 -alkyl (e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, and tert-butyl). In this case, it is preferable that neither R^2 nor R^3 is a tert-butyl).

[0100]

10 In a particularly favorable embodiment, R^1 is methyl and R^2 and R^3 are each hydrogen, or R^1 , R^2 , and R^3 are each hydrogen.

[0101]

Another preferable cyclic organic carbonate is vinylene carbonate of formula (IV) below.



15

[0102]

[0103]

Solvent(s) is(are) preferably used in the anhydrous state (i.e. a state with a water content in the range of 1 ppm to 30 ppm, wherein ppm refers to weight ppm), which can
20 be, for example, measured by Karl Fischer titration.

[0104]

The battery of the invention further includes one or more conductive salts. The suitable conductive salts are especially lithium salts. Examples of suitable lithium salts include salts of LiPF_6 , LiBF_4 , LiClO_4 , LiASF_6 , LiCF_3SO_3 , $\text{LiC}(\text{C}_n\text{F}_{2n+1}\text{SO}_2)_3$, lithium imide (e.g., $\text{LiN}(\text{C}_n\text{F}_{2n+1}\text{SO}_2)_2$, where n is an integer in the range 1 to 20), $\text{LiN}(\text{SO}_2\text{F})_2$, Li_2SiF_6 , LiSbF_6 , LiAlCl_4 , and the general formula $(\text{C}_n\text{F}_{2n+1}\text{SO}_2)_m\text{XLi}$. In this case, m is as defined below:

[0105]

$m = 1$ when X is selected from oxygen and sulfur,

[0106]

10 $m = 2$ when X is selected from nitrogen and phosphorus,

[0107]

and $m = 3$ when X is selected from carbon and silicon.

[0108]

The preferable conductive salts are selected from $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, LiPF_6 , LiBF_4 and LiClO_4 . Moreover, LiPF_6 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ are particularly preferred.

[0109]

In one embodiment of the present invention, the battery of the invention includes one or more separators that mechanically separate the electrodes. Suitable separators are polymer films, especially porous polymer films that are not reactive to metal lithium. Particularly suitable materials for separators are polyolefins, especially porous polyethylene in the film form and porous polypropylene in the film form.

[0110]

Separators made of polyolefin, especially polyethylene or polypropylenes, can have porosity in the range of 35 % to 45 %. The suitable pore diameter, for example, is in the range of 30 nm to 500 nm.

[0111]

In another embodiment of the present invention, the separator can be selected from a PET nonwoven fabric filled with inorganic particles. Such a separator has a porosity in the range of 40 % to 55 %. Suitable pore diameter, for example, is in the range of 80 nm to 750 nm.

[0112]

In another embodiment of the present invention, a separator made of fiberglass paper is selected.

[0113]

The battery of the invention further includes an housing that can have any desired
5 shape, e.g. cubic or cylindrical disk form. In a variation, the housing to be used is a metal foil that is elaborately treated as pouch.

[0114]

The battery of the invention provides a high electrical potential and is effective for its high energy density and favorable stability. More specifically, the battery of the
10 invention has high discharge capacitance when cycled against lithium elements at more than 4.3 V. It is observed that the battery of the invention shows only a very small drop (if exists) in potential during the cycling. During the cycling at 2.5 V to 4.55 V, the average discharge potential should exceed 3.5 V in 95 mA/g of a current rate in the material of the invention.

15 [0115]

The batteries of the invention can be combined with each other, and they can be, for example, connected in series or in parallel. Series connection is preferred.

[0116]

The present invention further provides a use of the battery of the invention, especially in mobile devices. Examples of mobile devices include motor vehicles (e.g.,
20 automobiles, motorcycles, aircrafts, or water vehicles such as boats or ships). Other examples of mobile devices include manually operated devices (e.g., computers [especially laptop devices], telephones, or power tools in the field of construction [especially drills, battery-powered drills or battery-powered tackers]).

25 [0117]

The use of the battery of the invention in the unit offers an advantage of a particularly high-volume energy density.

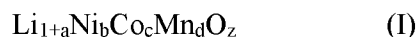
[0118]

The present invention also provides a manufacturing method of a battery
30 comprising:

[0119]

(A) the particle including a mixed oxide of General Formula (I) below that is completely or preferably partially coated with one or more fluorides:

[0120]



5 [0121]

(In the Formula (I),

[0122]

variables are each defined as follows:

[0123]

10 b is a number in the range of 0.25 to 0.45, preferably 0.37 to 0.42;

[0124]

c is a number in the range of 0.15 to 0.25, preferably 0.17 to 0.22;

[0125]

$$d = 1 - b - c;$$

15 [0126]

(1 + a) is in the range of 1.05 to 1.20, preferably 1.10 to 1.15;

[0127]

$$1.8 + a \leq z \leq 2.2 + a),$$

[0128]

20 (B) one or more carbon-containing materials having electric conductivity, and

[0129]

(C) one or more binders

[0130]

are mixed in one or more steps,

25 [0131]

in some cases; (D) these are applied to one or more metal foils or polymer films.

[0132]

The particle of the invention, carbon-containing material or the carbon (B), and the binder (C) are as defined above.

30 [0133]

Mixing may be performed in one or more steps.

[0134]

In a variation of the method according to the present invention, the particle of the invention, the carbon (B), and the binder (C) are mixed in a single step—for example in a mill, especially in a ball mill. The obtained mixture is then applied in a thin layer form to a support (e.g., the metal foil or polymer film (D)). The support can be removed before or during the integration into the battery. In another variation, the support is retained.

[0135]

In another variation of the method according to the present invention, the particle of the invention, the carbon (B), and the binder (C) are mixed in several steps, for example in a mill, especially in a ball mill. The particle of the invention and the carbon (B) can be mixed first. The mixture is combined with the binder (C) later. The obtained mixture is then applied in a thin layer form to a support (e.g., the metal foil or polymer film (D)). The support can be removed before or during the integration into the battery. In another variation, the support is not removed.

[0136]

In a variation of the method according to the present invention, the particle of the invention, the carbon (B) and the binder (C) are mixed in water or organic solvent (e.g., N-methylpyrrolidone or acetone). The obtained suspension is then applied in a thin layer form to a support (e.g., the metal foil or polymer film (D)), and the solvent is removed by heat treatment. The support can be removed before or during the integration into the battery. In another variation, the support is not removed.

[0137]

In the present invention, the thin layer can have a thickness in the range of 2 μm to 25 μm , for example.

[0138]

To improve the mechanical stability, the electrodes can be thermally or preferably mechanically treated (e.g., by pressing or calendaring).

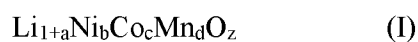
[0139]

The method according to the present invention is highly suitable for the formation of the electrode material of the invention and the electrodes that can be obtained from the electrode material.

[0140]

The present invention also provides a composite including the particle that particle is completely or partially coated with one or more fluorides, which includes one or more mixed oxides of General Formula (I) below, and one or more carbon-containing material having electric conductivity (also called as the carbon (B)):

5 [0141]



[0142]

(In the Formula,

[0143]

10 variables are each defined as follows:

[0144]

b is a number in the range of 0.25 to 0.45, preferably 0.37 to 0.42;

[0145]

c is a number in the range of 0.15 to 0.25, preferably 0.17 to 0.22;

15 [0146]

$d = 1 - b - c$;

[0147]

$(1 + a)$ is in the range of 1.05 to 1.20, preferably 1.10 to 1.15);

[0148]

20 $1.8 + a \leq z \leq 2.2 + a$),

[0149]

In the composite of the invention, the particle of the invention is treated (e.g., coated) with the carbon (B).

[0150]

25 In one embodiment of the invention, the particle of the invention and the carbon (B) are present in a weight ratio of 98:1 to 12:5, preferably 48:1 to 7:2, in the composite of the invention.

[0151]

30 The composite of the invention is particularly suitable for the formation of the electrode material of the invention. The manufacturing method is described above and is a part of the main subject of the invention.

[0152]

The present invention also provides the manufacturing method of the particle of the invention, which is also called a synthesis method according to the present invention. This method according to the present invention can be performed by calcining hydroxide, carbonate, oxyhydroxide, or basic carbonate of nickel, manganese, and cobalt in the presence of fluorides, and one or more lithium salts.

[0153]

Specifically, the procedure consists of first forming a precursor including the transition metals Ni, Co and Mn in a desired ratio, possibly including dopant(s), and then calcining it as described above. In a preferable variation, the procedure involves forming the precursor with the precipitation of a mixed carbonate or mixed oxyhydroxide, which may be basic. In the second step, mixing is first performed with a lithium compound, preferably with at least one lithium salt (e.g., with lithium hydroxide), or more preferably with Li_2CO_3 and one or more fluorides. Next, calcination is performed (e.g., under air flow) preferably at 875 °C to 950 °C for 3 hours to 12 hours.

[0154]

In one embodiment of the synthesis method, the calcination is performed at a maximum temperature in the range of 875 °C to 950 °C.

[0155]

In one embodiment of the present invention, the selected fluoride is ammonium fluoride, ammonium hydrogen fluoride, or a mixture of ammonium fluoride and ammonium hydrogen difluoride.

[0156]

The present invention will be explained with a reference of applicable examples below.

[Detailed Description of the Invention]

[0157]

General remarks: Numbers expressed in % are weight%, unless otherwise specified.

[0158]

The amount of dissolved salt is based on the number of kg of solution.

[0159]

I. Formation of Starting Materials

[0160]

I.1. Lithium Carbonate

[0161]

Commercial Li_2CO_3 was dried at 105°C for 16 hours before use, and particles
5 with a diameter of more than $50\text{ }\mu\text{m}$ were removed by sieving.

[0162]

I.2. Removal of Hydroxide (precursor)

[0163]

After solutions of NiSO_4 , CoSO_4 and MnSO_4 and aqueous solutions of ammonia
10 and NaOH were mixed by intensely stirring them at 55°C with at a feed rate
corresponding to 3 hours to 18 hours of residence time in the continuous reactor,
 $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ was added. Spherical particles of $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ were
precipitated. The resulting mixed metal oxide/hydroxides were filtered out.

[0164]

15 II. Formation of Material of the Invention and Material for Comparison

[0165]

II.1. Formation of Material C-M.1 for Comparison

[0166]

NCM-424, $\text{Li}/\text{metal} = 1.13$

20 [0167]

$\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ was dried under the air at 15°C for 16 hours.

[0168]

In an agate mortar, 6.34 g of Li_2CO_3 was initially filled according to I.1 and then
mixed well with 13.85 g of a dried $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ for 20 minutes. Thereafter, the
25 obtained mixture was calcined in a muffle furnace under the air with the execution of the
following temperature profile:

[0169]

First, the temperature per each case was increased from the room temperature to
 350°C by $3^\circ\text{C}/\text{min}$. The material was heated at 350°C for 4 hours. Thereafter, the
30 temperature was increased by 675°C . During this process, the temperature per each
case was increased by $3^\circ\text{C}/\text{min}$.

[0170]

The material was heated at 675 °C for 4 hours. The temperature was increased to 900 °C. During this process, the temperature per each case was increased by 3 °C/min.
[0171]

5 The calcination was performed at 900 °C for 6 hours. Through the overall heating and calcination, the air was passed through with the muffle furnace (100 l/h).
[0172]

After the completion of calcination, the material was cooled down at a cooling rate of 0.5 K/min. The comparison material C-M.1 of present invention was obtained with this process, and kept under the nitrogen before any additional use.
10 [0173]

II.2. Formation of Material M.2 of the Invention

[0174]

NCM-424, Li/metal = 1.13, F of 0.02 mol

[0175]

15 In the agate mortar, 6.34 g of Li_2CO_3 was initially filled according to I.1 and then mixed well with 13.85 g of the dried $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ for 10 minutes. After that, 0.13 g of NH_4F was added and the mixture was combined for 10 minutes. Thereafter, the obtained mixture was calcined in a muffle furnace under the air with the execution of the following temperature profile:

20 [0176]

First, the temperature per each case was increased from the room temperature to 350 °C by 3°C/min. The material was heated at 350 °C for 4 hours. Thereafter, the temperature was increased by 675 °C. During this process, the temperature per each case was increased by 3 °C/min.

25 [0177]

The material was heated at 675 °C for 4 hours. The temperature was increased to 900 °C. During this process, the temperature per each case was increased by 3 °C/min.
[0178]

30 The calcination was performed at 900 °C for 6 hours. Through the overall heating and calcination, the air was passed through with the muffle furnace (100 l/h).
[0179]

After the completion of calcination, the material was cooled down at a cooling rate of 0.5 K/min. The material M.2 of the invention was obtained with this process, and kept under the nitrogen before any additional use.

[0180]

5 II.3. Formation of Material M.3 of the Invention

[0181]

NCM-424, Li/metal = 1.13, F of 0.1 mol

[0182]

10 In the agate mortar, 6.34 g of Li_2CO_3 was initially filled according to I.1 and then mixed well with 13.85 g of the dried $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ for 10 minutes. After that, 0.57 g of NH_4F was added and the mixture was combined for 10 minutes. Thereafter, the obtained mixture was calcined in a muffle furnace under the air with the execution of the following temperature profile:

[0183]

15 First, the temperature per each case was increased from the room temperature to 350 °C by 3 °C/min. The material was heated at 350 °C for 4 hours. Thereafter, the temperature was increased by 675 °C. During this process, the temperature per each case was increased by 3 °C/min.

[0184]

20 The material was heated at 675 °C for 4 hours. The temperature was increased to 900 °C. During this process, the temperature per each case was increased by 3 °C/min.

[0185]

The calcination was performed at 900 °C for 6 hours. Through the overall heating and calcination, the air was passed through with the muffle furnace (100 l/h).

25 [0186]

After the completion of calcination, the material was cooled down at a cooling rate of 0.5 K/min. The material M.3 of the invention was obtained with this process, and kept under the nitrogen before any additional use.

[0187]

30 II.4. Formation of Material M.4 of the Invention

[0188]

NCM-424, Li/metal = 1.13, F of 0.2 mol

[0189]

In the agate mortar, 6.34 g of Li_2CO_3 was initially filled according to I.1 and then mixed well with 13.85 g of the dried $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ for 10 minutes. After that, 1.14 g of NH_4F was added and the mixture was combined for 10 minutes. Thereafter, the obtained mixture was calcined in a muffle furnace under the air with the execution of the following temperature profile:

[0190]

First, the temperature per each case was increased from the room temperature to $350\text{ }^\circ\text{C}$ by $3\text{ }^\circ\text{C/min}$. The material was heated at $350\text{ }^\circ\text{C}$ for 4 hours. Thereafter, the temperature was increased by $675\text{ }^\circ\text{C}$. During this process, the temperature per each case was increased by $3\text{ }^\circ\text{C/min}$.

[0191]

The material was heated at $675\text{ }^\circ\text{C}$ for 4 hours. The temperature was increased to $900\text{ }^\circ\text{C}$. During this process, the temperature per each case was increased by $3\text{ }^\circ\text{C/min}$.

[0192]

The calcination was performed at $900\text{ }^\circ\text{C}$ for 6 hours. Through the overall heating and calcination, the air was passed through with the muffle furnace (100 l/h).

[0193]

After the completion of calcination, the material was cooled down at a cooling rate of 0.5 K/min . The material M.4 of the invention was obtained with this process, and kept under the nitrogen before any additional use.

[0194]

II.5. Formation of Material M.5 of the Invention

[0195]

NCM-424, Li/metal = 1.2, F of 0.1 mol

[0196]

In the agate mortar, 6.74 g of Li_2CO_3 was initially filled according to I.1 and then mixed well with 13.85 g of the dried $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ for 10 minutes. After that, 0.57 g of NH_4F was added and the mixture was combined for 10 minutes. Thereafter, the obtained mixture was calcined in a muffle furnace under the air with the execution of the following temperature profile:

[0197]

First, the temperature per each case was increased from the room temperature to 350 °C by 3°C/min. The material was heated at 350 °C for 4 hours. Thereafter, the temperature was increased by 675 °C. During this process, the temperature per each case was increased by 3 °C/min.

5 [0198]

The material was heated at 675 °C for 4 hours. The temperature was increased to 900 °C. During this process, the temperature per each case was increased by 3 °C/min.

[0199]

The calcination is performed at 900 °C for 6 hours. Through the overall heating and calcination, the air was passed through with the muffle furnace (100 l/h).

[0200]

After the completion of calcination, the material was cooled down at a cooling rate of 0.5 K/min. The material M.5 of the invention was obtained with this process, and kept under the nitrogen before any additional use.

15 [0201]

III. Electrochemical Analysis:

[0202]

III.1. The Analysis of the Invention as the Half Cell

[0203]

20 To form the cathode (Kat-hz-2), the materials below were mixed in a screwtop container:

[0204]

88 % of M.2

[0205]

25 6 % of the polyvinylidene difluoride ("PVdF") (commercially available from Arkema Group, under the name "Kynar Flex® 2801")

[0206]

3 % of the carbon black with the BET surface area of 62 m²/g (commercially available from Timcal, under the name "Super P Li")

30 [0207]

3 % of the graphite (commercially available from Timcal, under the name "KS6")

[0208]

A sufficient amount of N-methylpyrrolidone (NMP) was added while stirring, and the mixture was stirred with Ultra-Turrax® until a smooth paste without lumps was obtained.

5 [0209]

The obtained paste was knife-coated with aluminum foils of thickness 20 μm . The paste was dried for 16 hours at 120 °C in a vacuum drying cabinet. The loading after the drying process was 1.1 mg/cm². After drying, a circular disk part was punched into an area of 3 cm². With this process, the cathode (Kat-hz-2) of the invention was
10 obtained.

[0210]

Anode (An-hz-1): A lithium disk was punched into an area of 3 cm². With this process, the anode (An-hz-1) of the invention was obtained.

[0211]

15 The test cell to be used was a setup according to Fig. 1. In a battery assembly, it was assembled from the bottom to the top based on a schematic diagram of Fig. 1. The anode is located on the very top, and the cathode is located at the very bottom in Fig. 1.

[0212]

Numbers in Fig. 1 indicate the following:

20 [0213]

1, 1' A bolt

[0214]

2, 2' A nut

[0215]

25 3, 3' Sealing ring (2 per each case; the second sealing ring that is slightly smaller per each case is not displayed on Fig. 1)

[0216]

4 Helical springs

[0217]

30 5 Output conductor made out of stainless steel

[0218]

6 Housing

[0219]

The cathode (Kat-hz-2) was applied to a bolt on the cathode side 1'. After application, the separator composed of glass fibers (thickness of 0.5 mm) was placed on the cathode (Kat-hz-2). A small amount of the electrolyte was set to flow. The anode
 5 (An-hz-1) was placed on a wet separator. The used output conductor 5 was a stainless steel plate that was applied to the anode directly. Later, seals 3 and 3' were added and fixed with a screw, together with the test cell. By the use of the helical springs 4 made of a steel spring and the pressure created by the screw connection with the anode bolt 1, the electronic contact was assured.

10 [0220]

The battery of the invention was similarly manufactured based on the material M.3 through M.5 or the comparison material C-M.1.

[0221]

The used electrolyte was a 1 M solution of LiPF_6 in ethyl methyl
 15 carbonate/diethyl carbonate (volume ratio of 1:1).

[0222]

With this process, the battery of the invention that was tested at 25 °C, especially with a potential range of the battery: 3.0 V through 4.6 V, was obtained.

[0223]

20 The following cycling programs were performed:

[0224]

The charge 0.1 C and the discharge 0.1 C 2x

[0225]

The charge 0.2 C and the discharge 0.2 C 5x

25 [0226]

The charge 0.2 C and the discharge 0.4 C 1x

[0227]

The charge 0.2 C and the discharge 0.8 C 1x

[0228]

30 The charge 0.2 C and the discharge 1.6 C 1x

[0229]

The charge 0.2 C and the discharge 3.2 C 1x

[0230]

The charge 0.2 C and the discharge 6.4 C 1x

[0231]

The charge 0.1 C and the discharge 0.1 C 2x (or 1x)

5 [0232]

The charge 0.2 C and the discharge 0.2 C 5x

[0233]

The charge 0.2 C and the discharge 1 C 1x

[0234]

10 The charge 0.4 C and the discharge 1 C 1x

[0235]

The charge 1 C and the discharge 1 C 53x

[0236]

The charge 0.2 C and the discharge 0.2 C 3x

15 [0237]

The charge 1 C and the discharge 1 C 53x

[0238]

The charge 0.2 C and the discharge 0.2 C 3x

[0239]

20 At the time of a fast discharge, the loss in capacitance in the half cell was extremely small.

[0240]

III.2. The Analysis of the Present Invention as the Full Cell

[0241]

25 Formation of the Full Cell:

[0242]

To form the cathode (Kat-vx-2), the materials below were mixed in a screwtop container:

[0243]

30 85.2 % of M.2

[0244]

8.3 % of the polyvinylidene difluoride ("PVdF") (commercially available from Arkema Group, under the name "Kynar Flex® 2801")

[0245]

3.2 % of the carbon black with the BET surface area of 62 m²/g (commercially available from Timcal, under the name "Super P Li")

[0246]

3.3 % of the graphite (commercially available from Timcal, under the name "KS6")

[0247]

A sufficient amount of N-methylpyrrolidone (NMP) was added while stirring, and the mixture was stirred with Ultra-Turrax® until a smooth paste without lumps was obtained.

[0248]

The obtained paste was knife-coated with aluminum foils of thickness 20 µm. The paste was dried for 16 hours at 120 °C in a vacuum drying cabinet. The loading after the drying process was 1.1 mg/cm². After drying, a circular disk part was punched into an area of 3 cm². With this process, the cathode (Kat-hz-2) of the invention was obtained.

[0249]

An electrochemical test was conducted at "Swagelok" cells. The used electrolyte was a 1 M solution of LiPF₆ in ethyl methyl carbonate/ethylene carbonate (volume ratio of 1:1).

[0250]

Separators: glass fibers; the anode: graphite; the temperature: 25°C; a potential range of the battery: 2.50 V through 4.525 V; a cycling program: 0.1 C (the first and the second cycles), 0.5 C (the third cycle), 1 C = 190 mA/g.

[0251]

Results:

[0252]

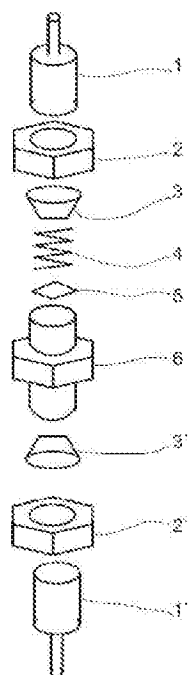
The loss in capacitance in the full cell according to Table 1 was calculated as follows: the difference between the average volume after 70 cycles and the average

volume after 2 cycles is divided by the average volume after 70 cycles and multiplied by 100 to obtain a loss in capacitance ("fading").

[0253]

Table 1	
The Results of Loss in Capacitance in the Analysis of the Full Cell	
The Used Cathode	Loss in Capacitance (%)
(kat-vz-2)	10
(kat-vz-3)	8

- 5 Fig. 1: a schematic structure of the battery discomposed for the test of the mixture of the present invention



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(54) 발명의 명칭 입자, 이의 제조 방법 및 이의 용도

(57) 요약

본 발명은 하기 일반식 (I) 의 혼합 산화물을 포함하는 입자로서, 하나 이상의 플루오라이드로 전체 또는 부분 코팅되는 입자에 관한 것이다:



[식 중,

변수는 각각 하기와 같이 정의됨:

b 는 0.25 내지 0.45 범위의 수이고,

c 는 0.15 내지 0.25 범위의 수이고,

d = 1 - b - c 이고,

(1+a) 는 1.05 내지 1.20 범위이고,

1.8 + a ≤ z ≤ 2.2 + a 임].

본 발명은 또한 본 발명에 따른 입자의 제조 방법 및 본 발명에 따른 입자의 용도에 관한 것이다.

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특허청구의 범위

청구항 1

하기 일반식 (I) 의 혼합 산화물을 포함하는 입자로서, 하나 이상의 플루오라이드로 전체 또는 부분 코팅되는 입자:



[식 중,

변수는 각각 하기와 같이 정의됨:

b 는 0.25 내지 0.45 범위의 수이고,

c 는 0.15 내지 0.25 범위의 수이고,

$1.8 + a \leq z \leq 2.2 + a$ 이고,

$d = 1 - b - c$ 이고,

(1+a) 는 1.05 내지 1.20 범위임].

청구항 2

제 1 항에 있어서, 일반식 (I) 의 혼합 산화물 중 전이 금속의 함에 대한 플루오라이드의 몰비가 0.02 내지 0.15 범위인 입자.

청구항 3

제 1 항 또는 제 2 항에 있어서, 입자 외부 표면의 5% 이상이 플루오라이드로 커버되는 입자.

청구항 4

제 1 항 내지 제 3 항 중 어느 한 항에 있어서, 플루오라이드가 LiF, NiF₂, CoF₂, MnF₂, 및 Ni, Mn 및 Co 에서 선택되는 하나 이상 금속의 옥시플루오라이드에서 선택되는 입자.

청구항 5

제 1 항 내지 제 4 항 중 어느 한 항에 있어서, 평균 직경 (D50) 이 1 내지 30 μm 범위인 입자.

청구항 6

제 1 항 내지 제 5 항 중 어느 한 항에 있어서, 본질적으로 구체인 입자.

청구항 7

제 1 항 내지 제 6 항 중 어느 한 항에 있어서, Li₂MnO₃ 을 포함하는 입자.

청구항 8

전극 제조를 위한, 제 1 항 내지 제 7 항 중 어느 한 항에 따른 입자의 용도.

청구항 9

제 1 항 내지 제 8 항 중 어느 한 항에 따른 입자, 하나 이상의 전기 전도성, 탄소함유 물질 및 하나 이상의 결합제를 포함하는 전극.

청구항 10

제 9 항에 있어서, 전기 전도성, 탄소함유 물질이 그래피트, 카본 블랙, 탄소 나노튜브, 그래핀 또는 상술한 물질 중 2 개 이상의 혼합물에서 선택되는 전극.

청구항 11

전지에서, 제 1 항 내지 제 7 항 중 어느 한 항에 따른 입자 또는 제 9 항 또는 제 10 항에 따른 전극의 용도.

청구항 12

제 1 항 내지 제 7 항 중 어느 한 항에 따른 입자 또는 제 9 항 또는 제 10 항에 따른 전극을 사용하는 전지를 제조하는 방법.

청구항 13

제 1 항 내지 제 7 항 중 어느 한 항에 따른 입자 또는 제 9 항 또는 제 10 항에 따른 전극을 사용하는 전극을 제조하는 방법.

청구항 14

제 1 항 내지 제 7 항 중 어느 한 항에 따른 전극 물질 또는 제 9 항 또는 제 10 항에 따른 하나 이상의 전극을 포함하는 전지.

청구항 15

모바일 장치에서의 동력원으로서의 제 14 항에 따른 전지의 용도.

청구항 16

모바일 장치가 자동차, 자전거, 항공기, 컴퓨터, 전화기 또는 전기 용품 (power tool) 인 제 14 항 또는 제 15 항에 따른 전지의 용도.

청구항 17

히드록시드, 카르보네이트, 옥시히드록시드 또는 니켈, 망간 및 코발트의 염기성 카르보네이트를 플루오라이드 및 하나 이상의 리튬 염의 존재 하에 하소하는 것을 포함하는, 제 1 항 내지 제 7 항 중 어느 한 항에 따른 입자를 제조하는 방법.

청구항 18

제 17 항에 있어서, 선택된 플루오라이드가 암모늄 플루오라이드 또는 암모늄 히드로젠디플루오라이드인 방법.

발명서

기술분야

[0001] 본 발명은 하기 일반식 (I) 의 혼합 산화물을 포함하는 입자에 관한 것이며:

[0002]
$$\text{Li}_{1+a}\text{Ni}_b\text{Co}_c\text{Mn}_d\text{O}_z \quad (I)$$

[0003] [식 중,

[0004] 변수는 각각 하기와 같이 정의됨:

[0005] b 는 0.25 내지 0.45 범위의 수이고,

[0006] c 는 0.15 내지 0.25 범위의 수이고,

[0007] $d = 1 - b - c$ 이고,

[0008] $1.8 + a \leq z \leq 2.2 + a$ 이고,

[0009] $(1+a)$ 는 1.05 내지 1.20 범위임],

[0010] 상기 입자는 하나 이상의 플루오라이드로 전체 또는 부분 코팅된다.

[0011] 본 발명은 또한 본 발명의 입자의 제조 방법에 관한 것이다. 본 발명은 또한 본 발명의 입자의 용도에 관한

것이다.

배경 기술

- [0012] 최대 작동 전압에서 높은 저장 용량을 갖는 전지에 대한 중요도가 증가하고 있다. 필요한 용량은 일반적으로 수성 시스템을 기반으로 작동하는 전지로는 얻기 어렵다.
- [0013] 리튬 이온 배터리에서, 전하 이동은 대략 수화 형태에서의 양성자에 의한 것이 아니라 비수성 용매 또는 비수성 용매계에서의 리튬 이온에 의해 보장된다. 전극 물질이 특정한 역할을 갖는다. 캐소드 물질에 대해 특히 높은 요구가 이루어지고 있다.
- [0014] 많은 경우, 높은 전압에서 작동하는 이들 캐소드는 높은 전압, 즉 예를 들어 4.3 V 이상에서 문제가 된다. 이러한 환경 하에, 종종 이의 중합과 조합된, 전해질의 산화 위험이 존재한다. 그러나 캐소드 상의 중합체 층은 가장 덜 바람직한 경우 절연체로서 작용할 수 있으며, 따라서 배터리 효율을 뚜렷하게 저하시킨다. 더욱이, 많은 캐소드 물질은 이러한 전압에서 사이클링 (cycling) 안정성이 결여된 것으로 발견되는데, 이는 방전 (탈리튬화) 과정에서 지나치게 많은 리튬이 구조에서 빠져나가고, 상응하는 캐소드 물질의 구조가 붕괴될 수 있기 때문이다.
- [0015] 따라서, 높은 전압, 즉 예를 들어 4.3 V 이상에서도, 그리고 특히 다수의 상당한 탈리튬화시에도 긴 수명을 갖는 캐소드 제조에 적합한 물질을 제공하는 것이 본 발명의 목적이다. 상응하는 캐소드로 추가 가공될 수 있는 물질을 제조할 수 있는 방법을 제공하는 것이 본 발명의 추가 목적이다. 높은 전압에서도, 그리고 특히 다수의 상당한 탈리튬화시에도 긴 수명을 갖는 전극 및 전지를 제공하는 것이 또한 본 발명의 목적이다.
- [0016] 따라서, 처음 정의한 입자가 발견되어, 이를 또한 본 발명의 맥락에 있어서 본 발명의 입자로 지칭한다.
- [0017] 본 발명의 맥락에 있어서, "사이클링 (cycling)" 은 배터리 또는 전지를 다시 충전하고 방전시키는 것을 지칭한다.

발명의 내용

- [0018] 본 발명의 입자는 하기 일반식 (I) 의 하나 이상의 혼합 산화물을 포함하며:
- [0019]
$$\text{Li}_{1+a}\text{Ni}_b\text{Co}_c\text{Mn}_d\text{O}_z \quad (\text{I})$$
- [0020] [식 중,
- [0021] 변수는 각각 하기와 같이 정의됨:
- [0022] b 는 0.25 내지 0.45, 바람직하게는 0.37 내지 0.42 범위의 수이고,
- [0023] c 는 0.15 내지 0.25, 바람직하게는 0.17 내지 0.22 범위의 수이고,
- [0024] $d = 1 - b - c$ 이고,
- [0025] $(1+a)$ 는 1.05 내지 1.20, 바람직하게는 1.10 내지 1.15 범위이고,
- [0026] $1.8 + a \leq z \leq 2.2 + a$ 임],
- [0027] 상기 입자는 하나 이상의 플루오라이드로 전체, 또는 바람직하게는 부분 코팅된다.
- [0028] 본 발명의 한 구현예에서, 본 발명의 입자는 일반식 (I) 의 둘 이상의 혼합 산화물을 포함한다. 본 발명의 또 다른 구현예에서, 본 발명의 입자는 일반식 (I) 의 정확히 하나의 혼합 산화물을 포함한다.
- [0029] 본 발명의 한 구현예에서 본 발명의 입자는, 일반식 (I) 의 혼합 산화물 외에, 임의의 추가 Mn-, Co- 또는 Ni- 함유 산화 화합물을 포함하지 않는다. 본 발명의 또 다른 구현예에서, 본 발명의 입자는 일반식 (I) 의 화합물을 기준으로 예를 들어 5 내지 22 mol% 범위의 Li_2MnO_3 을 포함할 수 있다.
- [0030] 본 발명의 한 구현예에서, 본 발명의 입자는 일반식 (I) 의 혼합 산화물 중 전이 금속의 합에 대한 플루오라이드의 몰비가 0.02 내지 0.15 의 범위이다.
- [0031] 본 발명의 한 구현예에서, 본 발명의 물질은 본질적으로 층 구조를 가지며, 즉 층으로 이루어진 산화물이다. 각각의 결정 격자의 구조는 자체적으로 알려져 있는 방법, 예를 들어 X-선 회절 또는 전자 회절, 특히 X-선

분말 회절 분석에 의해 측정될 수 있다.

- [0032] 본 발명의 한 구현예에서, 본 발명의 입자는 예를 들어 DIN ISO 9277:2003-05 에 따라 예컨대 질소 흡착에 의해 측정된, 0.1 내지 5 m²/g 범위의 BET 표면적을 가질 수 있다.
- [0033] 본 발명의 한 구현예에서, 본 발명의 물질은 전체 화합물 (I) 을 기준으로 Na, K, Rb, Cs, 알칼리 토금속, Ti, V, Cr, Fe, Cu, Ag, Zn, B, Al, Zr, Mo, W, Nb, Si, Ga 및 Ge 의 양이온에서 선택되는 금속 이온 총 2 중량% 이하, 바람직하게는 총 1 중량% 이하로 도핑될 수 있다. 본 발명의 바람직한 구현예에서, 본 발명의 물질은 다른 금속 이온으로 도핑되지 않는다.
- [0034] "도핑" 은 본 발명의 물질 제조 동안, 하나 이상의 단계에서, Na, K, Rb, Cs, 알칼리 토금속, Ti, V, Cr, Fe, Cu, Ag, Zn, B, Al, Zr, Mo, W, Nb, Si, Ga 및 Ge 의 양이온에서 선택되는 하나 이상의 양이온을 갖는 하나 이상의 화합물이 첨가되는 것을 의미하는 것으로 이해될 것이다. 본 발명의 물질을 기준으로 0.1 내지 100 ppm 범위의 나트륨 이온과 같은, 출발 물질의 약간의 오염으로 인해 도입된 불순물은 본 발명의 맥락에 있어서 도핑으로 지칭되지 않을 것이다.
- [0035] 본 발명의 한 구현예에서, 본 발명의 입자는 최대 1 중량% 이하의 술페이트 또는 카르보네이트를 포함한다. 본 발명의 또 다른 구현예에서, 본 발명의 물질은 임의의 검출가능한 비율의 술페이트 및/또는 카르보네이트를 갖지 않는다.
- [0036] 본 발명의 한 구현예에서, 일반식 (I) 의 화합물은 결정질 분말의 형태이다.
- [0037] 본 발명의 한 구현예에서, 본 발명의 입자는 본질적으로 구체이다. 본 발명의 한 구현예에서, 본 발명의 입자는 본질적으로 구체인, 제 1 입자의 제 2 응집물이다. 제 2 응집물의 입자 직경 (D50) 은 1 내지 30 μm 범위, 바람직하게는 2 내지 25 μm 범위, 보다 바람직하게는 4 내지 20 μm 범위일 수 있다. 본 발명의 맥락에 있어서 입자 직경 (D50) 은 예를 들어 광 산란 또는 전자 현미경에 의한 평가에 의해 측정가능한 바와 같은 평균 입자 직경 (중량 평균) 을 지칭한다.
- [0038] "본질적으로 구체" 는 본 발명의 입자가 정확히 구체이거나 둥근 형상을 갖는다는 것을 의미하는 것으로 이해되며, 이러한 경우 최대 지점에서의 직경 및 최소 지점에서의 직경은 서로 10% 초과로 상이하지 않다.
- [0039] 본 발명의 입자는 하나 이상의 플루오라이드로 전체 또는 부분 코팅되는데, 이는 본 발명의 입자가 하나 이상의 플루오라이드를 갖는 코팅물을 갖는다는 것을 의미한다. 상기 코팅물은 본 발명의 입자의 일부로 고려될 것이다.
- [0040] 본 발명의 한 구현예에서, 본 발명의 입자 외부 표면의 5% 이상이 플루오라이드로 코팅된다. 이는 평균 값을 의미한다. 바람직한 구현예에서, 본 발명의 입자 외부 표면의 10 내지 90% 가 플루오라이드로 커버된다. 커버리지는 예를 들어 광전자 분광계 (XPS) 또는 전자 현미경 (SEM, TEM) 에 의해 측정될 수 있다.
- [0041] 본 발명의 입자를 코팅하는 플루오라이드는 결정질이거나 비정질 형태일 수 있다.
- [0042] 본 발명의 한 구현예에서, 플루오라이드는 LiF, NiF₂, CoF₂, MnF₂, 및 임의로는 Mn, Ni 및 Co 에서 선택되는 2 개 이상 금속의 혼합 플루오라이드, 및 Ni, Mn 및 Co 에서 선택되는 하나 이상 금속의 옥시플루오라이드에서 선택된다. —LiF, NiF₂, CoF₂ 및 MnF₂ 에서 선택되는 플루오라이드가 바람직하다.
- [0043] 본 발명의 한 구현예에서, 본 발명의 입자는 플루오라이드의 혼합물, 예를 들어 LiF, NiF₂, CoF₂, MnF₂ 및 Ni, Mn 및 Co 에서 선택되는 하나 이상 금속의 옥시플루오라이드에서 선택되는 둘 이상의 플루오라이드로 전체 또는 부분 코팅된다.
- [0044] 본 발명의 한 구현예에서, 플루오라이드(들) 는 본 발명의 입자 외부 표면 상에 단일 결정의 형태, 또는 비정질 또는 결정질 층의 형태로 배열된다.
- [0045] 본 발명의 한 구현예에서, 플루오라이드는 본 발명의 입자의 외부 표면 상에 존재하나, 기공에는 존재하지 않는다. 본 발명의 또 다른 구현예에서, 플루오라이드는 외부 표면 상에 존재할 뿐 아니라 본 발명의 입자의 기공에, 특히 제 1 입자의 응집으로 인해 유래한 기공에 존재한다.
- [0046] 본 발명의 입자를 사용하여, 양호한 특성을 갖는 전지를 제조할 수 있다. 보다 특히, 일반식 (I) 의 화합물로 제조된 전지가 3.0 V 내지 4.6 V 에서 리튬 원소에 대해 사이클링되는 경우 높은 방전 용량을 가지며, 해당

전지가, 존재한다면, 사이클링 동안 전위에 있어서 매우 적은 감소만을 나타낸다는 것이 관찰된다. 리튬 원소에 대해 3.0 V 내지 4.6 V 에서 사이클링 동안, 본 범위의 물량의 25 mA/g 의 전해 유량에서, 평균 반전 전위는 3.5 V 초과여야 한다.

금반열등 또한 금반열의 입자를 포함하는 전극을 제공한다.

분배면의 양자를 또한, 분배면의 백라에 있어서 물질 (A)로 지칭할 수 있다.

본 반명의 한 구절에 있어서, 본 반명의 임자는 본 반명의 전극에서 전기 전도성, 탄소 함유 물질을 갖는 복합체로서 사용된다. 예를 들어, 본 반명의 임자는 처리, 예를 들어 전기 전도성, 탄소 함유 물질로 코팅될 수 있다. 이러한 복합체는 마찬가지로 본 반명의 주제의 일부를 형성한다.

전기 전도성, 탄소함유 물질을 예를 들어, 그래피트, 카본 블랙, 탄소 나노튜브, 탄소 나노튜브 또는 사슬한 물질 중 2 개 이상의 혼합물에서 선택될 수 있다. 본 발명의 맥락에 있어서, 전기 전도성, 탄소함유 물질을 또한 하여서 탄소(B)로 지칭할 수 있다.

온 환경의 한 구획에서, 전기 전도성, 탄소 함유 물질은 카본 블랙이다. 카본 블랙은 예를 들어, 램프 블랙, 펄스 (furnace black), 플레임 (flame) 블랙, 썬열 (thermal) 블랙, 아세틸렌 블랙 및 산업적 (industrial) 블랙에서 선택될 수 있다. 카본 블랙은 불순물, 예를 들어 탄화수소, 특히 방향족 탄화수소, 또는 산소-함유 화합물 또는 산소-함유 기, 예를 들어 OH 기를 포함할 수 있다. 추가로, 황-또는 철-함유 불순물이 카본 블랙 내에 존재할 수 있다.

한 변형에서, 전기 전도성, 탄소함유 물질을 부분 산화된 카본 블랙이다.

문 환경의 한 구획에 있어, 전기 전도성, 탄소 함유 물량은 탄소 나노튜브를 포함한다. 탄소 나노튜브 (줄여서 CNT), 예를 들어 단일-벽 탄소 나노튜브 (SW CNT) 및 다중벽 탄소 나노튜브 (MW CNT)가 자체적으로 알려져 있다. 이외 제조 방법 및 일부 특성은 예를 들어 [Chemie Ingenieur Technik 2006, 78, 94-100]에서 A. Jess 등에 의해 기재되어 있다.

본 실험의 한 구현예에서, 탄소 나노튜브는 직경이 0.4 내지 50 nm, 바람직하게는 1 내지 25 nm 범위이다.

다.

단소나 노름트는 자체적으로 알려져 있는 방법에 의해 제조될 수 있다. 예를 들어, 환반성 탄소 화합물, 예를 들어 메탄 또는 일산화탄소, 아세틸렌 또는 에틸렌, 또는 환반성 탄소 화합물의 혼합물, 예를 들어 합성 가스는 하나 이상의 환원제, 예를 들어 수소 및/또는 추가의 가스, 예를 들어 질소의 존재 하에 분해될 수 있다. 또 다른 적합한 가스 혼합물은 일산화탄소와 에틸렌의 혼합물이다. 분해를 위한 적합한 온도는 예를 들어 400 내지 1000°C, 바람직하게는 500 내지 800°C 이다. 분해를 위한 적합한 압력 조건은 예를 들어 표준 압 내지 100 bar, 바람직하게는 10 bar 까지의 범위이다.

예를 들어, 특이 문제의 존재 또는 부재와, 기어공 아크 (arc) 중에서의 탄소 화합물의 분해에 의해, 단 원 - 또는 다중벽 탄소 나노튜브가 수득될 수 있다.

본 판면의 맥락에 있어서, 그레핀은 단일 그레핀 층과 유사한 구조를 갖는 거의 동일하거나 동일하 2 차원 6차원 탄소 결정을 의미하는 것으로 이해된다.

굴판명어의 한 구예에서, 굴판명어의 전극에서, 굴판명어의 양자 대 전기 전도성, 탄소함유 물질의 종류는 200:1 내지 5:1, 바람직하게는 100:1 내지 10:1 범위이다.

곧 반명의 추가적인 양태는 결국, 특히 케오드(곧 반명의 양자, 하나 이상의 전기 전도성, 탄소함유 물결 및 하나 이상의 결합체를 포함함)이다. 곧 반명의 양자, 하나 이상의 전기 전도성, 탄소함유 물결 및 하나의 결합체는 결국 물결이 형성되도록 조합되며, 이는 마찬가지로 곧 반명의 주체 일부를 형성한다.

본 편문의 명자 및 전기 전도성, 탄소함유 물결은 차기에서 기재되어 있다.

적합한 생활제는 바람직하게는 유기 (문) 생활제에서 선택된다. 적합한 (문) 생활제, 즉 단일 생활제 또는 군 생활제는 예를 들어, 용이온, 축배적 또는 자유-라디칼 (문) 생활에 의해 수득가능한 (문) 생활제, 특히 플라이에틸

렌, 폴리아크릴로니트릴, 폴리부타디엔, 폴리스티렌, 및 에틸렌, 프로필렌, 스티렌, (메트)아크릴로니트릴 및 1,3-부타디엔에서 선택되는 둘 이상의 공단량체의 공중합체에서 선택될 수 있다. 폴리프로필렌이 또한 적합하다. 폴리이소프렌 및 폴리아크릴레이트가 추가적으로 적합하다. 폴리아크릴로니트릴이 바람직하다.

[0064] 본 발명의 맥락에 있어서, 폴리아크릴로니트릴은 폴리아크릴로니트릴 단일중합체 뿐 아니라 아크릴로니트릴과 1,3-부타디엔 또는 스티렌의 공중합체를 의미하는 것으로 이해된다. 폴리아크릴로니트릴 단일중합체가 바람직하다.

[0065] 본 발명의 맥락에 있어서, 폴리에틸렌은 호모폴리에틸렌 뿐 아니라, 50 mol% 이상의 공중합된 에틸렌 및 50 mol% 이하의 하나 이상의 추가 공단량체를 포함하는 에틸렌의 공중합체, 예를 들어 α -올레핀 에컨대 프로필렌, 부틸렌 (1-부텐), 1-헥센, 1-옥텐, 1-데센, 1-도데센, 1-펜텐 및 또한 이소부텐, 비닐방향족, 예를 들어 스티렌, 및 또한 (메트)아크릴산, 비닐 아세테이트, 비닐 프로피오네이트, (메트)아크릴산의 C_1 - C_{10} -알킬 에스테르, 특히 메틸 아크릴레이트, 메틸 메타크릴레이트, 에틸 아크릴레이트, 에틸 메타크릴레이트, n-부틸 아크릴레이트, 2-에틸헥실 아크릴레이트, n-부틸 메타크릴레이트, 2-에틸헥실 메타크릴레이트, 및 또한 말레산, 말레산 무수물 및 이타콘산 무수물을 의미하는 것으로 이해된다. 폴리에틸렌은 HDPE 또는 LDPE 일 수 있다.

[0066] 본 발명의 맥락에 있어서, 폴리프로필렌은 호모폴리프로필렌 뿐 아니라, 50 mol% 이상의 공중합된 프로필렌 및 50 mol% 이하의 하나 이상의 추가 공단량체를 포함하는 프로필렌의 공중합체, 예를 들어 에틸렌 및 α -올레핀 에컨대 부틸렌, 1-헥센, 1-옥텐, 1-데센, 1-도데센 및 1-펜텐을 의미하는 것으로 이해된다. 폴리프로필렌은 바람직하게는 이소택틱이거나 본질적으로 이소택틱인 폴리프로필렌이다.

[0067] 본 발명의 맥락에 있어서, 폴리스티렌은 스티렌의 단일중합체 뿐 아니라, 아크릴로니트릴, 1,3-부타디엔, (메트)아크릴산, (메트)아크릴산의 C_1 - C_{10} -알킬 에스테르, 디비닐벤젠, 특히 1,3-디비닐벤젠, 1,2-디페닐에틸렌 및 α -메틸스티렌과의 공중합체를 의미하는 것으로 이해된다.

[0068] 또 다른 바람직한 결합제는 폴리부타디엔이다.

[0069] 다른 적합한 결합제는 폴리에틸렌 옥시드 (PEO), 셀룰로오스, 카르복시메틸셀룰로오스, 폴리이미드 및 폴리비닐 알코올에서 선택된다.

[0070] 본 발명의 한 구현예에서, 결합제는 평균 분자량 M_w 가 50 000 내지 1 000 000 g/mol, 바람직하게는 500 000 g/mol 까지의 범위인 이들 (공)중합체에서 선택된다.

[0071] 결합제는 가교되거나 비가교된 (공)중합체일 수 있다.

[0072] 본 발명의 특히 바람직한 구현예에서, 결합제는 할로젠화 (공)중합체, 특히 불소화 (공)중합체에서 선택된다. 할로젠화 또는 불소화 (공)중합체는 분자 당 하나 이상의 할로젠 원자 또는 하나 이상의 불소 원자를 갖는, 바람직하게는 분자 당 2 개 이상의 할로젠 원자 또는 2 개 이상의 불소 원자를 갖는 하나 이상의 (공)중합된 (공)단량체를 포함하는 이들 (공)중합체를 의미하는 것으로 이해된다.

[0073] 그 예는 폴리비닐 클로라이드, 폴리비닐리덴 클로라이드, 폴리테트라플루오로에틸렌, 폴리비닐리덴 플루오라이드 (PVdF), 테트라플루오로에틸렌-헥사플루오로프로필렌 공중합체, 비닐리덴 플루오라이드-헥사플루오로프로필렌 공중합체 (PVdF-HFP), 비닐리덴 플루오라이드-테트라플루오로에틸렌 공중합체, 퍼플루오로알킬 비닐 에테르 공중합체, 에틸렌-테트라플루오로에틸렌 공중합체, 비닐리덴 플루오라이드-클로로트리플루오로에틸렌 공중합체 및 에틸렌-클로로플루오로에틸렌 공중합체이다.

[0074] 적합한 결합제는 특히 폴리비닐 알코올 및 할로젠화 (공)중합체, 예를 들어 폴리비닐 클로라이드 또는 폴리비닐리덴 클로라이드, 특히 불소화 (공)중합체 에컨대 폴리비닐 플루오라이드 및 특히 폴리비닐리덴 플루오라이드 및 폴리테트라플루오로에틸렌이다.

[0075] 한 구현예에서, 본 발명의 전극에서, 전기 전도성, 탄소 함유 물질은 그래피트, 카본 블랙, 탄소 나노튜브, 그래핀 또는 상술한 물질 중 2 개 이상의 혼합물에서 선택된다.

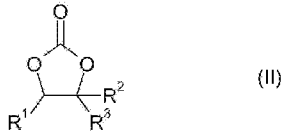
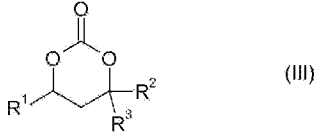
[0076] 본 발명의 한 구현예에서, 본 발명의 전극 물질은:

[0077] (A) 60 내지 98 중량%, 바람직하게는 70 내지 96 중량% 범위의 본 발명의 입자,

[0078] (B) 1 내지 25 중량%, 바람직하게는 2 내지 20 중량% 범위의 전기 전도성, 탄소 함유 물질,

- [0079] (C) 1 내지 20 중량%, 바람직하게는 2 내지 15 중량% 범위의 결합제
를 포함한다.
- [0081] 본 발명의 전극의 기하학적 구조는 광범위한 한도 내에서 선택될 수 있다. 본 발명의 전극을, 예를 들어 10 μm 내지 250 μm , 바람직하게는 20 내지 130 μm 범위의 두께를 갖는 박층 내에서 구성시키는 것이 바람직하다.
- [0082] 본 발명의 한 구현예에서, 본 발명의 전극은 호일, 예를 들어 금속 호일, 특히 알루미늄 호일, 또는 중합체 필름, 예를 들어 폴리에스테르 필름 (미처리되거나 처리된)을 포함한다.
- [0083] 본 발명은 또한 전지에서 본 발명의 전극 물질 또는 본 발명의 전극의 용도를 제공한다. 본 발명은 또한 이 본 발명의 전극 물질을 사용하는 전지 제조 방법을 제공한다. 본 발명은 또한 이 상의 본 발명의 전극 물질 또는 하나 이상의 본 발명의 전극을 포함하는 전지를 제공한다.
- [0084] 정의상, 본 발명의 전지에서 본 발명의 전극은 캐소드로서 역한다. 본 발명의 전지는 반대-전극을 포함하며, 이는 본 발명의 맥락에 있어서 애노드로서 정의되고, 예를 들어 탄소 애노드, 특히 그래파이트 애노드, 리튬 애노드, 구소 애노드 또는 리튬 티타네이트 애노드일 수 있다.
- [0085] 본 발명의 전지는 예를 들어 배터리 또는 아큐뮬레이터 (accumulator) 일 수 있다.
- [0086] 본 발명의 전지는 애노드 및 본 발명의 전극에 추가로, 추가의 구성성분, 예를 들어 전도성 염, 비수성 용매, 분리기, 산물 도제 (예를 들어 금속 또는 합금으로 제조된), 및 또한 케이를 연결부 및 하우징을 포함할 수 있다.
- [0087] 본 발명의 한 구현예에서, 본 발명의 전지는 실온에서 액체 또는 고체일 수 있는, 바람직하게는 중합체, 시클릭 또는 비시클릭 에테르, 시클릭 및 비시클릭 아세탈 및 시클릭 또는 비시클릭 유기 카르보네이트에서 선택되는 하나 이상의 비수성 용매를 포함한다.
- [0088] 적합한 중합체의 예는 특히 폴리아렌 클리콜, 바람직하게는 폴리-C₁-C₄-알렌 클리콜 및 특히 폴리에틸렌 클리콜이다. 이들 폴리아렌 클리콜은 20 mol% 이하의 하나 이상의 C₁-C₄-알렌 클리콜을 중합된 형태로 포함할 수 있다. 폴리아렌 클리콜은 바람직하게는 메틸 또는 에틸에 의해 이중-중합된 폴리아렌 클리콜이다.
- [0089] 적합한 폴리아렌 클리콜 및 특히 적합한 폴리에틸렌 클리콜의 분자량 M_n는 400 g/mol 이상일 수 있다. 적합한 폴리아렌 클리콜 및 특히 적합한 폴리에틸렌 클리콜의 분자량 M_n는 5 000 000 g/mol 이하, 바람직하게는 2 000 000 g/mol 이하일 수 있다.
- [0091] 적합한 비시클릭 에테르의 예는, 예컨대 다이소프로판 에테르, 다-n-부틸 에테르, 1,2-디메톡시에탄, 1,2-디에톡시에탄이고, 1,2-디메톡시에탄이 바람직하다.
- [0092] 적합한 시클릭 에테르의 예는 테트라히드로푸란 및 1,4-디옥산이다.
- [0093] 적합한 비시클릭 아세탈의 예는 예컨대 디메톡시메탄, 디에톡시메탄, 1,1-디메톡시에탄 및 1,1-디에톡시에탄이다.
- [0094] 적합한 시클릭 아세탈의 예는 1,3-디옥산 및 특히 1,3-디옥솔란이다.
- [0095] 적합한 비시클릭 유기 카르보네이트의 예는 디메틸 카르보네이트, 에틸 메틸 카르보네이트 및 디에틸 카르보네이트이다.

[0096] 적합한 시클릭 유기 카르보네이트의 예는 하기 일반식 (II) 및 (III) 의 화합물이다:



[0097]

[0098] [식 중,

[0099] R^1 , R^2 및 R^3 은 동일하거나 상이할 수 있으며 수소 및 C_1 - C_4 -알킬, 예를 들어 메틸, 에틸, n-프로필, 이소프로필, n-부틸, 이소부틸, sec-부틸 및 tert-부틸에서 선택되고, 이때 R^2 및 R^3 은 바람직하게는 둘 모두 tert-부틸이 아님].

[0100] 특히 바람직한 구현예에서, R^1 은 메틸이고 R^2 및 R^3 은 각각 수소이거나, R^1 , R^2 및 R^3 은 각각 수소이다.

[0101] 또 다른 바람직한 시클릭 유기 카르보네이트는 하기 식 (IV) 의 비닐렌 카르보네이트이다:



[0102]

[0103] 용매(들) 는 바람직하게는 무수 상태, 즉, 예를 들어 칼 피셔 (Karl Fischer) 적정에 의해 측정가능한, 1 ppm 내지 30 ppm 범위 (ppm 은 중량 ppm 을 지칭함) 의 물 함량을 갖는 상태로써 알려져 있는 바로 사용된다.

[0104] 본 발명의 전지는 하나 이상의 전도성 염을 추가로 포함한다. 적합한 전도성 염은 특히 리튬 염이다. 적합한 리튬 염의 예는 $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiAsF_6$, $LiCF_3SO_3$, $LiC(C_nF_{2n+1}SO_2)_3$, 리튬 이미드 예컨대 $LiN(C_nF_{2n+1}SO_2)_2$ (이때, n 은 1 내지 20 범위의 정수임), $LiN(SO_2F)_2$, Li_2SiF_6 , $LiSbF_6$, $LiAlCl_4$, 및 일반식 $(C_nF_{2n+1}SO_2)_mLi$ 의 염이며, 이때, m 은 하기와 같이 정의된다:

[0105] X 가 산소 및 황에서 선택되는 경우 $m = 1$ 이고,

[0106] X 가 질소 및 인에서 선택되는 경우 $m = 2$ 이고,

[0107] X 가 탄소 및 규소에서 선택되는 경우 $m = 3$ 이다.

[0108] 바람직한 전도성 염은 $LiC(CF_3SO_2)_3$, $LiN(CF_3SO_2)_2$, $LiPF_6$, $LiBF_4$, $LiClO_4$ 에서 선택되며, $LiPF_6$ 및 $LiN(CF_3SO_2)_2$ 가 특히 바람직하다.

[0109] 본 발명의 한 구현예에서, 본 발명의 전지는 전극을 기계적으로 분리시키는 하나 이상의 분리기를 포함한다. 적합한 분리는 중합체 필름, 특히, 금속성 리튬에 대해 미반응성인 다공성 중합체 필름이다. 분리기용으로 특히 적합한 물질은 폴리올레핀, 특히 필름 형태의 다공성 폴리에틸렌 및 필름 형태의 다공성 폴리프로필렌이다.

[0110] 폴리올레핀, 특히 폴리에틸렌 또는 폴리프로필렌으로 만들어진 분리기는 35 내지 45% 범위의 다공도를 가질 수 있다. 적합한 기공 직경은 예를 들어 30 내지 500 nm 범위이다.

[0111] 본 발명의 또 다른 구현예에서, 분리기는 무기 입자로 충전된 PET 부직포에서 선택될 수 있다. 이러한 분리기는 40 내지 55% 범위의 다공도를 가질 수 있다. 적합한 기공 직경은 예를 들어 80 내지 750 nm 범위이다.

[0112] 본 발명의 또 다른 구현예에서, 유리섬유지 (fiberglass paper) 로 만들어진 분리기가 선택된다.

- [0113] 본 발명의 전지는 임의의 원하는 형상, 예를 들어 입방형 또는 원통형 디스크 형태를 가질 수 있는 하우징을 추가로 포함한다. 한 변형에서, 사용한 하우징은 파우치로서 정교하게 처리된 금속 호일이다.
- [0114] 본 발명의 전지는 높은 전위를 제공하며 높은 에너지 밀도 및 양호한 안정성으로 유용하다. 보다 특히, 4.3 V 초과에서 리튬 원소에 대해 사이클링되는 경우, 본 발명의 전지가 높은 방전 용량을 갖고, 상기 본 발명의 전지는, 존재한다면, 사이클링 동안 전위에 있어서 단지 매우 작은 감소만을 나타낸다는 것이 관찰된다. 2.5 V 내지 4.55 V 에서, 및 본 발명의 물질의 95 mA/g 의 현재 유량에서 사이클링 동안 평균 방전 전위는 3.5 V 초과여야 한다.
- [0115] 본 발명의 전지는 서로 조합될 수 있으며, 예를 들어 직렬로 연결되거나 병렬로 연결될 수 있다. 직렬 연결이 바람직하다.
- [0116] 본 발명은 장치, 특히 모바일 장치에서의 본 발명의 전지의 용도를 추가로 제공한다. 모바일 장치의 예는 자동차 (motor vehicle), 예를 들어 자동차 (automobile), 자전거, 항공기, 또는 수중 장치 (water vehicle) 예컨대 보트 또는 선박이다. 모바일 장치의 다른 예는 수동으로 움직이는 것들, 예를 들어 컴퓨터, 특히 휴대용 컴퓨터, 전화기, 또는 예를 들어 건축 분야에서의 전기 용품 (power tool), 특히 드릴, 배터리-동력 드릴 또는 배터리-동력 택커 (tacker) 이다.
- [0117] 유닛에서의 본 발명의 전지 사용으로, 특히 높은 체적 에너지 밀도의 이점이 제공된다.
- [0118] 본 발명은 또한:
- [0119] (A) 하기 일반식 (I) 의 혼합 산화물을 포함하는 입자로서, 하나 이상의 플루오라이드로 전체, 또는 바람직하게는 부분 코팅된 입자:
- [0120]
$$\text{Li}_{1-a}\text{Ni}_b\text{Co}_c\text{Mn}_d\text{O}_z \quad (I)$$
- [0121] [식 중,
- [0122] 변수는 각각 하기와 같이 정의됨:
- [0123] b 는 0.25 내지 0.45, 바람직하게는 0.37 내지 0.42 범위의 수이고,
- [0124] c 는 0.15 내지 0.25, 바람직하게는 0.17 내지 0.22 범위의 수이고,
- [0125] $d = 1 - b - c$ 이고,
- [0126] $(1+a)$ 는 1.05 내지 1.20, 바람직하게는 1.10 내지 1.15 범위이고,
- [0127] $1.8 + a \leq z \leq 2.2 + a$ 임], 및
- [0128] (B) 하나 이상의 전기 전도성, 탄소 함유 물질 및
- [0129] (C) 하나 이상의 결합제
- [0130] 를 하나 이상의 단계에서 서로 혼합하고, 임의로는 이들을
- [0131] (D) 하나 이상의 금속 호일 또는 중합체 필름에 적용하는 것을 포함하는, 전극 제조 방법을 제공한다
- [0132] 본 발명의 입자, 전기 전도성, 탄소 함유 물질 또는 탄소 (B) 및 결합제 (C) 는 상기에서 정의하였다.
- [0133] 혼합은 하나 이상의 단계에서 이루어질 수 있다.
- [0134] 본 발명에 따른 방법의 한 변형에서, 본 발명의 입자, 탄소 (B) 및 결합제 (C) 는 한 단계에서, 예를 들어 밀 (mill) 에서, 특히 볼 밀 (ball mill) 에서 혼합된다. 이후, 이에 따라 수득가능한 혼합물은 박층에서 담체, 예를 들어 금속 호일 또는 중합체 필름 (D) 에 적용된다. 전지에 혼입하기 전 또는 혼입시, 담체는 제거될 수 있다. 다른 변형에서, 담체는 보유된다.
- [0135] 본 발명에 따른 방법의 또 다른 변형에서, 본 발명의 입자, 탄소 (B) 및 결합제 (C) 는 다수 단계에서, 예를 들어 밀에서, 특히 볼 밀에서 혼합된다. 예를 들어, 본 발명의 입자 및 탄소 (B) 를 서로 먼저 혼합할 수 있다. 그 이후 결합제 (C) 와 혼합한다. 이후, 이에 따라 수득가능한 혼합물은 박층에서 담체, 예를 들어 금속 호일 또는 중합체 필름 (D) 에 적용된다. 전지에 혼입하기 전 또는 혼입시, 담체는 제거될 수 있다. 다른 변형에서, 담체는 제거되지 않는다.

- [0136] 본 발명에 따른 방법의 한 변형에서, 본 발명의 입자, 탄소 (B) 및 결합제 (C) 는 물 또는 유기 용매 (예를 들어 N-메틸피롤리돈 또는 아세톤) 중에서 혼합된다. 이에 따라 수득가능한 현탁액은 박층에서 담체, 예를 들어 금속 호일 또는 중합체 필름 (D) 에 적용되고, 용매는 열 처리에 의해 제거된다. 전지에 혼입하기 전 또는 혼입시, 담체는 제거될 수 있다. 다른 변형에서, 담체는 제거되지 않는다.
- [0137] 본 발명의 맥락에 있어서 박층은 예를 들어 2 μm 내지 250 μm 이하 범위의 두께를 갖는다.
- [0138] 기계적 안정성을 향상시키기 위해서, 전극은 열 처리되거나 바람직하게는 기계적으로 처리, 예를 들어 압축되거나 캘린더링 (calendering) 될 수 있다.
- [0139] 본 발명에 따른 방법은 본 발명의 전극 물질 및 그로부터 수득가능한 전극의 제조에 매우 적합하다.
- [0140] 본 발명은 또한 하기 일반식 (I) 의 하나 이상의 혼합 산화물을 포함하는 입자 (상기 입자는 하나 이상의 플루오라이드로 전체 또는 부분 코팅됨), 및 하나 이상의 전기 전도성, 탄소 함유 물질 (또한 탄소 (B) 로 지칭함) 을 포함하는 복합체를 제공한다:
- [0141] $\text{Li}_{1+a}\text{Ni}_b\text{Co}_c\text{Mn}_d\text{O}_z$ (I)
- [0142] [식 중,
- [0143] 변수는 각각 하기와 같이 정의됨:
- [0144] b 는 0.25 내지 0.45, 바람직하게는 0.37 내지 0.42 범위의 수이고,
- [0145] c 는 0.15 내지 0.25, 바람직하게는 0.17 내지 0.22 범위의 수이고,
- [0146] $d = 1 - b - c$ 이고,
- [0147] $(1+a)$ 는 1.05 내지 1.20, 바람직하게는 1.10 내지 1.15 범위이고,
- [0148] $1.8 + a \leq z \leq 2.2 + a$ 임].
- [0149] 본 발명의 복합체에서, 본 발명의 입자는 처리, 예를 들어 탄소 (B) 로 코팅된다.
- [0150] 본 발명의 한 구현예에서, 본 발명의 복합체에서, 본 발명의 입자 및 탄소 (B) 는 98:1 내지 12:5, 바람직하게는 48:1 내지 7:2 범위의 중량비로 존재한다.
- [0151] 본 발명의 복합체는 본 발명의 전극 물질의 제조에 특히 적합하다. 이의 제조 방법이 상기 기재되며 이는 마찬가지로 본 발명의 주제 일부를 형성한다.
- [0152] 본 발명은 또한 본 발명의 입자 제조 방법을 제공하며, 이는 본 발명에 따른 합성 방법으로도 지칭된다. 본 발명에 따른 합성 방법은 히드록시드, 카르보네이트, 옥시히드록시드 또는 니켈, 망간 및 코발트의 염기성 카르보네이트를 플루오라이드 및 하나 이상의 리튬 염의 존재 하에 하소함으로써 수행될 수 있다.
- [0153] 특히, 그 절차는 먼저 전이 금속 Ni, Co 및 Mn 을 원하는 비율로, 그리고 도판트(들) 를 임의로 포함하는 전구체를 제조한 후 상기 기재한 바와 같이 하소하는 것일 수 있다. 바람직한 변형에서, 절차는 염기성일 수 있는 혼합 카르보네이트, 또는 혼합 옥시히드록시드의 침전에 의해 전구체를 제조하는 것이다. 제 2 단계에서, 혼합은 먼저 리튬 화합물, 바람직하게는 하나 이상의 리튬 염, 예를 들어 수산화리튬 또는 보다 바람직하게는 Li_2CO_3 과, 그리고 하나 이상의 플루오라이드와 이루어진다. 이후 바람직하게는 875 내지 950°C 에서 3 내지 12 시간 동안, 예를 들어 공기 흐름 하에 하소를 실행한다.
- [0154] 본 합성 방법의 한 구현예에서, 하소는 875 내지 950°C 범위의 최대 온도에서 이루어진다.
- [0155] 본 발명의 한 구현예에서, 선택된 플루오라이드는 암모늄 플루오라이드 또는 암모늄 히드로젠디플루오라이드, 또는 암모늄 플루오라이드 및 암모늄 히드로젠디플루오라이드의 혼합물이다.
- [0156] 본 발명을 하기 작용 실시예에 의해 설명한다.

발명을 실시하기 위한 구체적인 내용

- [0157] 일반적 언급: 달리 나타내지 않는 한, % 로의 수치는 중량% 이다.
- [0158] 용해된 염의 나타난 양은 용액의 kg 을 기준으로 한다.

- [0159] I. 출발 물질의 제조
- [0160] I.1. 리튬 카르보네이트
- [0161] 이의 사용 전에, 시판 Li_2CO_3 을 16 시간에 걸쳐 105°C 에서 건조시킨 후, 체질에 의해 $50\ \mu\text{m}$ 초과와 직경을 갖는 입자를 제거하였다.
- [0162] I.2. 히드록시드 (전구체) 의 제거
- [0163] 55°C 에서, 연속 반응기 내에서 3 내지 18 시간의 체류 시간에 상응하는 공급 속도로, 격렬히 교반하면서 NiSO_4 , CoSO_4 및 MnSO_4 의 용액과 암모니아 및 NaOH 의 수용액을 조합하여, $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ 를 첨가하였다. $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ 의 구체 입자가 침전되었다. 형성된 혼합 금속 산화물/수산화물을 여과해냈다.
- [0164] II. 본 발명의 물질 및 비교용 물질의 제조
- [0165] II.1. 비교용 물질 C-M.1 의 제조
- [0166] NCM-424, Li/금속 = 1.13
- [0167] 16 시간에 걸쳐 105°C 에서 공기 하에 $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ 를 건조시켰다.
- [0168] 마노 절구 (agate mortar) 에, I.1 에 따라 6.34 g 의 Li_2CO_3 을 초기 충전하고, 이를 20 분에 걸쳐 13.85 g 의 건조 $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ 와 잘 혼합하였다. 그 후, 이에 따라 수득가능한 혼합물을, 하기 온도 프로파일을 실행하여 공기 하 머플 퍼니스 (muffle furnace) 에서 하소시켰다:
- [0169] 먼저, 각각의 경우 $3^\circ\text{C}/\text{분}$ 으로 온도를 실온에서 350°C 로 증가시켰다. 4 시간에 걸쳐 350°C 에서 가열하였다. 이후 온도를 675°C 로 증가시키고, 이 과정에서 각각의 경우 온도를 $3^\circ\text{C}/\text{분}$ 으로 증가시켰다.
- [0170] 4 시간에 걸쳐 675°C 에서 가열하였다. 이후 온도를 900°C 로 증가시키고, 이 과정에서 각각의 경우 온도를 $3^\circ\text{C}/\text{분}$ 으로 증가시켰다.
- [0171] 6 시간에 걸쳐 900°C 에서 하소를 실행하였다. 전체 가열 및 하소에 걸쳐, 머플 퍼니스를 통해 공기를 통과시켰다 ($100\ \text{l/h}$).
- [0172] 하소 종료 후, $0.5\ \text{K}/\text{분}$ 의 냉각 속도로 냉각하였다. 이로 인해 비교용 물질 C-M.1 을 수득하여, 추가 사용 전에 질소 하에 보관하였다.
- [0173] II.2. 본 발명의 물질 M.2 의 제조
- [0174] NCM-424, Li/금속 = 1.13, 0.02 mol 의 F
- [0175] 마노 절구에, I.1 에 따라 6.34 g 의 Li_2CO_3 을 초기 충전하고, 이를 10 분에 걸쳐 13.85 g 의 건조 $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ 와 잘 혼합하였다. 그 후, 0.13 g 의 NH_4F 를 첨가하고 혼합물을 10 분에 걸쳐 다시 혼합하였다. 그 후, 이에 따라 수득가능한 혼합물을, 하기 온도 프로파일을 실행하여 공기 하 머플 퍼니스에서 하소시켰다:
- [0176] 먼저, 각각의 경우 $3^\circ\text{C}/\text{분}$ 으로 온도를 실온에서 350°C 로 증가시켰다. 4 시간에 걸쳐 350°C 에서 가열하였다. 이후 온도를 675°C 로 증가시키고, 이 과정에서 각각의 경우 온도를 $3^\circ\text{C}/\text{분}$ 으로 증가시켰다.
- [0177] 4 시간에 걸쳐 675°C 에서 가열하였다. 이후 온도를 900°C 로 증가시키고, 이 과정에서 각각의 경우 온도를 $3^\circ\text{C}/\text{분}$ 으로 증가시켰다.
- [0178] 6 시간에 걸쳐 900°C 에서 하소를 실행하였다. 전체 가열 및 하소에 걸쳐, 머플 퍼니스를 통해 공기를 통과시켰다 ($100\ \text{l/h}$).
- [0179] 하소 종료 후, $0.5\ \text{K}/\text{분}$ 의 냉각 속도로 냉각하였다. 이로 인해 본 발명의 물질 M.2 를 수득하여, 추가 사용 전에 질소 하에 보관하였다.
- [0180] II.3. 본 발명의 물질 M.3 의 제조
- [0181] NCM-424, Li/금속 = 1.13, 0.1 mol 의 F

- [0182] 마노 절구에, I.1 에 따라 6.34 g 의 Li_2CO_3 을 초기 충전하고, 이를 10 분에 걸쳐 13.85 g 의 건조 $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ 와 잘 혼합하였다. 그 후, 0.57 g 의 NH_4F 를 첨가하고 혼합물을 10 분에 걸쳐 다시 혼합하였다. 그 후, 이에 따라 수득가능한 혼합물을, 하기 온도 프로파일을 실행하여 공기 하 머플 퍼니스에서 하소시켰다:
- [0183] 먼저, 각각의 경우 3°C/분으로 온도를 실온에서 350°C 로 증가시켰다. 4 시간에 걸쳐 350°C 에서 가열하였다. 이후 온도를 675°C 로 증가시키고, 이 과정에서 각각의 경우 온도를 3°C/분으로 증가시켰다.
- [0184] 4 시간에 걸쳐 675°C 에서 가열하였다. 이후 온도를 900°C 로 증가시키고, 이 과정에서 각각의 경우 온도를 3°C/분으로 증가시켰다.
- [0185] 6 시간에 걸쳐 900°C 에서 하소를 실행하였다. 전체 가열 및 하소에 걸쳐, 머플 퍼니스를 통해 공기를 통과시켰다 (100 l/h).
- [0186] 하소 종료 후, 0.5 K/분의 냉각 속도로 냉각하였다. 이로 인해 본 발명의 물질 M.3 을 수득하여, 추가 사용 전에 질소 하에 보관하였다.
- [0187] II.4. 본 발명의 물질 M.4 의 제조
- [0188] NCM-424, Li/금속 = 1.13, 0.2 mol 의 F
- [0189] 마노 절구에, I.1 에 따라 6.34 g 의 Li_2CO_3 을 초기 충전하고, 이를 10 분에 걸쳐 13.85 g 의 건조 $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ 와 잘 혼합하였다. 그 후, 1.14 g 의 NH_4F 를 첨가하고 혼합물을 10 분에 걸쳐 다시 혼합하였다. 그 후, 이에 따라 수득가능한 혼합물을, 하기 온도 프로파일을 실행하여 공기 하 머플 퍼니스에서 하소시켰다:
- [0190] 먼저, 각각의 경우 3°C/분으로 온도를 실온에서 350°C 로 증가시켰다. 4 시간에 걸쳐 350°C 에서 가열하였다. 이후 온도를 675°C 로 증가시키고, 이 과정에서 각각의 경우 온도를 3°C/분으로 증가시켰다.
- [0191] 4 시간에 걸쳐 675°C 에서 가열하였다. 이후 온도를 900°C 로 증가시키고, 이 과정에서 각각의 경우 온도를 3°C/분으로 증가시켰다.
- [0192] 6 시간에 걸쳐 900°C 에서 하소를 실행하였다. 전체 가열 및 하소에 걸쳐, 머플 퍼니스를 통해 공기를 통과시켰다 (100 l/h).
- [0193] 하소 종료 후, 0.5 K/분의 냉각 속도로 냉각하였다. 이로 인해 본 발명의 물질 M.4 를 수득하여, 추가 사용 전에 질소 하에 보관하였다.
- [0194] II.5. 본 발명의 물질 M.5 의 제조
- [0195] NCM-424, Li/금속 = 1.2, 0.1 mol 의 F
- [0196] 마노 절구에, I.1 에 따라 6.74 g 의 Li_2CO_3 을 초기 충전하고, 이를 10 분에 걸쳐 13.85 g 의 건조 $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}(\text{OH})_2$ 와 잘 혼합하였다. 그 후, 0.57 g 의 NH_4F 를 첨가하고 혼합물을 10 분에 걸쳐 다시 혼합하였다. 그 후, 이에 따라 수득가능한 혼합물을, 하기 온도 프로파일을 실행하여 공기 하 머플 퍼니스에서 하소시켰다:
- [0197] 먼저, 각각의 경우 3°C/분으로 온도를 실온에서 350°C 로 증가시켰다. 4 시간에 걸쳐 350°C 에서 가열하였다. 이후 온도를 675°C 로 증가시키고, 이 과정에서 각각의 경우 온도를 3°C/분으로 증가시켰다.
- [0198] 4 시간에 걸쳐 675°C 에서 가열하였다. 이후 온도를 900°C 로 증가시키고, 이 과정에서 각각의 경우 온도를 3°C/분으로 증가시켰다.
- [0199] 6 시간에 걸쳐 900°C 에서 하소를 실행하였다. 전체 가열 및 하소에 걸쳐, 머플 퍼니스를 통해 공기를 통과시켰다 (100 l/h).
- [0200] 하소 종료 후, 0.5 K/분의 냉각 속도로 냉각하였다. 이로 인해 본 발명의 물질 M.5 를 수득하여, 추가 사용 전에 질소 하에 보관하였다.
- [0201] III. 전기화학적 분석:

- [0202] III.1. 본 발명의 반전지 (half cell) 로의 분석
- [0203] 캐소드 (Kat-hz-2) 를 제조하기 위해서, 하기의 것을 스크류탑 (screwtop) 용기에서 서로 혼합하였다:
- [0204] 88% M.2
- [0205] 6% 폴리비닐리덴 디플루오라이드 ("PVdF") (Arkema Group 에서 Kynar Flex® 2801 로 시판),
- [0206] BET 표면적이 $62 \text{ m}^2/\text{g}$ 인 3% 카본 블랙 (Timcal 사에서 "Super P Li" 로 시판),
- [0207] 3% 그래피트 (Timcal 사에서 KS6 으로 시판),
- [0208] 교반하면서, 충분한 N-메틸피롤리돈 (NMP) 을 첨가하고, 뭉뚱하고 덩어리를 갖지 않는 페이스트가 수득될 때까지 혼합물을 Ultraturrax 에서 교반하였다.
- [0209] 이에 따라 수득한 페이스트를 $20 \mu\text{m}$ 두께의 알루미늄 호일에 나이프-코팅하고, 16 시간 동안 120°C 에서 진공 건조 캐비넷 내에서 건조시켰다. 건조 후 로딩은 $1.1 \text{ mg}/\text{cm}^2$ 였다. 이후, 원형 디스크 형태의 부분을 3 cm^2 의 면적으로 구멍내었다. 이로 인해 본 발명의 캐소드 (Kat-hz-2) 를 수득하였다.
- [0210] 애노드 (An-hz-1): 리튬 디스크 (면적 3 cm^2) 를 구멍내었다. 이로 인해 애노드 (An-hz-1) 를 수득하였다.
- [0211] 사용한 시험 전지는 도 1 에 따른 셋업이었다. 전지의 어셈블리에서, 이를 도 1 의 모식적 도해에 따라 바닥으로부터 위쪽으로 조립하였다. 도 1 에서, 애노드 쪽이 맨 위에 있고, 캐소드 쪽이 맨 아래에 있다.
- [0212] 도 1 에서의 표시는 하기를 위미한다:
- [0213] 1, 1' 볼트
- [0214] 2, 2' 너트
- [0215] 3, 3' 씰링 링 (Sealing ring) - 각 경우 2 개, 각 경우 약간 더 작은 두 번째 씰링 링은 도면에 나타나지 않음
- [0216] 4 나선형 스프링
- [0217] 5 스테인레스 스틸로 만들어진 산출 도체
- [0218] 6 하우징
- [0219] 캐소드 (Kat-hz-2) 를 캐소드 쪽 1' 에서 볼트에 적용하였다. 이후, 유리 섬유로 구성된 분리기 (두께 0.5 mm) 를 캐소드 (Kat-hz-2) 상에 놓았다. 전해질을 분리기 상에 소량씩 흐르게 하였다. 애노드 (An-hz-1) 를 젖은 분리기 상에 놓았다. 사용한 산출 도체 5 는 애노드에 직접 적용한 스테인레스 스틸 플레이트였다. 이후, 씰 3 및 3' 를 첨가하고 시험 전지의 부분을 함께 나사로 고정시켰다. 나선형 스프링 4 로 구성된 스틸 스프링을 사용하고 애노드 볼트 1 과의 나사 연결에 의해 생성된 압력에 의해, 전기 접촉을 확실하게 하였다.
- [0220] 본 발명의 물질 M.3 ~ M.5 또는 비교용 물질 C-M.1 을 기반으로 한 본 발명의 전지를 유사하게 제조하였다.
- [0221] 사용한 전해질은 에틸 메틸 카르보네이트/디에틸 카르보네이트 (부피비 1:1) 중 LiPF_6 의 1 M 용액이었다.
- [0222] 이로 인해, 25°C , 특히 전지의 전위 범위: $3.0 \text{ V} - 4.3 \text{ V}$ 또는 $3.0 \text{ V} - 4.6 \text{ V}$ 에서 시험한 본 발명의 전지를 수득하였다.
- [0223] 하기의 사이클링 프로그램을 실행하였다:
- [0224] 충전 0.1 C , 방전 0.1 C 2x
- [0225] 충전 0.2 C , 방전 0.2 C 5x
- [0226] 충전 0.2 C , 방전 0.4 C 1x
- [0227] 충전 0.2 C , 방전 0.8 C 1x
- [0228] 충전 0.2 C , 방전 1.6 C 1x

- [0229] 충전 0.2 C, 방전 3.2 C 1x
- [0230] 충전 0.2 C, 방전 6.4 C 1x
- [0231] 충전 0.1 C, 방전 0.1 C 2x (또는 1x)
- [0232] 충전 0.2 C, 방전 0.2 C 5x
- [0233] 충전 0.2 C, 방전 1 C 1x
- [0234] 충전 0.4 C, 방전 1 C 1x
- [0235] 충전 1 C, 방전 1 C 53x
- [0236] 충전 0.2 C, 방전 0.2 C 3x
- [0237] 충전 1 C, 방전 1 C 53x
- [0238] 충전 0.2 C, 방전 0.2 C 3x.
- [0239] 신속 방전시 방전지에서의 용량 손실은 매우 작았다.
- [0240] III.2 . 본 발명의 풀 (full) 전지로의 분석
- [0241] 풀 전지의 제조:
- [0242] 캐소드 (Kat-vz-2) 를 제조하기 위해서, 스크류탑 용기 내에서 하기를 서로 혼합하였다:
- [0243] 85.2% M.2
- [0244] 8.3% 폴리비닐리덴 디플루오라이드 ("PVdF") (Arkema Group 에서 Kynar Flex® 2801 로 시판),
- [0245] BET 표면적 $62 \text{ m}^2/\text{g}$ 인 3.2% 카본 블랙 (Timcal 사에서 "Super P Li" 로 시판),
- [0246] 3.3% 그래피트 (Timcal 사에서 KS6 으로 시판).
- [0247] 교반하면서, 충분한 N-메틸피롤리돈 (NMP) 을 첨가하고, 뭉뚱하고 덩어리를 갖지 않는 페이스트가 수득될 때까지 혼합물을 Ultraturrax 에서 교반하였다.
- [0248] 이에 따라 수득한 페이스트를 $20 \text{ }\mu\text{m}$ 두께의 알루미늄 호일에 나이프-코팅하고, 16 시간 동안 120°C 에서 진공 건조 캐비넷 내에서 건조시켰다. 건조 후 로딩은 $1.1 \text{ mg}/\text{cm}^2$ 였다. 이후, 원형 디스크 형태의 부분을 1.13 cm^2 의 면적으로 구멍내었다. 이로 인해 본 발명의 캐소드 (Kat-vz-2) 를 수득하였다.
- [0249] 전기화학적 시험을 "Swagelok" 전지에서 수행하였다. 사용한 전해질은 에틸 메틸 카르보네이트/에틸렌 카르보네이트 (부피비 1:1) 중 LiPF_6 의 1 M 용액이었다.
- [0250] 분리기: 유리 섬유. 에노드: 그래피트. 온도: 25°C . 전지의 전위 범위: $2.50 \text{ V} - 4.525 \text{ V}$. 사이클링 프로그램: 0.1 C (제 1 및 제 2 사이클), 0.5 C (제 3 사이클). 1 C = 190 mA/g .
- [0251] 결과:
- [0252] 표 1 에 따른 풀 전지에서의 용량 손실을 하기와 같이 계산하였다: 70 사이클 후 및 2 사이클 후 평균 용량의 차이를 70 사이클 후 평균 용량으로 나누고, 100 을 곱하여, 용량 손실을 얻었다 ("페이딩 (fading)").

표 1

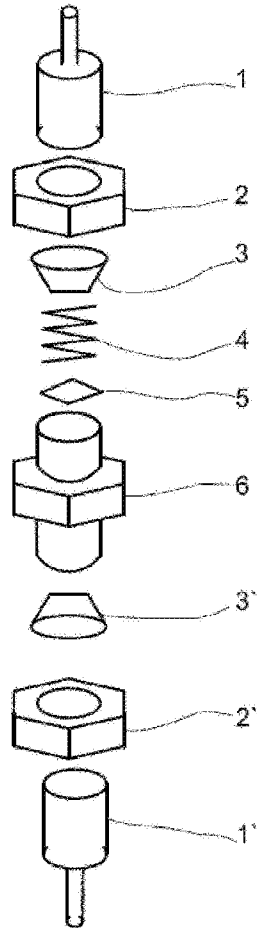
[0253]

풀 전지 분석에서의 용량 손실 결과	
사용한 캐소드	용량 손실 [%]
(kat-vz-2)	10
(kat-vz-3)	8

도면

도 1

도 1: 본 발명의 현상물 시험을 위해 분해된 전자의 모식적 구조



Electronic Patent Application Fee Transmittal

Application Number:	16923494			
Filing Date:	08-Jul-2020			
Title of Invention:	POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING LITHIUM COBALTATE COATED WITH LITHIUM TITANATE AND MAGNESIUM OXIDE			
First Named Inventor/Applicant Name:	Teruaki OCHIAI			
Filer:	John F. Hayden/April Saunders-Fuller			
Attorney Docket Number:	12732-2003004			
Filed as Large Entity				
Filing Fees for Utility under 35 USC 111(a)				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
PETITION FEE- 37 CFR 1.17(H) (GROUP III)	1464	1	140	140
RCE- 1ST REQUEST	1801	1	1360	1360
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
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 (\$)				1500



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Alexandria, VA 22313-1450
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Decision Date : April 9, 2021

In re Application of :

Teruaki OCHIAI

DECISION ON PETITION

UNDER CFR 1.313(c)(2)

Application No : 16923494

Filed : 08-Jul-2020

Attorney Docket No : 12732-2003004

This is an electronic decision on the petition under 37 CFR 1.313(c)(2), filed April 9, 2021 , to withdraw the above-identified application from issue after payment of the issue fee.

The petition is **GRANTED**.

The above-identified application is withdrawn from issue for consideration of a submission under 37 CFR 1.114 (request for continued examination). See 37 CFR 1.313(c)(2).

Petitioner is advised that the issue fee paid in this application cannot be refunded. If, however, this application is again allowed, petitioner may request that it be applied towards the issue fee required by the new Notice of Allowance.

Telephone inquiries concerning this decision should be directed to the Patent Electronic Business Center (EBC) at 866-217-9197.

This application file is being referred to Technology Center AU 1725 for processing of the request for continuing examination under 37 CFR 1.114 .

Office of Petitions

Electronic Acknowledgement Receipt

EFS ID:	42398269
Application Number:	16923494
International Application Number:	
Confirmation Number:	3273
Title of Invention:	POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING LITHIUM COBALTATE COATED WITH LITHIUM TITANATE AND MAGNESIUM OXIDE
First Named Inventor/Applicant Name:	Teruaki OCHIAI
Customer Number:	26171
Filer:	John F. Hayden/April Saunders-Fuller
Filer Authorized By:	John F. Hayden
Attorney Docket Number:	12732-2003004
Receipt Date:	09-APR-2021
Filing Date:	08-JUL-2020
Time Stamp:	16:37:42
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	\$ 1500
RAM confirmation Number	E202149G37381251
Deposit Account	061050
Authorized User	April Saunders-Fuller

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

37 CFR 1.17 (Patent application and reexamination processing fees)

37 CFR 1.19 (Document supply fees)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Petition automatically granted by EFS	petition-request.pdf	31691	no	2
			a13ccf4a3059d08dd38a140c2cd9464a1bd a1998		

Warnings:**Information:**

2	Request for Continued Examination (RCE)	12732-2003004-RCE.pdf	697599	no	3
			c64f0a0031dfecad05c3a277843c334bed7e 12f9		

Warnings:**Information:**

3		12732-2003004-QPIDS.pdf	218996	yes	3
			47f9efddda94fc42c43858e4e8a5ac9f34322 f92		

Multipart Description/PDF files in .zip description

	Document Description	Start	End
	Quick Path Information Disclosure Statement	1	2
	Information Disclosure Statement (IDS) Form (SB08)	3	3

Warnings:**Information:**

4	Foreign Reference	KR20150062724.pdf	6863520	no	53
			b2509e045df2ab37937a44253c731f26987 a4666		

Warnings:**Information:**

5	Foreign Reference	KR20140125856.pdf	1704272	no	51
			98790fc0a661ede94f8b6147b90252a2b98 8803b		

Warnings:**Information:**

6	Fee Worksheet (SB06)	fee-info.pdf	32265	no	2
			04b3819c6ce403be04afa4c27ee1e737191d0c68		

Warnings:

Information:

Total Files Size (in bytes):	9548343
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This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Doc Code: PET.AUTO Document Description: Petition automatically granted by EFS-Web		PTO/SB/140 U.S. Patent and Trademark Office Department of Commerce
Electronic Petition Request	PETITION TO WITHDRAW AN APPLICATION FROM ISSUE AFTER PAYMENT OF THE ISSUE FEE UNDER 37 CFR 1.313(c)	
Application Number	16923494	
Filing Date	08-Jul-2020	
First Named Inventor	Teruaki OCHIAI	
Art Unit	1725	
Examiner Name	SEAN CULLEN	
Attorney Docket Number	12732-2003004	
Title	POSITIVE ELECTRODE ACTIVE MATERIAL INCLUDING LITHIUM COBALTATE COATED WITH LITHIUM TITANATE AND MAGNESIUM OXIDE	
<p>An application may be withdrawn from issue for further action upon petition by the applicant. To request that the Office withdraw an application from issue, applicant must file a petition under this section including the fee set forth in § 1.17(h) and a showing of good and sufficient reasons why withdrawal of the application from issue is necessary.</p> <p>APPLICANT HEREBY PETITIONS TO WITHDRAW THIS APPLICATION FROM ISSUE UNDER 37 CFR 1.313(c).</p> <p>A grantable petition requires the following items:</p> <p>(1) Petition fee; and</p> <p>(2) One of the following reasons:</p> <p>(a) Unpatentability of one or more claims, which must be accompanied by an unequivocal statement that one or more claims are unpatentable, an amendment to such claim or claims, and an explanation as to how the amendment causes such claim or claims to be patentable;</p> <p>(b) Consideration of a request for continued examination in compliance with § 1.114 (for a utility or plant application only); or</p> <p>(c) Express abandonment of the application. Such express abandonment may be in favor of a continuing application, but not a CPA under 37 CFR 1.53(d).</p>		
Petition Fee		
<div style="border: 1px solid black; padding: 5px; margin-bottom: 5px;"> ☐ Small Entity </div> <div style="border: 1px solid black; padding: 5px; margin-bottom: 5px;"> ☐ Micro Entity </div> <div style="border: 1px solid black; padding: 5px;"> ☒ Regular Undiscounted </div>		
Reason for withdrawal from issue		

- ☐ One or more claims are unpatentable
- ☒ Consideration of a request for continued examination (RCE) (List of Required Documents and Fees)
- ☐ Applicant hereby expressly abandons the instant application (any attorney/agent signing for this reason must have power of attorney pursuant to 37 CFR 1.32(b)).

RCE request, submission, and fee.

- ☐ I certify, in accordance with 37 CFR 1.4(d)(4) that :
- ☐ The RCE request ,submission, and fee have already been filed in the above-identified application on
- ☒ Are attached.

THIS PORTION MUST BE COMPLETED BY THE SIGNATORY OR SIGNATORIES

I certify, in accordance with 37 CFR 1.4(d)(4) that I am:

- ☒ An attorney or agent registered to practice before the Patent and Trademark Office who has been given power of attorney in this application.
- ☐ An attorney or agent registered to practice before the Patent and Trademark Office, acting in a representative capacity.
- ☐ A sole inventor
- ☐ A joint inventor; I certify that I am authorized to sign this submission on behalf of all of the inventors as evidenced by the power of attorney in the application
- ☐ A joint inventor; all of whom are signing this e-petition

Signature	/John F. Hayden/
Name	John F. Hayden
Registration Number	37640



United States Patent and Trademark Office

Office of the Chief Financial Officer

Document Code:WFEE

User :71530

Sale Accounting Date:05/04/2021

Sale Item Reference Number

16923494

Effective Date

04/09/2021

Document Number

I202154G28322001

Fee Code

1806

Fee Code Description

SUBMISSION- INFORMATION
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/923,494	07/08/2020	Teruaki OCHIAI	12732-2003004	3273
26171	7590	05/13/2021		
FISH & RICHARDSON P.C. (DC)			EXAMINER	
P.O. BOX 1022			CULLEN, SEAN P	
MINNEAPOLIS, MN 55440-1022				
			ART UNIT	PAPER NUMBER
			1725	
			NOTIFICATION DATE	DELIVERY MODE
			05/13/2021	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

PATDOCTC@fr.com

Supplemental Notice of Allowability	Application No. 16/923,494	Applicant(s) OCHIAI et al.	
	Examiner Sean P Cullen, Ph.D.	Art Unit 1725	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to the IDS filed on 09 April 2021.
☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on ____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on ____; the restriction requirement and election have been incorporated into this action.

3. ☒ The allowed claim(s) is/are 1,3-6,13 and 15-18. As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

4. ☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a) ☒ All b) ☐ Some *c) ☐ None of the:

1. ☐ Certified copies of the priority documents have been received.

2. ☒ Certified copies of the priority documents have been received in Application No. 15/638,449.

3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

* Certified copies not received: ____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date ____.

Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)	5. ☒ Examiner's Amendment/Comment
2. ☒ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____.	6. ☐ Examiner's Statement of Reasons for Allowance
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.	7. ☐ Other _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date _____.	

/Sean P Cullen, Ph.D./ Primary Examiner, Art Unit 1725	
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DETAILED ACTION

Notice of Pre-AIA or AIA Status

1. The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Status of Claims

2. **Claim(s) 1, 3–6, 13, and 15–18** is/are pending.
3. **Claim(s) 2, 7–12, 14, and 19–25** is/are canceled.

Information Disclosure Statement

4. The information disclosure statement (IDS) submitted on 09 April 2021 was filed after the mailing date of the Notice of Allowance on 22 February 2021. The submission complies with the provisions of 37 CFR 1.97. Accordingly, the information disclosure statement is being considered by the examiner.

Conclusion

5. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Sean P Cullen, Ph.D. whose telephone number is (571)270-1251. The examiner can normally be reached on Monday to Thursday 6:00 am to 4:00 pm CT, Friday 6:00 am to 12:00 pm CT.

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is

encouraged to use the USPTO Automated Interview Request (AIR) at
<http://www.uspto.gov/interviewpractice>.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Basia A Ridley can be reached on (571)272-1453. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <https://ppair-my.uspto.gov/pair/PrivatePair>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Sean P Cullen, Ph.D./
Primary Examiner, Art Unit 1725

PTO/SB/08A (07-06)

Approved for use through 03/31/2007. OMB 0651-0031

U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Use as many sheets as necessary)				Complete if Known	
				Application Number	16/923,494
				Filing Date	July 8, 2020
				First Named Inventor	Teruaki OCHIAI
				Art Unit	1725
				Examiner Name	S. CULLEN
				Attorney Docket Number	12732-2003004
Sheet	1	of	1		

U. S. PATENT DOCUMENTS

[illegible]

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No. ¹	Foreign Patent Document	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	T ⁶
		Country Code ³ -Number ⁴ -Kind Code ⁵ (if known)				
		KR-2015-0062724A	06-08-2015			Full
		KR-2014-0125856A	10-29-2014			Full

Examiner Signature	/Sean P Cullen, Ph.D./	Date Considered	05/05/2021
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*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. 1 Applicant's unique citation designation number (optional). 2 See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. 3 Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). 4 For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. 5 Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.15 if possible. 6 Applicant is to place a check mark here if English language Translation is attached.

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450. **DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 (1-800-786-9199) and select option 2.

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May 13, 2021 03:56:11 AM

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Application	Document	Mailroom Date	Attorney Docket No.
16923494	NOA	05/13/2021	12732-2003004
	1449	05/13/2021	12732-2003004

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Effective Date	Sale Item Reference Number	Refund Total
04/09/2021	16923494	\$1,360.00

Document Number	Fee Code	Fee Code Description	Amount Paid	Payment Method	Account Number
I20215HD27263101	1801	RCE- 1ST REQUEST	\$1,360.00	DA	061050



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04/09/2021	05/18/2021	16923494

Document Number	Fee Code	Fee Code Description	Amount Paid	Payment Method
I20215HD27263101	1801	RCE- 1ST REQUEST	\$1,360.00	DA



APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/923,494	06/22/2021	11043660	12732-2003004	3273

26171 7590 06/02/2021

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MINNEAPOLIS, MN 55440-1022

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b) (application filed on or after May 29, 2000)

The Patent Term Adjustment is 0 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (<http://pair.uspto.gov>).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site <http://pair.uspto.gov> for additional applicants):

Teruaki OCHIAI, Atsugi, JAPAN;
SEMICONDUCTOR ENERGY LABORATORY CO., LTD., ATSUGI-SHI, JAPAN;
Takahiro KAWAKAMI, Atsugi, JAPAN;
Mayumi MIKAMI, Atsugi, JAPAN;
Yohei MOMMA, Isehara, JAPAN;
Masahiro TAKAHASHI, Atsugi, JAPAN;
Ayae TSURUTA, Atsugi, JAPAN;

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Application	Document	Mailroom Date	Attorney Docket No.
16923494	ISSUE.NTF	06/02/2021	12732-2003004

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