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(54) Title: SYNTHESIS AND CHARACTERIZATION OF LITHIUM NICKEL MANGANESE COBALT PHOSPHOROUS OXIDE

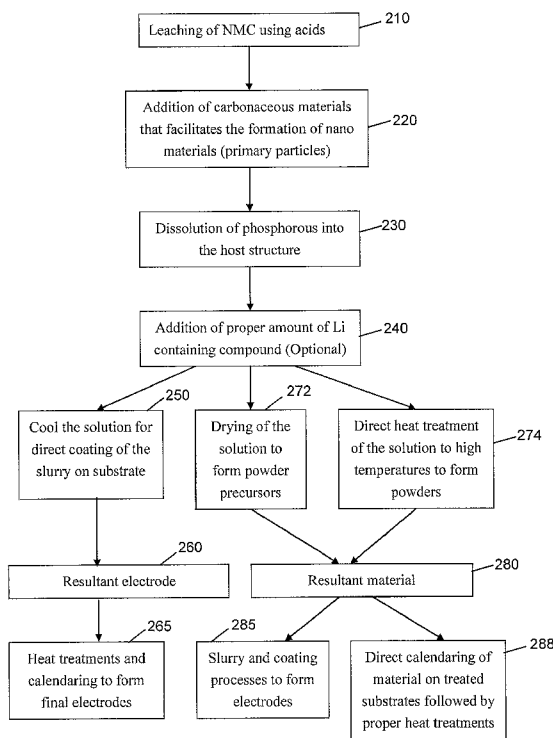


FIG. 2

(57) Abstract: Disclosed herein are certain embodiments of a novel chemical synthesis route for lithium ion battery applications. Accordingly, various embodiments are focused on the synthesis of a new active material using NMC (Lithium Nickel Manganese Cobalt Oxide) as the precursor for a phosphate material having a layered crystal structure. Partial phosphate generation in the layer structured material stabilizes the material while maintaining the large capacity nature of the layer structured material. Materials having a composition represented by:  $Lix Ni_{1/4} Mn_{1/4} Co_{1/4} P_{(1/3-y)} O_2$ , wherein  $0 \leq x \leq 1$ ,  $0.001 \leq y \leq 0.25$  and by:  $Lix X_{(2/3+y)} P_{(1/3-y)} O_2$ , wherein  $0 \leq x \leq 1$ ,  $0.001 \leq y \leq 0.33$ , and X is Nickel or a combination of transition metal elements, can be prepared.

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## Synthesis and Characterization of Lithium Nickel Manganese Cobalt Phosphorous Oxide

### CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the priority benefit of U.S. Patent Application No. 13/889,514, filed on May 8, 2013.

### TECHNICAL FIELD

[0002] The present disclosure is generally concerned with processing techniques for materials synthesis for lithium ion batteries.

### BACKGROUND

[0003] Conventional phosphate material (e.g.,  $\text{LiFePO}_4$ ,  $\text{LiMnPO}_4$ ) materials are structurally stable materials that do not exhibit decomposition of the material when charged to high voltages (e.g., higher than 4.5V). The structure stability is also reflected by the fact that very small or no exothermic reactions are observed when heated to high temperatures without the presence of lithium residing in the structure. However, the phosphate materials do exhibit smaller theoretical capacity (around 170mAh/g) and lower electrical conductivity. As a result, conventional phosphate material is restrictive or picky on the synthesis conditions and electrode preparation methods for lithium ion battery applications.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0004] Many aspects of the disclosure can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale, emphasis instead being placed upon clearly illustrating the principles of certain embodiments of the present disclosure. Moreover, in the drawings, like reference numerals designate corresponding parts throughout the several views.

[0005] FIG. 1(a) is an illustrative view of a crystal structure of a conventional structured  $\text{LiNiO}_2$ .

[0006] FIG. 1(b) is a diagram of an X-Ray Diffraction pattern for  $\text{LiNiPO}_2$  in accordance with embodiments of the present disclosure.

[0007] FIG. 1(c) is a diagram of an X-Ray Diffraction pattern for  $\text{Li}_3\text{Ni}_2\text{PO}_6$  in accordance with embodiments of the present disclosure.

[0008] FIG. 2 is a flow chart diagram depicting an exemplary synthesis process for phosphate material in accordance with embodiments of the present disclosure.

[0009] FIGS. 3(a)-3(b) are diagrams illustrating results of an examination of synthesized materials using X-ray diffraction in accordance with embodiments of the present disclosure.

[00010] FIG. 4(a) is a diagram illustrating results of an examination of synthesized materials using X-ray diffraction in accordance with embodiments of the present disclosure.

[00011] FIGS. 4(b)-4(d) are diagrams illustrating results of an examination of synthesized materials and precursor materials using scanning electron microscope for comparison analysis.

**[00012]** FIG. 5 is a diagram showing phase evolution data for synthesized materials during varying heat treatments in accordance with an exemplary embodiment of the present disclosure.

**[00013]** FIGS. 6(a)-(c) are diagrams showing electrochemical properties of exemplary electrodes in accordance with embodiments of the present disclosure.

**[00014]** FIG. 7 is a diagram of an exemplary embodiment of a furnace and a heat treatment environment for the synthesis of materials in accordance with the present disclosure.

### DETAILED DESCRIPTION

**[00015]** Disclosed herein are certain embodiments of a novel chemical synthesis route for lithium ion battery applications. Accordingly, various embodiments are focused on the synthesis of a new active material using NMC (Lithium Nickel Manganese Cobalt Oxide) as the precursor for a phosphate material having a layered crystal structure. Partial phosphate generation in the layer structured material stabilizes the material while maintaining the large capacity nature of the layer structured material.

**[00016]** For comparison, conventional phosphate material (e.g.,  $\text{LiFePO}_4$ ,  $\text{LiMnPO}_4$ ) materials are structurally stable materials that do not exhibit decomposition of the material when charged to high voltages (e.g., higher than 4.5V). The structure stability is also reflected by the fact that very small or no exothermic reactions are observed when heated to high temperatures without the presence of lithium residing in the structure. However, the phosphate materials do exhibit smaller theoretical capacity (around

170mAh/g) and lower electrical conductivity. In contrast, the layer structured materials exhibit higher theoretical capacity (around 270mAh/g) with better materials intrinsic electrical conductivity.

[00017] In accordance with an embodiment of the present disclosure, a targeted phosphate material is  $\text{Li}_3\text{Ni}_2\text{PO}_6$  (1/3 of the transition metal sites are replaced by phosphorous) and its derivatives (less than 1/3 of transition metal sites are replaced by phosphorous). This material has a higher theoretical capacity of 305mAh/g. Meanwhile, this new class of material can be modified to stabilize the layer structured material by incorporating a different amount of phosphate (or phosphorous oxide) that renders this new class of material as exhibiting high capacity and safety dual characteristics. As an example, the crystal structure (only 1 unit cell) of conventional layer structured  $\text{LiNiO}_2$  is shown for illustration in FIG. 1(a). A total of 12 atom layers are repeated in the Li-O-Ni-O order. If 1/3rd of the Ni sites are replaced by the phosphorous atoms, the material will be  $\text{Li}_3\text{Ni}_2\text{PO}_6$  as mentioned earlier. If 1/6th of the Ni sites are replaced by the phosphorous atoms, the material will become  $\text{Li}_3\text{Ni}_{2.5}\text{P}_{0.5}\text{O}_6$  (i.e.,  $\text{Li}_6\text{Ni}_5\text{PO}_{12}$ ), and so on. For simplicity, a general formula may be given as  $\text{LiNi}_{(1-x)}\text{P}_x\text{O}_2$  for this new class of material. The phosphorous will range from 0.33 to 0.01. The simulated XRD (X-Ray Diffraction) patterns for  $\text{LiNiPO}_2$  and  $\text{Li}_3\text{Ni}_2\text{PO}_6$  are shown in FIG. 1(b) and FIG. 1(c), respectively, for illustrating the iso-structural nature of the phosphorous replaced material. Further, from the enclosed experimental results, it is also apparent to synthesize materials with general formula of  $\text{Li}_x\text{X}_{2/3+y}\text{P}_{1/3-y}\text{O}_2$ ,  $0 \leq x \leq 1$ ,  $0.001 \leq y \leq 0.33$ , where X can be Ni or a combination of transition metal elements, such as Cobalt, Nanganese, Nickel, etc.

**[00018]** For one embodiment, NMC material (Lithium Nickel Manganese Cobalt oxide,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ) is particularly chosen as the synthesis starting material (i.e., precursor). A reason, among others, is to leach out Manganese in the solution state that could expedite the diffusion of Phosphorous ions (or phosphate ions) to the original positioned residing Mn ions. Furthermore, the leached Mn can be re-grown on the surface of the skeletal material (the material being leached) and ensure good electrical conductivity of the synthesized material.

**[00019]** FIG. 2 shows the general synthesis steps utilized in an exemplary embodiment of the present disclosure. To begin, NMC is leached (210) using acids. Next, the addition of carbonaceous materials facilitates (220) the formation of nano materials (primary particles). Then, phosphorous is dissolved (230) into the host structure, and a proper amount of lithium (Li) containing compound may be optionally added (240). To form (260) a resultant electrode, the resulting solution is cooled (250) for direct coating of the slurry on a substrate. After which, heat treatments and calendaring may be applied to form (265) final electrodes.

**[00020]** Alternatively, to form a resultant material (280), the resulting solution may be dried (272) to form powder precursors, or direct heat treatment (to high temperatures) may be applied (274) to the resulting solution to form powders. After which, slurry and coating processes may be applied to form (285) electrodes. Alternatively, direct calendaring of the resultant material on treated substrates followed by proper heat treatments may be performed (288).

[00021] For clarity, exemplary synthesis routes are described using the following examples, in accordance with embodiments of the present disclosure.

#### EXAMPLE 1

Characterization of the occurrence of the phosphorous replaced layer structured material with general formula of  $\text{Li}_x\text{Ni}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{P}_{(1/4-y)}\text{O}_2$

[00022] 1. Initially, dissolve oxalic acid (22.5g (0.25 mole)) in CMC (carboxymethyl cellulose 1wt% solution) (40g) at 80°C.

[00023] 2. Add  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (97g (1 mole)) to the solution. At this time, purplish foam evolves implying the dissolution of Mn into the solution. Keep the solution at 80°C for two more hours until reaction is completed.

[00024] Remarks: Step 1 and 2 are used for leaching Mn from  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ . The acid used in step 1 is not limited to oxalic acid. Formic acid, acetic acid, hydrochloric acid, or nitric acid may also be used. However, organic acids are preferred in certain embodiments.

[00025] 3. Add proper amount of carbonaceous materials. In this case, sucrose (67.5g) was added into the solution. React for 2 more hours.

[00026] Remarks: Step 3 is used in facilitating the formation of nano crystalline materials. The carbonaceous material is not limited to sucrose. Methyl cellulose (MC), Methylcarboxymethyl cellulose (CMC), Cellulose acetate, starch, or styrene butadiene rubber may be used in achieving the same goal.

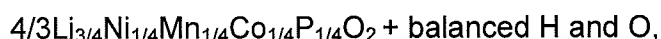
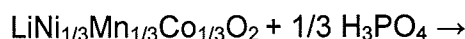
[00027] 4. Then, titrate phosphoric acid (38.3g (0.33 mole, 85% in  $\text{H}_3\text{PO}_4$  content)) to the solution slowly (in half an hour).

[00028] 5. Cool down the solution. At this moment, the solution is good

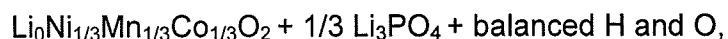
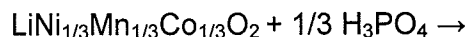
for direct coating on Al foil or can be dried to form powders for later on reaction. That is, the solution can be used in making the electrode directly or can be used in making powder materials.

[00029] In the case of direct coating process, since manganese oxalate (transition metal source), phosphate ions (phosphorous source), and aluminum substrates (aluminum source) are all present, the coated solution can adhere to the substrate when heat treated to high temperatures, as described in U.S. Patent Application No. 13/865,962, entitled "Methods and System for Making an Electrode Free from a Polymer Binder," which is incorporated herein by reference in its entirety.

[00030] In the case of powder formation process, the methods in drying the solution can be flexible. This is usually conducted at 150°C for several hours. FIG. 3(a) and FIG. 3(b) show the XRD data for the as-prepared powder (dried at 150°C) being heat treated at 250°C and 330°C separately for 4 hours in air. From FIG. 3(a) it can be seen that the resultant material consists of two layer structured materials with different lattice parameters. With the sample being heat treated at 330°C, the two (003) peaks merged into only one broadened peak as a new material. This new material can be described with the following reactions:



with the creation of 25% Li vacancies or



with the creation of 100% Li vacancies.

**[00031]** Since trace  $\text{Li}_3\text{PO}_4$  is observed in the resultant material, it may be concluded that the resultant material is between the two extreme cases (i.e., partial phosphorous incorporated layer structured material) with residual  $\text{Li}_3\text{PO}_4$ .

**[00032]** It should be mentioned that no olivine structured materials were observed from the XRD data. So, the occurrence of layer structured, partial replacement of transition metal sites with phosphorous ions can be concluded as the structure of the resultant material. If a microscopic view is implemented in this example, one can also conclude that the resultant material is comprised of layer structured materials with different lattice parameters.

## EXAMPLE 2

Characterization of the occurrence of nano crystalline formation during the transformation of NMC to  $\text{Li}_x\text{Ni}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{P}_{(1/4-y)}\text{O}_2$

**[00033]** 1. Initially, dissolve oxalic acid (22.5g (0.25 mole)) in CMC (carboxymethyl cellulose 1wt% solution) (40g) at 80°C.

**[00034]** 2. Add  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (97g (1 mole)) to the solution. At this time, purplish foam evolves implying the dissolution of Mn into the solution. Keep the solution at 80°C for two more hours until reaction is completed.

**[00035]** Remarks: Step 1 and 2 are used for leaching Mn from  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ . The acid used in step 1 is not limited to oxalic acid. Formic acid, acetic acid, hydrochloric acid, or nitric acid may also be used. However, organic acids are preferred in certain embodiments.

**[00036]** 3. Add proper amount of carbonaceous materials. In this case, methyl cellulose (MC) (67.5g) was added into the solution. React for 1 hour.

**[00037]** 4. Add 30g of n-Butanol for 3 more hours of reaction.

**[00038]** Remarks: Step 3 and 4 are used in facilitating the formation of nano crystalline materials. The carbonaceous material is not limited to sucrose. Methyl cellulose (MC), Methylcarboxymethyl cellulose (CMC), Cellulose acetate, starch, or styrene butadiene rubber may be used in achieving the same goal.

**[00039]** 5. Then, titrate phosphoric acid (38.3g (0.33 mole, 85% in H<sub>3</sub>PO<sub>4</sub> content)) to the solution slowly (in an hour).

**[00040]** Remarks: Steps 5 was utilized in dissolving phosphorous into the structure. Then, the resultant slurry was transferred to a metallic aluminum boat and heat treated to 300°C for 4 hours in air in a box furnace. The heat treated material's XRD data is shown in FIG. 4(a). Meanwhile, FIG. 4(b) and FIG. 4(c) are the SEM (scanning electron microscope) pictures representing the heat treated material (20kX) and the original NMC material (10kX) (before any treatment) for comparisons. It can be seen that the morphology of the heat treated materials is nano particles (primary particle) in nature, which is very different from the original NMC materials morphology.

**[00041]** FIG. 4(d) is an additional SEM picture conducted by cross sectioning the heat treated material. It can be seen that the heat treated material is pretty much porous in nature which can be reflected by the physical data shown in Table 1 as the surface area has been increased from 0.4 to 6 m<sup>2</sup>/g.

Table 1

	Particle size Data (um)			Surface Area Data (BET) (m <sup>2</sup> /g)
	D10	D50	D100	
LiNi <sub>1/3</sub> Mn <sub>1/3</sub> Co <sub>1/3</sub> O <sub>2</sub>	6.06	11.84	38.88	0.3867
Heat Treated Material †	6.08	12.84	42.69	6.0663

Physical properties of the precursor NMC (LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>) and the Example 2 heat treated material (300°C for 4 hours).

† Heat treated material was obtained after heat treating the sample at 300°C for 4 hours.

### EXAMPLE 3

Synthesis and characterization of Li<sub>x</sub>Ni<sub>1/4</sub>Mn<sub>1/4</sub>Co<sub>1/4</sub>P<sub>(1/4-y)</sub>O<sub>2</sub> with the addition of Li content

**[00042]** 1. Initially, dissolve formic acid (47g (1 mole)) in MC (Methyl cellulose 1wt% water solution) (40g) at 80°C.

**[00043]** 2. Add LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> (97g) (1 mole) to the solution. At this time, purplish foam evolves implying the dissolution of Mn into the solution. Keep the solution at 80°C for two more hours until reaction is completed.

**[00044]** Remarks: Step 1 and 2 are used for leaching Mn from LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>. The acid used in step 1 is not limited to formic acid. Oxalic acid, acetic acid, hydrochloric acid, or nitric acid may also be used. However, organic acids are preferred in certain embodiments.

**[00045]** 3. Add proper amount of carbonaceous materials. In this case, methyl cellulose (MC) (20g) was added into the solution. React for 1 hour.

**[00046]** 4. Add 30g of n-Butanol for 1 more hour of reaction.

**[00047]** Remarks: Step 3 and 4 are used in facilitating the formation of nano crystalline materials.

**[00048]** 5. Then, titrate phosphoric acid (28.8g (0.25 mole, 85% in H<sub>3</sub>PO<sub>4</sub> content)) to the solution slowly (in an hour).

**[00049]** 6. Prepare the solution containing lithium on the side by dissolving Li<sub>2</sub>CO<sub>3</sub> (18.5g) in formic acid/water (ratio 30g/60g) solution. 18.5g Li<sub>2</sub>CO<sub>3</sub> is equivalent to 0.5 mole of Li content.

**[00050]** 7. Add the solution prepared in step 6 to the solution resulted from step 5.

**[00051]** Remarks: Step 5 was utilized in dissolving phosphorous into the structure and step 6 was used in increasing the lithium content (e.g., decreasing Li vacancies in the structure as mentioned in Example 1).

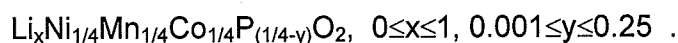
**[00052]** 8. Then, increase the solution temperature from 80°C (kept from step 1 to 6) to 110°C for drying the solution. The dried xerogel was crushed into powder form to be ready for the following heat treatments.

**[00053]** FIG. 5 shows the phase evolution data for the as-prepared powder and the samples being heat treated at 300°C, 380°C, 450°C, 550°C, and 650°C separately for 4 hours in oxygen. Original NMC precursor is also placed for comparisons. From FIG. 5, it can be seen that the heat treated materials showed broadened peaks implying the formation of phosphorized material with new nano crystallines formed on the surface of the resultant materials. Before the heat treatments, the as-prepared powder shows a mixture of manganese formate (hydrated and non-hydrated) and the leached NMC materials. So, it is apparent that the newly formed nano crystalline materials can result from the formation of LiMn<sub>2</sub>O<sub>4</sub>, or nano (amorphous) LiMnPO<sub>4</sub> during the heat treatment processes. Other impurities such as Li<sub>3</sub>PO<sub>4</sub> can be a consequence of excess or non-reacted lithium and

phosphate ions.

**[00054]** From the data described in Examples 1, 2, and 3, several new findings may be mentioned. First, it can be concluded that during the processes disclosed in the present disclosure, the NMC material can be phosphorized. Second, during the formation of the phosphorized layer structured material, new nano crystallines can be formed on the surface of the precursor material with the presence of the porous structure of the final material. It is apparent that the porous structure is formed during the leaching process, and the leached material can re-grow onto the parent material in the form of nano crystalline materials. The broadening of the peaks can be comprehended as the result of the existence of phosphorized layer structured material and the newly formed nano materials. The newly formed nano materials are originated mainly from the presence of leached manganese (formate). Next, heat treatments to elevated temperatures (please refer to the phase evolution study shown in FIG. 5) does not change the peak broadening nature of the material implying the stability of the phosphorized phase can be maintained with the increase of temperature.

**[00055]** Accordingly, from the aforementioned examples, occurrence of phosphate material was observed corresponding to the general formula:



**[00056]** The following examples may be used in characterizing the materials described above. Two exemplary methods used in making exemplary electrodes in accordance with the present disclosure are described.

### Method 1

Conventional method in making the slurry and coating on the aluminum substrate

**[00057]** Example electrode preparation: Active material (5g), Super P® (1g) and SBR (Styrene-Butadiene Rubber) (0.3g) were used in the slurry making. After coating using doctor blade, the coated electrode was dried at 110°C for 3 hours followed by punching of the electrode. After vacuum drying again at 110°C for overnight, the electrodes were transferred to the glove box for test cell assembly. The test cell was three-electrode design with Li as the reference electrode.

### Method 2

Direct formation of the material on the substrate

**[00058]** For example electrode preparation:

**[00059]** 1. Load the active battery material on top of the as made substrate by spreading the active material powder through a 250 mesh sieve of a calendaring machine.

**[00060]** 2. Pass the as made (active material loaded) electrode through the calendaring machine again for compacting the electrode.

**[00061]** 3. Send the as made electrode to the box furnace for various heat treatments.

**[00062]** 4. Punch the heat treated electrode and vacuum dry the samples at 110°C for overnight. The dried electrodes were then transferred to the glove box for test cell assembly.

**[00063]** For substrate preparation:

**[00064]** i. Prepare 5M Phosphoric acid/n-Butanol solution (dissolve 23g phosphoric acid and add n-Butanol to 40ml in volume).

**[00065]** ii. Soak a substrate (Al plate) in the prepared solution that was kept at 50°C for 2 minutes. Then, transfer the substrate to 100ml n-Butanol for rinsing. After rinsing, keep the substrate upright and dry at 50°C.

**[00066]** iii. Allow MnO<sub>2</sub> powders to pass through a 250 mesh sieve and spread on the substrate. Then, take the loaded substrate for calendaring followed by a gentle heat treatment at 330°C for 2 hours in air.

#### EXAMPLE 4

**[00067]** Electrochemical characterizations for the electrodes were made using the as-prepared powders described in Example 3, followed by heat treating the electrode at 330°C for 4 hours in air. The electrode was made using the method 2 described above in which an average of 5.3mg of active material was loaded on the substrate.

**[00068]** For the exemplary electrode, a charge capacity of 251mAh/g was observed. The first discharge capacity was calculated to be 334mAh/g with two plateaus observed (please refer to FIG. 6(a)). The extremely high first discharge capacity could be attributed to the new nano crystalline material (oxides) formed on the surface of the skeletal material.

#### EXAMPLE 5

**[00069]** Electrochemical characterizations for the electrodes were made using the as-prepared powders described in Example 3, followed by heat

treating the electrode at 700°C for 4 hours in oxygen. The electrode was made using the method 2 described above.

**[00070]** For the exemplary electrode, it was observed that the aluminum substrate was able to sustain a heat treatment of 700°C under oxygen atmosphere. It should be noted that if the aluminum substrate is coated with active material on two sides, the aluminum substrate will be even stronger due to the strong oxidizing environment. In this case, an electrode with 2.1mg loading of active material was tested.

**[00071]** A charge capacity of 231.7mAh/g was observed. The first discharge capacity was calculated to be 114.7mAh/g with no obvious plateaus observed (please refer to FIG. 6(b)). The loss of charge capacity could be a result from the presence of the impurity phase observed shown in the phase evolution study.

#### EXAMPLE 6

**[00072]** Electrochemical characterizations for the material synthesized using the as-prepared powders described in Example 3 were made by heat treating the as-prepared powders to 700°C for 4 hours in oxygen. The electrode was made using the conventional slurry making and coating method as described in method 1.

**[00073]** In this example, an electrode with 2.8mg loading (using the recipe described in method 1, active material is 81%) was tested. A charge capacity of 108.5mAh/g was observed. The first discharge capacity was calculated to be 52.6mAh/g with no obvious plateaus observed (please refer to FIG. 6(c)).

The shortage in capacity can be attributed to too small sample size used for the test. A corresponding c-rate of about c/3 was used for testing the sample.

**[00074]** Any process descriptions should be understood as representing steps in an exemplary process, and alternate implementations are included within the scope of the disclosure in which steps may be executed out of order from that shown or discussed, including substantially concurrently or in reverse order, depending on the functionality involved, as would be understood by those reasonably skilled in the art of the present disclosure.

**[00075]** FIG. 7 shows the design of a furnace and a heat treatment environment for the synthesis of the materials presently disclosed. FIG. 7 shows reaction vessel 1, which is open to air in furnace 2. The furnace is open to the atmosphere at 3a and 3b so as to maintain substantially atmospheric pressure in the furnace. Flow of gases into or out of the furnace is dependent on heating and cooling cycles of the furnace and chemical reactions taking place with materials in the furnace. Air is free to enter the furnace, and air and/or products of a chemical reaction of materials 4 in the reaction vessel 1 are free to exit the furnace. Materials 4 in vessel 1 react chemically during heating steps to form cathode materials in accordance with the present disclosure. Materials 4 in vessel 1, which face air found in the furnace, are covered by a layer of a high temperature inert blanket 5, which is porous to air and escaping gases caused by the heating step. Heating coils of the furnace are indicated at 6.

**[00076]** It should be emphasized that the above-described embodiments are merely possible examples of implementations, merely set forth for a clear understanding of the principles of the disclosure. Many variations and

modifications may be made to the above-described embodiment(s) without departing substantially from the spirit and principles of the disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims.

**CLAIMS**

At least the following is claimed:

1. A lithium nickel manganese cobalt phosphorous oxide material having a composition represented by:  
$$\text{Li}_x\text{Ni}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{P}_{(1/4-y)}\text{O}_2,$$
wherein  $0 \leq x \leq 1$ ,  $0.001 \leq y \leq 0.25$ .
2. The lithium nickel manganese cobalt phosphorous oxide material according to claim 1, wherein the material is comprised of layer structured materials with different lattice parameters.
3. The lithium nickel manganese cobalt phosphorous oxide material according to claim 1, wherein the material comprises newly formed nano crystalline materials resulting from a formation of  $\text{LiMn}_2\text{O}_4$  or nano (amorphous)  $\text{LiMnPO}_4$  during a heat treatment process.
4. A positive electrode material for a lithium secondary battery comprising the lithium nickel manganese cobalt phosphorous oxide material according to claim 1.

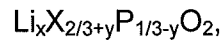
5. The positive electrode material according to claim 4, wherein the positive electrode material further comprises phosphorized material with nano crystallines formed on a surface of the lithium nickel manganese cobalt phosphorous oxide material.

6. The positive electrode material according to claim 5, wherein the nano crystallines comprise  $\text{LiMn}_2\text{O}_4$  formed during a heat treatment process of the lithium nickel manganese cobalt phosphorous oxide material.

7. The positive electrode material according to claim 5, wherein the nano crystallines comprise nano (amorphous)  $\text{LiMnPO}_4$  formed during a heat treatment process of the lithium nickel manganese cobalt phosphorous oxide material.

8. The positive electrode material according to claim 5, wherein the nano crystallines comprise  $\text{Li}_3\text{PO}_4$  formed from excess or non-reacted lithium and phosphate ions.

9. A lithium metal phosphorous oxide material having a composition represented by:



wherein  $0 \leq x \leq 1$ ,  $0.001 \leq y \leq 0.33$ , and

X is Nickel or a combination of transition metal elements.

10. The lithium metal phosphorous oxide material according to claim 9, wherein X is a combination of Nickel, Cobalt, and Manganese elements.

11. The lithium nickel manganese cobalt phosphorous oxide according to claim 9, wherein the material is comprised of layer structured materials with different lattice parameters.

12. A positive electrode material for a lithium secondary battery comprising the lithium nickel manganese cobalt phosphorous oxide material according to claim 9.

13. A process for producing lithium nickel manganese cobalt phosphorous oxide material comprising:

leaching manganese from Lithium Nickel Manganese Cobalt Oxide (NMC) within a solution;

facilitating formation of nano materials with addition of carbonaceous materials to the solution; and

dissolving phosphorous within a resulting host structure of the solution.

14. The process according to claim 13, further comprising:

cooling the resulting solution for direct coating of a slurry on an aluminum substrate;

applying a heat treatment and calendaring to form an electrode comprising the lithium nickel manganese cobalt phosphorous oxide material.

15. The process according to claim 13, further comprising:

drying or applying a direct heat treatment to the resulting solution to form a resultant active material powder.

16. The process according to claim 15, further comprising:  
direct calendaring the active material powder on an aluminum substrate to form a compacted electrode;  
applying a heat treatment to the compacted electrode; and  
drying the heated electrode to form a final electrode comprising the lithium nickel manganese cobalt phosphorous oxide material.

17. The process according to claim 16, wherein the heated electrode is treated at approximately 330°C for approximately 4 hours in air.

18. The process according to claim 13, further comprising:  
adding a lithium containing compound to the solution after the phosphorous is dissolved.

19. The process according to claim 16, wherein the heated electrode is treated at approximately 700°C for approximately 4 hours in oxygen.

20. The process according to claim 15, further comprising:  
applying a heat treatment to an aluminum substrate; and  
directly coating the heated substrate with the resultant active material powder to form a final electrode comprising the lithium nickel manganese cobalt phosphorous oxide material, wherein the resultant active material powder adheres to the heated substrate.

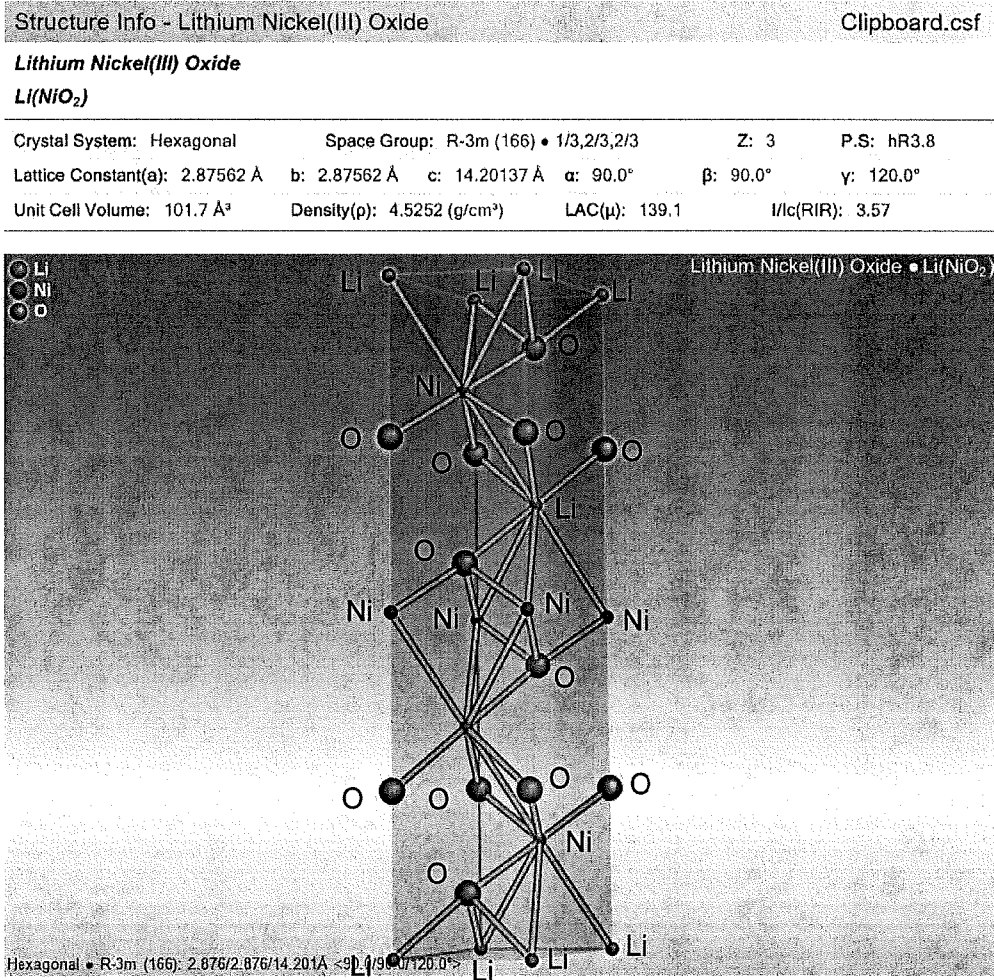


FIG. 1(a)

ID	S.F.	Site	Fill	x	y	z	B(iso)
Li1	Li+1	3 a	1.0	0.0	0.0	0.0	0.5*
Ni2	Ni+3	3 b	1.0	0.0	0.0	0.5	0.5*
O1	O -2	6 c	1.0	0.0	0.0	0.2417	0.5*

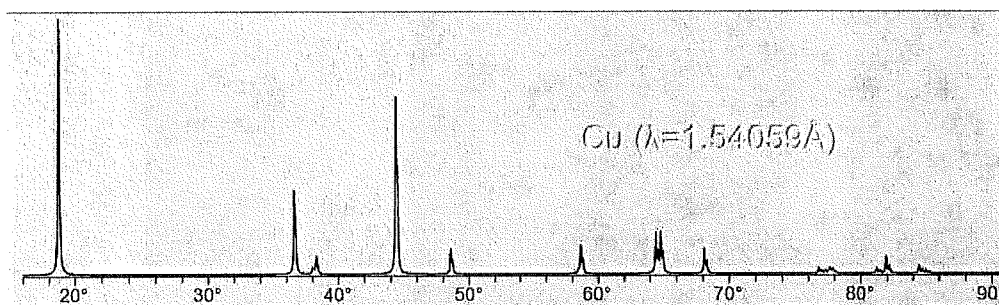


FIG. 1(b)

ID	S.F.	Site	Fill	x	y	z	B(iso)
Li1	Li+1	3 a	1.0	0.0	0.0	0.0	0.5*
P	P +4	3 b	0.33	0.0	0.0	0.5	0.5*
Ni1	Ni	3 b	0.67	0.0	0.0	0.5	0.5*
O1	O -2	6 c	1.0	0.0	0.0	0.2417	0.5*

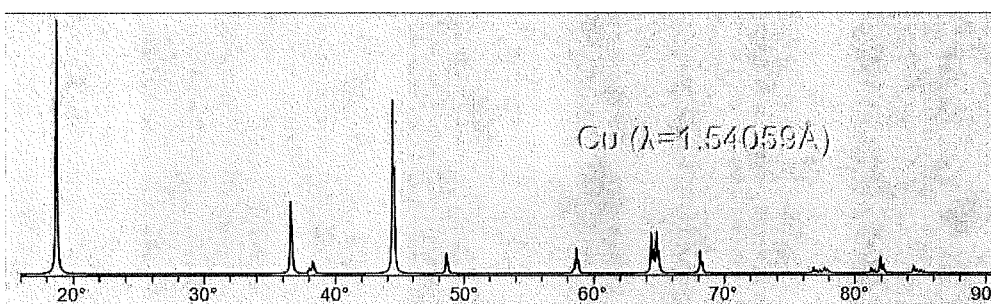


FIG. 1(c)

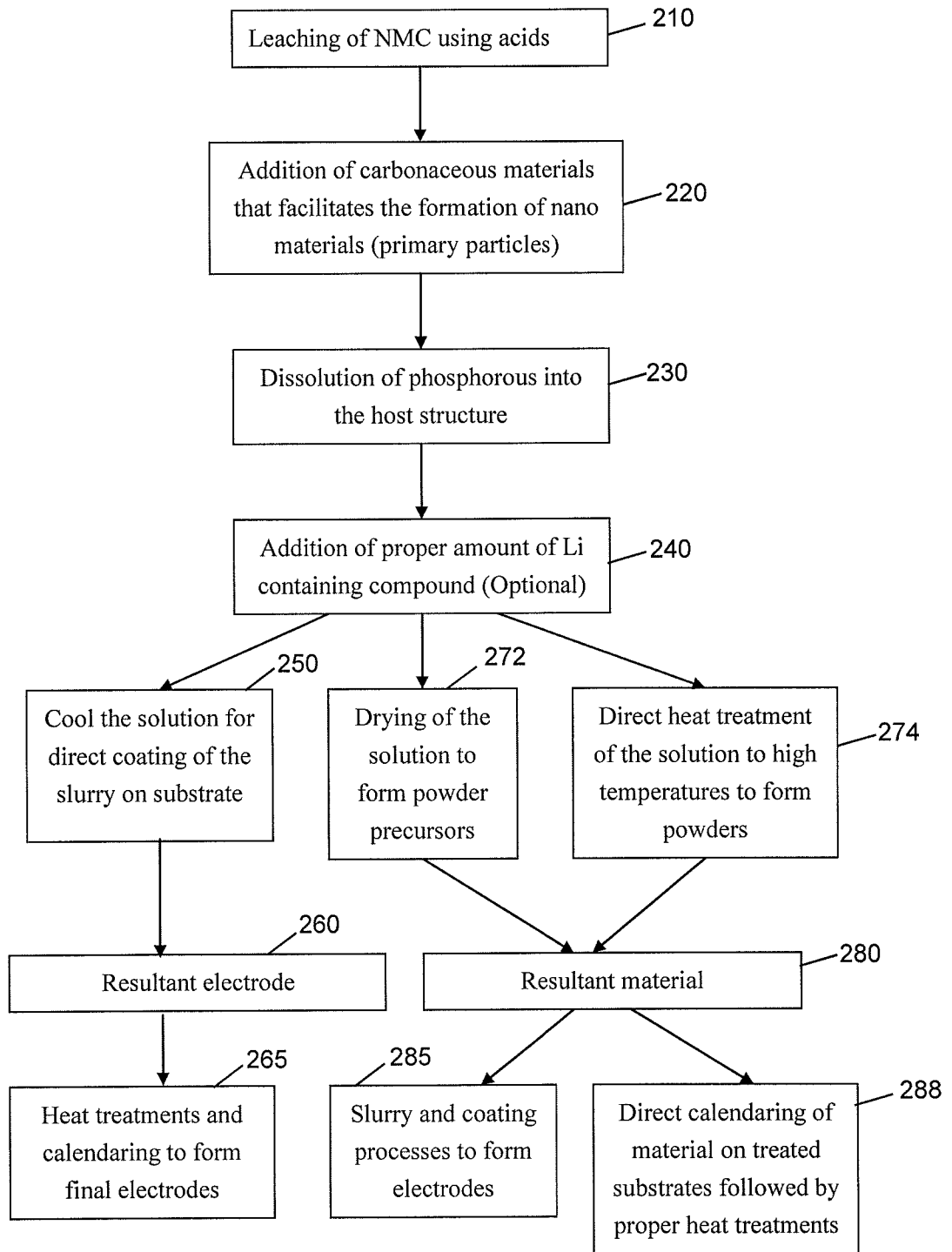


FIG. 2

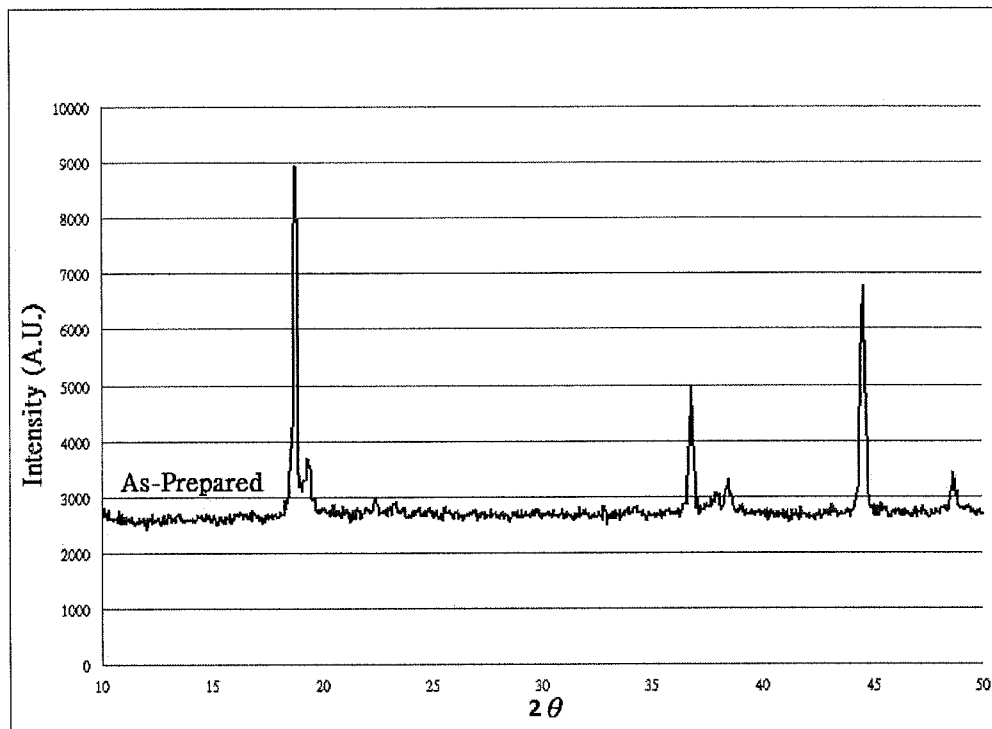


FIG. 3(a)

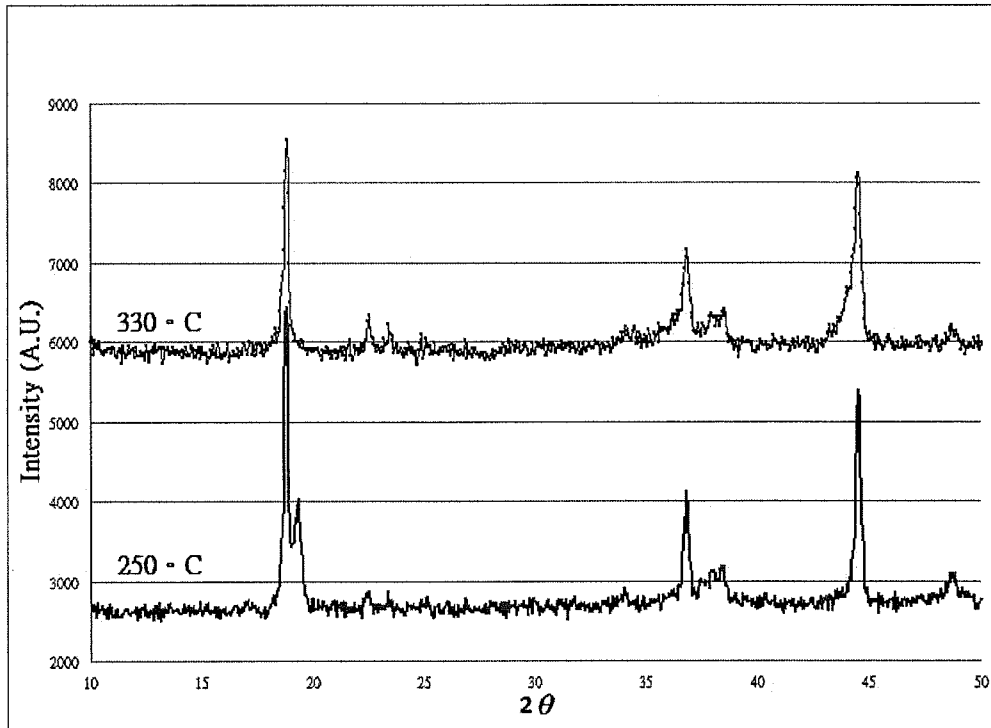


FIG. 3(b)

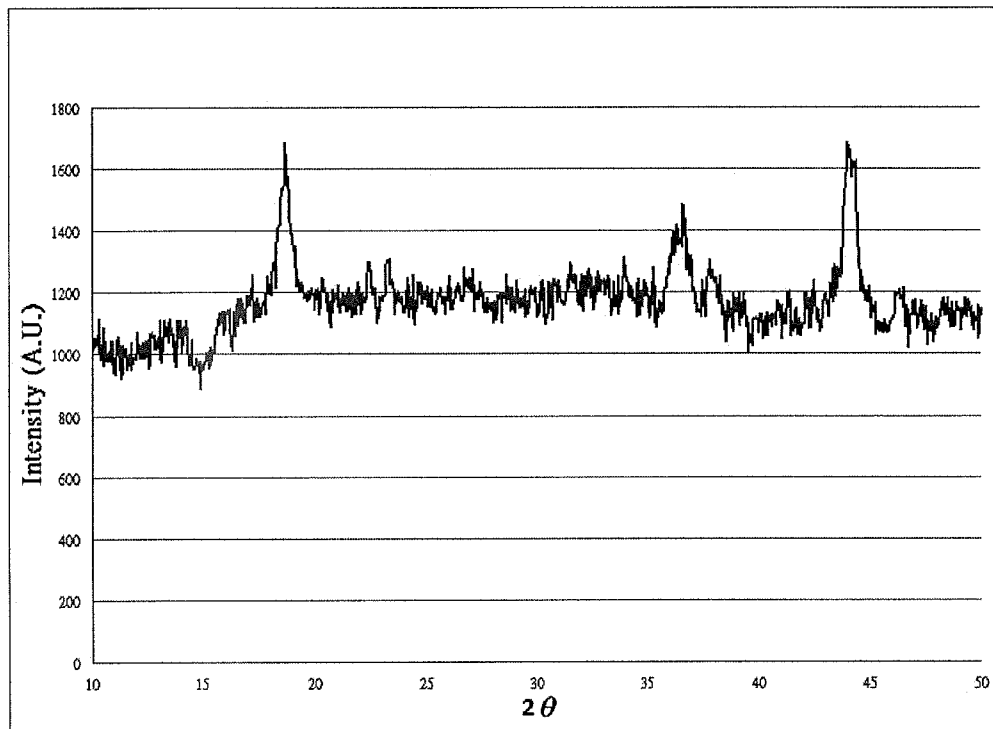


FIG. 4(a)

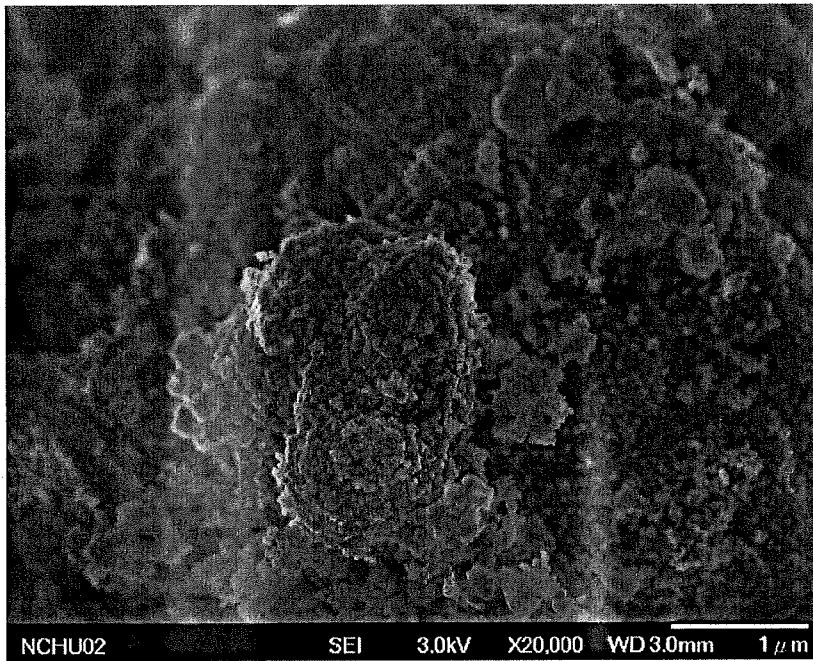


FIG. 4(b)

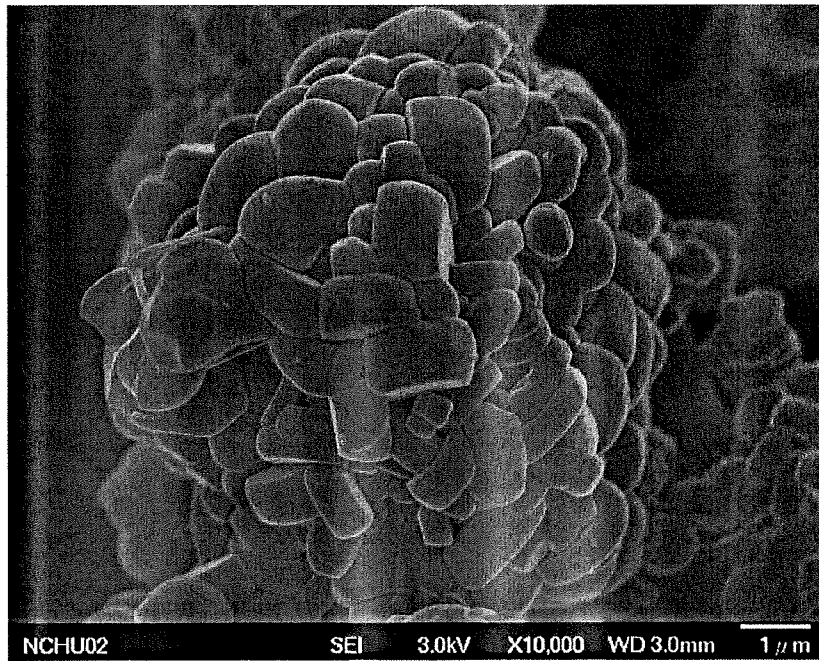


FIG. 4(c)

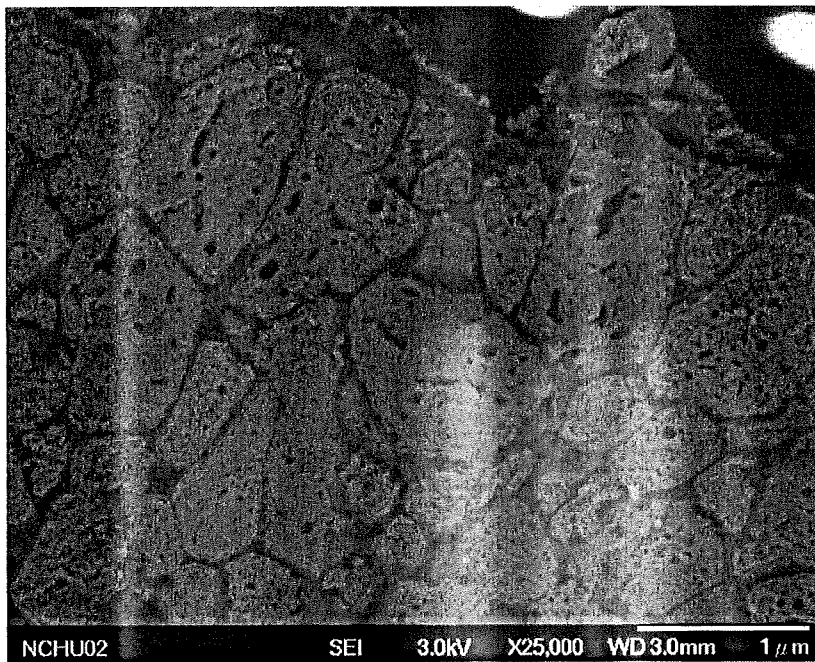


FIG. 4(d)

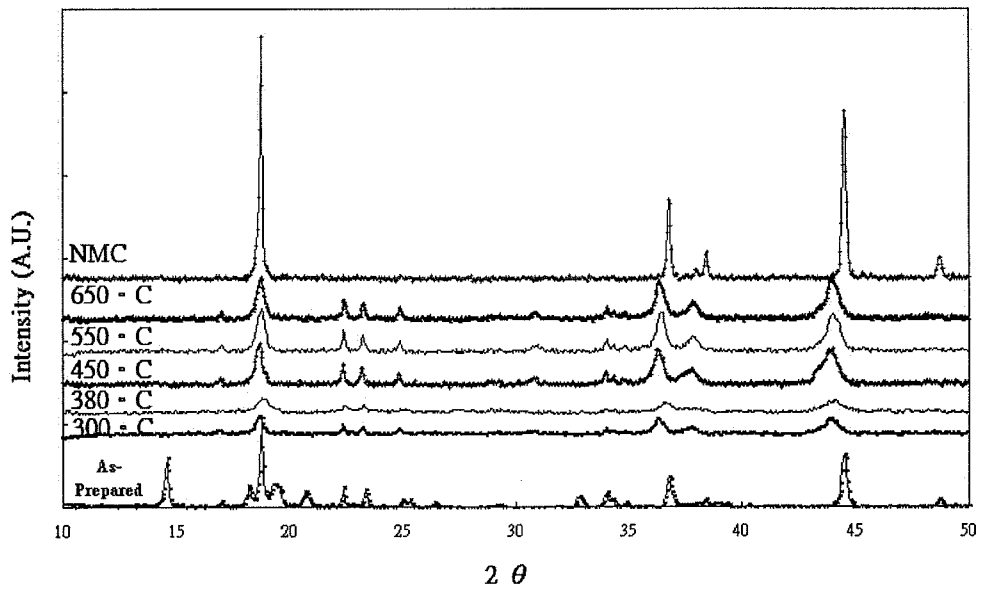


FIG. 5

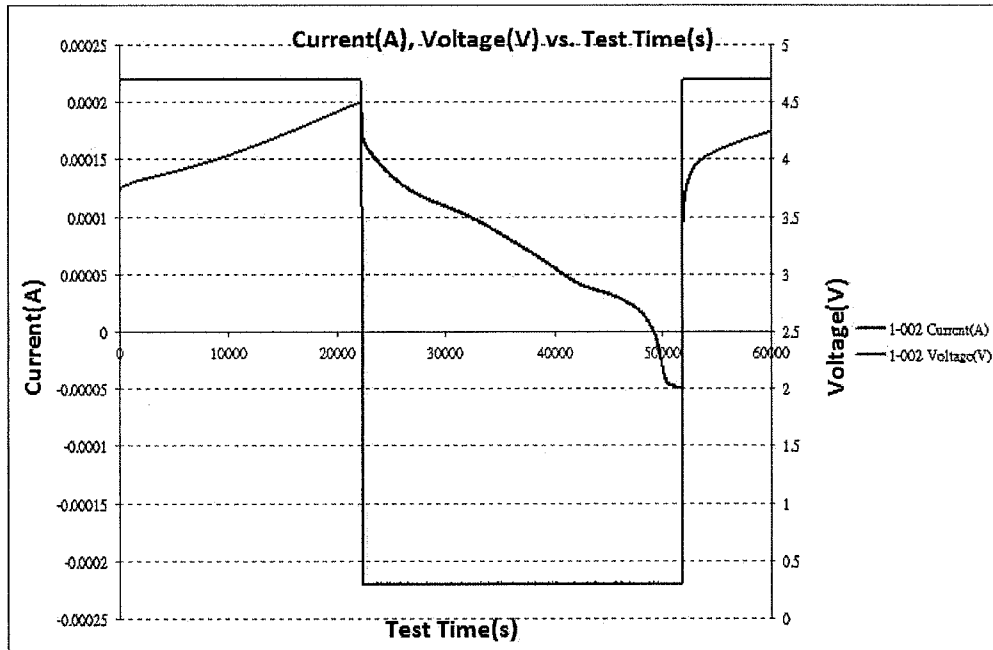


FIG. 6(a)

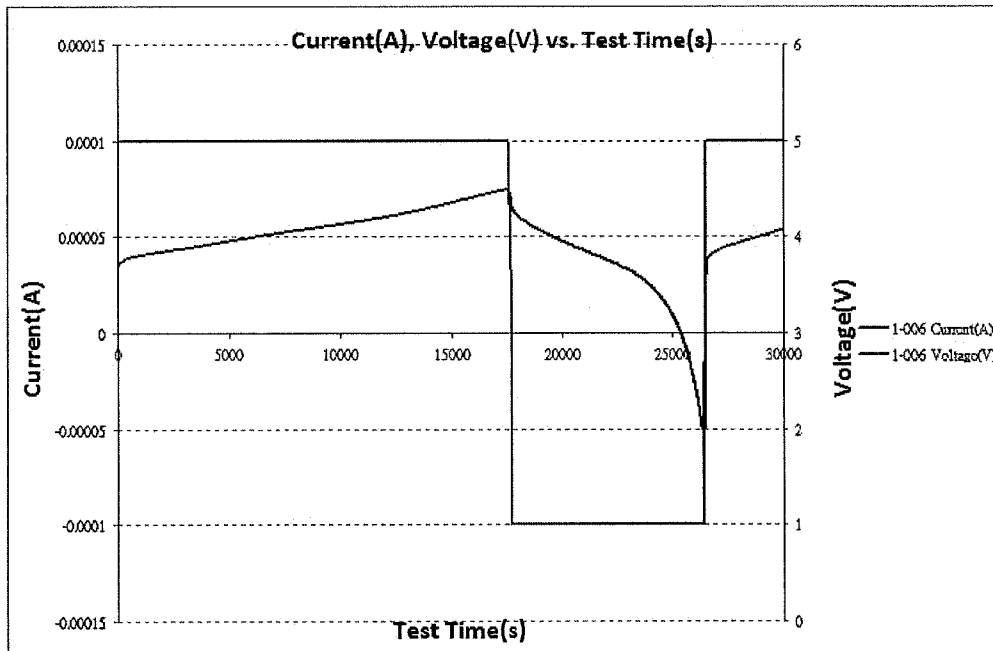


FIG. 6(b)

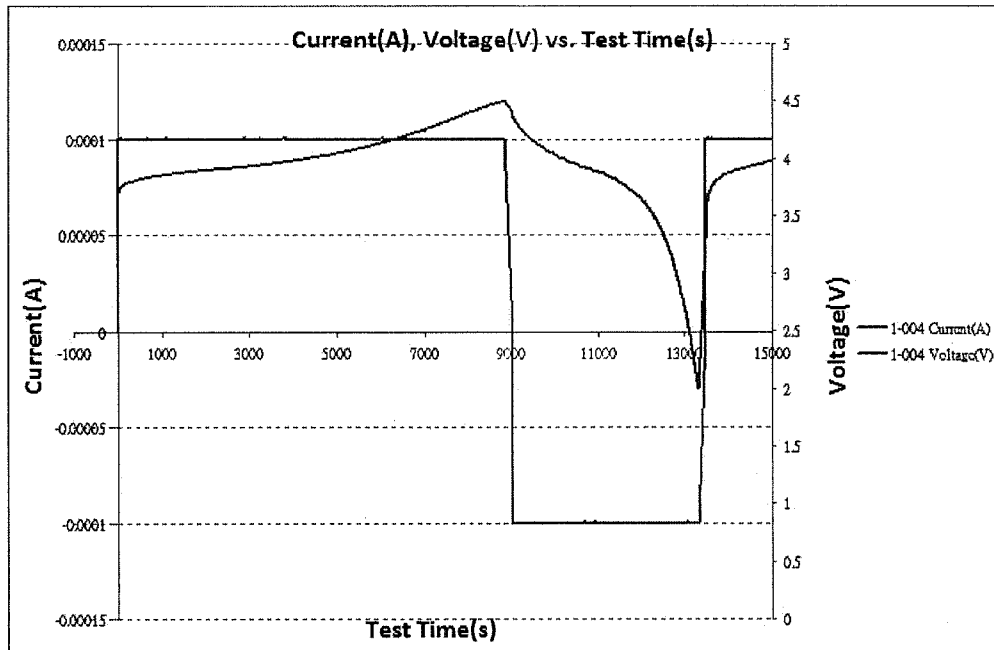


FIG. 6(c)

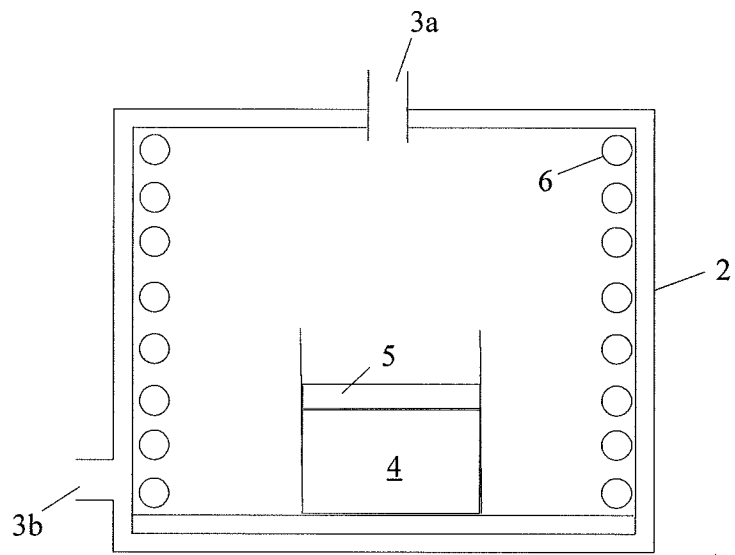


FIG. 7

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/IB2014/001067

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C01B25/16 C01B25/45 C01G53/00 H01M4/505 H01M4/525  
ADD.  
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
Minimum documentation searched (classification system followed by classification symbols)  
C01B C01G H01M  
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/038412 A1 (BASF SE [DE]; SCHULZ-DOBRICK MARTIN [DE]; EWALD BASTIAN [DE]; LAMPERT) 29 March 2012 (2012-03-29) page 2, line 5 - page 3, line 34; claims page 4, lines 9-11 page 10, line 26 - line 29 -----	1-8, 13-20
X	US 2007/281212 A1 (THACKERAY MICHAEL M [US] ET AL) 6 December 2007 (2007-12-06) paragraphs [0004], [0009] - [0010], [0039], [0042], [0045] - [0046] -----	1-8, 13-20
X	EP 1 808 918 A1 (NIPPON MINING CO [JP] JX NIPPON MINING & METALS CORP [JP]) 18 July 2007 (2007-07-18) -----	1-8
A	paragraphs [0011], [0013] - [0014], [0023] - [0025], [0040] - [0042]; tables 10-11 -----	13-20

Further documents are listed in the continuation of Box C.  See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search <b>16 April 2015</b>	Date of mailing of the international search report <b>17/08/2015</b>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer <b>Marucci, Alessandra</b>
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2014/001067

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO 2012038412	A1	29-03-2012	CN 103221345 A	24-07-2013
			EP 2619139 A1	31-07-2013
			JP 2013541147 A	07-11-2013
			KR 20130097778 A	03-09-2013
			TW 201219981 A	16-05-2012
			WO 2012038412 A1	29-03-2012
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US 2007281212	A1	06-12-2007	US 2007281212 A1	06-12-2007
			US 2012141860 A1	07-06-2012
			US 2013130095 A1	23-05-2013
			WO 2008054547 A2	08-05-2008
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EP 1808918	A1	18-07-2007	CN 101048899 A	03-10-2007
			EP 1808918 A1	18-07-2007
			JP 4425915 B2	03-03-2010
			KR 20070058678 A	08-06-2007
			TW I282638 B	11-06-2007
			US 2009121198 A1	14-05-2009
			WO 2006049001 A1	11-05-2006
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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IB2014/001067

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-8, 13-20

### Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

## 1. claims: 1-8, 13-20

A lithium nickel manganese cobalt phosphorous oxide material having a composition represented by:

$\text{Li}_x \text{Ni}_{1/4} \text{Mn}_{1/4} \text{Co}_{1/4} \text{P}_{(1/4-y)} \text{O}_2$ , wherein  $0 < x < 1$ ,  $0.001 < y < 0.25$ .

Method for producing the same and positive electrode material for a lithium secondary battery comprising the same.

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## 2. claims: 9-12

A lithium metal phosphorous oxide material having a composition represented by:

$\text{Li}_x \text{X}_{(2/3+y)} \text{P}_{(1/3-y)} \text{O}_2$ , wherein  $0 < x < 1$ ,  $0.001 < y < 0.33$ , and X is

Nickel or a combination of transition metal elements  
A positive electrode material for a lithium secondary battery comprising the same.

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