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(54) Title: REDUCED STRAIN CATHODE MATERIALS FOR SOLID STATE LITHIUM ION BATTERIES

(57) Abstract: The present invention relates to mixed oxides of formula LiM_2O_4 with reduced strain properties, where M can be one or more transition metals from the first row (Sc to Zn) and/or other elements selected from the group consisting of: Mg, Al, Si, Ga, Ge, Zr, Nb, La and Ta. In preferred embodiments of the present invention, in the mixed oxides of formula LiM_2O_4 of the present invention, M is a mixture of Mn, Mg and Cr. Methods of producing the mixed oxides are also provided as well as an all-solid-state lithium ion secondary battery comprising a positive electrode containing a positive electrode active material comprising the mixed oxide.



reduced strain cathode materials for solid state lithium ion batteriesField of the Invention

5 The present invention relates to the design of a cathode material for a solid state lithium ion battery with zero or reduced expansion and contraction upon charge and discharge in order to improve its reversibility and performance.

Background Art

10 When a Li-ion battery is charged and discharged, Li^+ ions are removed and inserted into host structures at the anode and cathode. This process generates a change in the structure of the host, resulting in mechanical stress and strain, which is responsible for cracks on/in the particles and loss of contact with the conductive agents and the current collector. In conventional Li-ion
15 batteries this phenomenon is countered by using binders, which accommodate the structural expansion and contraction and keep the composite electrode assembly together. In solid-state batteries, however, this is not possible. In a system where the electrode materials are enclosed in a rigid framework, they cannot freely expand and contract: this exacerbates the mechanical stress and
20 strain and leads to poor battery performance.

Currently, an anode material for Li-ion batteries with zero strain is available [Non-patent document 1]. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been extensively investigated and its zero-strain capabilities have been confirmed many times. On the other hand, there are no zero-strain cathode materials reported in the literature. Cho
25 et al [Non-patent document 2] reported that coating LiCoO_2 with ZrO_2 would suppress the typical structural changes in the lithium cobaltate, thus enhancing its reversibility. However, it was later reported by Chen and Dahn [Non-patent documents 3 and 4] that LiCoO_2 within the coating would undergo the same expansion and contraction as the uncoated material, and that the improvement

of performance was due to a limited interaction between the material and the liquid electrolyte.

There does not therefore appear to be any concrete example of a material exhibiting zero-strain properties which can be used as cathode in a solid state Li-ion battery.

Non-patent documents:

[1] J. Electrochem. Soc. 1995, Volume 142, issue 5, 1431-1435

[2] Angewandte Chemie International Edition, 2001, Volume 40, Issue 18, pages 3367–3369

[3] Electrochem. Solid-State Lett. 2002, Volume 5, issue 10, A213-A216

[4] Electrochimica Acta, Volume 49, Issue 7, 15 March 2004, Pages 1079–1090

Problem to be solved

In the light of the above, the present inventors have sought to design new electrode materials with zero or low strain that may be used in solid-state lithium batteries.

After a theoretical study of volume change upon delithiation for a large range of LiM_2O_4 -type materials (for a number of different M species), certain specific mixed oxides of lithium, manganese, chromium and magnesium were proven experimentally to show low volume change.

Summary of the invention

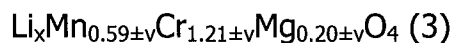
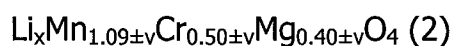
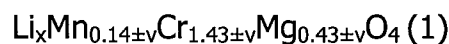
As a result of the research effort of the present inventors, mixed oxides with promising properties for solid-state lithium batteries have been identified.

In one aspect, the present invention relates to mixed oxides of formula LiM_2O_4 with reduced strain properties, where M can be one or more transition metals from the first row (Sc to Zn) and/or other elements selected from the

group consisting of: Mg, Al, Si, Ga, Ge, Zr, Nb, La and Ta, wherein the "reduced strain properties" are characterized by an change in cell volume of less than or equal to 5% between the fully lithiated and delithiated state of the mixed oxide. Preferably the change in cell volume (experimentally observed) will be less than
 5 or equal to 2%, more preferably less than or equal to 1%.

In preferred embodiments of the present invention, in the mixed oxides of formula LiM_2O_4 of the present invention, M is a mixture of Mn, Mg and Cr.

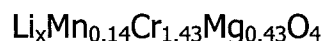
In a specially advantageous embodiment, the present invention relates to a mixed oxide according to claim 1 or 2, having any one of the following
 10 formulae (1), (2) or (3):



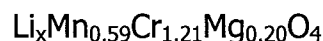
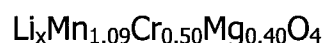
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where v is less than or equal to 0.05. More preferably v is less than or equal to 0.02, and most preferably v is less than or equal to 0.01.

Compounds having the formulae:



20



are specifically comprised within the present invention.

The present invention, in another aspect also provides a method of producing a mixed oxide of Li, Mn, Cr and Mg, including the specific mixed
 25 oxides defined above. The method comprises the steps of:

(a) mixing a lithium source, a manganese source, a chromium source, and a magnesium source; and

(b) calcining the mixture obtained in step (a) in an oxygen-containing atmosphere, such as atmospheric air, at a temperature of between 700°C and 1100 °C for a time between 6 and 24 hours.

Appropriately, in the method of the present invention, each of the lithium source, manganese source, chromium source, and/or magnesium source are, independently of one another, metal sources in the form of carbonates, sulfates, nitrates, oxalates, chlorides, hydroxides and/or oxides. In a particularly preferred embodiment, the lithium source, manganese source, chromium source, and/or magnesium source is (are) nitrate(s).

In a further aspect, the present invention also provides an all-solid-state lithium ion secondary battery comprising:

- a positive electrode containing a positive electrode active material comprising a mixed oxide as defined hereinabove, which may advantageously be one of the specific mixed oxides defined hereinabove based on Li, Mn, Cr and Mg;

- a negative electrode containing a negative electrode active material capable of releasing and accepting lithium ions; and

- a solid electrolyte layer sandwiched between the positive electrode and the negative electrode.

Brief summary of the Figures

Figure 1 shows a representation of volume change vs. Li content in LiM_2O_4 , as determined using theoretical calculations.

Figure 2 shows the theoretically calculated strain characteristics of three specific preferred embodiments of mixed oxides of Li, Mn, Cr and Mg according to the invention.

Figure 3 shows X-ray diffraction (XRD) data obtained for pristine materials corresponding to three specific preferred embodiments of mixed

oxides of Li, Mn, Cr and Mg according to the invention. "Pristine" here is used in the sense of "as synthesized" without further processing.

Figure 4 shows the results obtained upon the first charge of conventional liquid-type batteries containing three specific preferred embodiments of mixed oxides of Li, Mn, Cr and Mg according to the invention.

Figure 5a, 5b, 5c show, respectively, XRD patterns, after charging, of the three specific preferred embodiments $\text{Li}_x\text{Mn}_{0.14}\text{Cr}_{1.43}\text{Mg}_{0.43}\text{O}_4$ (1), $\text{Li}_x\text{Mn}_{1.09}\text{Cr}_{0.5}\text{Mg}_{0.4}\text{O}_4$ (2) and $\text{Li}_x\text{Mn}_{0.59}\text{Cr}_{1.21}\text{Mg}_{0.2}\text{O}_4$ (3).

Figure 6 shows reduced volume expansion for the materials described in the present invention vs. the state-of-the-art materials.

Detailed Description of the Invention

In the theoretical study carried out by the present inventors, which was the first step in the genesis of the present invention, in the first stage, the volume change upon delithiation was calculated for all basic constituents LiM_2O_4 . Here, M can be one or more transition metals from the first row (Sc to Zn) and/or other elements selected from the group consisting of: Mg, Al, Si, Ga, Ge, Zr, Nb, La and Ta. The aim was to identify mixed oxides with reduced strain i.e. a minimum change of volume according to the change in lithium content. Preferably, "reduced strain properties" are characterized by a change in cell volume of less than or equal to 5% between the fully lithiated and delithiated state of the mixed oxide, more preferably less than or equal to 2%, still more preferably less than or equal to 1%.

In Figure 1, the volume change trend as calculated is shown, the volume change according to the lithium content from 0 to 1 being calculated.

Specifically, the volume change for a compound $\text{Li}_x(\text{MnM}^1\text{M}^2)_2\text{O}_4$ was calculated from interpolation and averaging, M^1 and M^2 being metals selected from the M group as set out above. It was desired to design a predictive tool to find materials with the desired property (i.e. low strain). Cell parameter (and

consequently cell volume) changes are very often governed by an empirical rule called "Vegard's Law". In essence, this rule supposes that, if two elements or compounds are taken and a solid solution is made of them, the variation of the cell parameters will show linear dependence on the solid solution composition.

- 5 Thus, if component 1 has a cell parameter of 5 Å and component 2 has a cell parameter of 3 Å, a 50/50 solution of 1 and 2 will have a cell parameter of 4 Å.

In the work underlying the present invention, the variation of the cell parameter was calculated for basic constituents LiM_2O_4 (cf. Figure 1), and then these were mixed in different proportions in a search for systems where the
10 cell parameter would remain constant regardless of the Li content. Cell volumes at a Li content of 0.0, 0.5 and 1.0 were calculated. Interpolation and averaging were used in this process of minimizing the volume change. Computer software available for such calculations uses both known crystal structure data as well as theoretical calculations. Simulations were performed
15 using Density Functional Theory (DFT) through MedeA® software.

Here, the cell volume, typically given in cubic angstroms ($\text{\AA}^3$), may be referred to as Ω .

Particular attention was given in the present invention to ternary mixtures where M includes Mg, Cr and Mn. Mg has the unique property, as
20 shown in Figure 1, of having a cell volume that actually decreases as Li content increases, which is important for balancing the more-or-less pronounced opposite trend for other metals (cf. Figure 1). Magnesium (Mg) has no ability to vary oxidation state as Li content varies. Manganese (Mn) is a basic structural component and a part of known LiMn_2O_4 spinel oxides used in
25 lithium batteries. Mn also has oxidation state variability (in particular through Mn(II) and Mn(IV) states). Chromium (Cr) shows further oxidation state variability (oxidation up to Cr(VI) being possible), which allows the mixed oxide to manage the charge variation as Li^+ ions are removed from the structure during charge of the battery.

The theoretical study detailed above led to the discovery of three compounds of interest. A first compound was identified and was predicted to have zero strain, with no volume change upon lithium removal, according to the simulation result (as shown in Figure 2). This first compound has the formula $\text{Li}_x\text{Mn}_{0.14}\text{Cr}_{1.43}\text{Mg}_{0.43}\text{O}_4$. Compounds 2 and 3 identified in the theoretical study were predicted to show low strain and have formulae $\text{LiMn}_{1.09}\text{Cr}_{0.5}\text{Mg}_{0.4}\text{O}_4$ and $\text{LiMn}_{0.59}\text{Cr}_{1.21}\text{Mg}_{0.2}\text{O}_4$. The low strain behavior was compared to the benchmark known mixed oxide compound $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

After this theoretical part of the study, these three materials were prepared by coprecipitation starting from nitrates of the metal precursors, followed by calcination at 900°C for several hours.

For composition 1, 1.408 g of LiNO_3 , 0.724 g of $\text{Mn}(\text{NO}_3)_2$, 11.677 g of $\text{Cr}(\text{NO}_3)_3$ and 2.224 g of $\text{Mg}(\text{NO}_3)_2$ were mixed and ground in an agate mortar. For composition 2, 1.408 g of LiNO_3 , 5.64 g of $\text{Mn}(\text{NO}_3)_2$, 4.04 g of $\text{Cr}(\text{NO}_3)_3$ and 2.07 g of $\text{Mg}(\text{NO}_3)_2$ were mixed and ground in an agate mortar. For composition 3, 1.408 g of LiNO_3 , 3.053 g of $\text{Mn}(\text{NO}_3)_2$, 9.78 g of $\text{Cr}(\text{NO}_3)_3$ and 1.034 g of $\text{Mg}(\text{NO}_3)_2$ were mixed and ground in an agate mortar. The nitrate mixtures were then transferred to alumina crucibles and heated at 100°C/hour up to 900°C. The samples were kept at 900°C for 10 hours, and then cooled at the natural cooling rate of the oven.

In a synthesis based on metal nitrate precursors, in order to calculate the right amount of source material, it is considered that no oxygen is lost, as the calcination is carried out in air so that O_2 is supplied by the environment. Nitrates are decomposed as nitrogen oxides (NO_x) and are lost, and the starting mixture is calculated stoichiometrically based only on the metal content of the nitrates, adjusted for the purity of the starting precursor (for example some are of 97% purity, others 98% and so on).

The XRD patterns of the three materials prepared are shown in Figure 3. XRD patterns were acquired on a Rigaku Miniflex II diffractometer with $\text{CuK}\alpha$

radiation. The sample powders were ground in an agate mortar and placed in a flat, rotating sample holder. The pattern was acquired between 2θ values of 10 and 90 degrees in continuous mode with a scan rate of 0.5 degrees per minute. The diffraction patterns were analyzed with the Fullprof software.

5 In order to estimate the volume change upon charging, the materials were charged up to the stability limit of the electrolyte ($\sim 5V$ vs. Li^+/Li) as shown in Figure 4. Electrodes for battery testing were prepared by mixing the active material powders (75 wt%) with carbon additives (15 wt%) and a polymeric binder (PVDF, 10 wt%). The components were suspended in N-
10 Methyl Pyrrolidone (NMP) and mixed until a homogeneous slurry was obtained. The slurry was cast using the "Doctor Blade" technique on an aluminum foil with a wet thickness of 0.5mm. The electrode was dried overnight in a vacuum oven at $80^\circ C$. Round electrodes with a diameter of 16 mm were cut from the dried sheet and used to assemble swagelok-type two-electrode cells where a
15 disc of lithium metal served as counter and pseudo-reference electrode. The electrolyte used was a 1 M $LiPF_6$ solution in ethylene carbonate : dimethylcarbonate 50:50 in weight (commercially known as LP30).

After charging, the electrodes were recovered and an XRD pattern was taken to assess the change in cell parameter. Electrodes were recovered from
20 the swagelok cells in an argon-filled glove box and washed in dimethylcarbonate to remove the electrolyte residue. Each sample was then placed on an XRD sample holder and covered with Kapton tape in order to avoid contact with air. The samples were then measured in a Rigaku Miniflex II diffractometer with CuK radiation. The pattern was acquired between 2θ values
25 of 10 and 90 degrees in continuous mode with a scan rate of 0.5 degrees per minute. The diffraction patterns were analyzed with the Fullprof software.

The XRD patterns for the three materials after charging, compared to the pristine ones, are shown in figure 5a-5b-5c.

From the cell parameter "a", the cell volume was calculated according to $V = a^3$ (considering the cubic symmetry of the three materials) and compared to the values for the benchmark $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ obtained from Journal of the Electrochemical Society, 2006, 153(7), A1345. This material was chosen as benchmark and state-of-the-art as it is a high-voltage material suitable for use in solid-state batteries. The result shown in Figure 6 clearly indicates the strong reduction of volume change coming with the invention of the new materials.

An all-solid-state lithium ion secondary battery according to the present invention has a configuration in which a solid electrolyte layer is sandwiched between a positive electrode containing a positive electrode active material capable of accepting and releasing lithium ions and a negative electrode containing a negative electrode active material capable of releasing and accepting lithium ions. The solid electrolyte layer is made of an electronically insulating material capable of transferring lithium ions between anode and cathode.

In the all-solid-state lithium ion secondary battery, the positive electrode active material, which is contained in the positive electrode, can include, in addition to the mixed oxides of the invention, also contain minor amounts of other positive electrode active materials insofar as the latter do not materially affect the functioning of the invention, and in particular do not significantly increase strain upon delithiation. The other positive electrode active materials are preferably present at not more than 10 %, more preferably not more than 5 %, and more preferably not more than 1 % by mass with respect to the positive electrode active materials of the invention, and may include: a sulfide containing a transition metal element or an oxide containing lithium and a transition metal element. Examples of such further positive electrode active materials include transition metal sulfides such as TiS_2 , TiS_3 , MoS_3 , and FeS_2 ; lithium-manganese composite oxides such as LiMnO_2 and LiMn_2O_4 ; lithium-cobalt composite oxides such as LiCoO_2 ; lithium-nickel composite oxides such as

LiNiO₂; lithium-manganese-cobalt composite oxides such as LiMnCoO₄; lithium-iron composite oxides such as LiFeO₂; lithium-iron-phosphorus composite oxides such as LiFePO₄; lithium-vanadium composite oxides such as LiV₂O₄; and transition metal oxides such as V₂O₅. As set out hereinabove, the positive electrode active material in preferred embodiments of the present invention will contain a mixed lithium-manganese-chromium-magnesium oxide as detailed in the present invention because such a material has the potential to show one or more of the following favourable properties: low strain properties, safe operation and high temperature resistance.

The positive electrode may consist only of one or more positive-electrode active materials or may consist of a mixture of one or more positive-electrode active materials, one or more binders, one or more conductive agents, one or more electrolytes and so on.

Examples of the binder(s) include polyvinylidene fluoride, polytetrafluoroethylene, polyvinyl acetate, polymethyl methacrylate and polyethylene.

Examples of the conductive agent(s) include metals, conductive ceramics, natural graphite, artificial graphite, acetylene black and vapor-grown carbon fiber (VGCF).

As the electrolyte, oxides such as Li-conducting garnets or perovskites or spinels can be used. Other materials include Li-conducting sulfides, phosphates or glasses. The inclusion of the solid electrolyte material also in the positive electrode makes exchange of electrons and ions between the positive electrode and the solid electrolyte layer smoother.

For example, the positive electrode can be obtained by mixing the positive-electrode active material and the optional materials including the binder, the conductive agent and the electrolyte, and pressing the resulting mixture into a pellet form. When a sheet (foil) of a metal or an alloy thereof is used as the positive-electrode active material, it can be used as-is.

The positive electrode may be formed on a current collector such as aluminum or copper.

In the all-solid-state lithium ion secondary battery, examples of the negative electrode active material, which is contained in the negative electrode, include metallic lithium, carbonaceous materials capable of releasing and occluding lithium ions, lithium-containing alloys such as Li-Al and Li-Zn, indium-containing alloys such as In-Sb and Cu-In-Sn, oxides such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and WO_2 , lanthanum-nickel compounds such as $\text{La}_3\text{Ni}_2\text{Sn}_7$, and conductive polymers. In particular, the negative electrode active material is preferably $\text{Li}_4\text{Ti}_5\text{O}_{12}$ because such a material has zero strain properties, safe operation and high temperature resistance.

The negative electrode may consist only of one or more negative-electrode active materials or may consist of a mixture of one or more negative-electrode active materials, one or more binders, one or more conductive agents, one or more electrolytes and so on.

Examples of the binders include polyvinylidene fluoride, polytetrafluoroethylene, polyvinyl acetate, polymethyl methacrylate and polyethylene.

Examples of the conductive agent include metals, conductive ceramics, natural graphite, artificial graphite, acetylene black and vapor-grown carbon fiber (VGCF).

As the electrolyte, oxides such as Li-conducting garnets or perovskites or spinels can be used. Other materials include Li-conducting sulfides, phosphates or glasses. The inclusion of the solid electrolyte material also in the positive electrode makes exchange of electrons and ions between the positive electrode and the solid electrolyte layer smoother.

For example, the negative electrode can be obtained by mixing the negative-electrode active material and the optional materials including the binder, the conductive agent and the electrolyte, and pressing the resulting

mixture into a pellet form. When a sheet (foil) of a metal or an alloy thereof is used as the negative-electrode active material, it can be used as-is.

The negative electrode may be formed on a current collector such as aluminum or copper.

5 In the all-solid-state lithium ion secondary battery, a process for preparing the positive or negative electrode is not particularly limited and a vapor or solid phase process can be used to prepare the positive or negative electrode. Examples of the vapor phase process include pulse laser deposition (PLD), sputtering, vapor deposition, and chemical vapor deposition (CVD)
10 including metal-organic Chemical vapor deposition (MOCVD). Examples of the solid phase process include a sintering process, a sol-gel process, a doctor blade process, a screen printing process, a slurry casting process, and powder pressing. The following solvent can be used to prepare slurry by a doctor blade process or a similar process: an aromatic hydrocarbon solvent such as toluene
15 or xylene or an alcoholic solvent such as ethanol or propanol. When the slurry contains a resin binder, the resin binder may be, for example, a polyvinyl resin. In the case of manufacturing the all-solid-state lithium ion secondary battery by powder pressing, all of the positive electrode active material, the negative electrode active material, and the solid electrolyte may be powdery.
20 Alternatively, the solid electrolyte may be solid and the positive and negative electrode active materials may be powdery. Alternatively, the solid electrolyte may be powdery and the positive and negative electrode active materials may be solid.

 The all solid-state lithium secondary battery of the present invention can
25 be obtained by stacking the positive electrode, the electrolyte layer and the negative electrode, and pressing them, for example.

 The all-solid-state lithium ion secondary battery is not particularly limited in shape and may have a coin shape, a button shape, a sheet shape, a multilayer shape, a cylindrical shape, a flat shape, a rectangular shape, or

another shape. Those identical to the all-solid-state lithium ion secondary battery may be connected to each other in series so as to form a power supply for electric vehicles. Examples of the electric vehicles include battery electric vehicles powered by batteries only, hybrid electric vehicles powered by internal combustion engines and motors, and fuel-cell electric vehicles powered by fuel cells.

The technical teaching of all patent and non-patent references cited hereinabove are incorporated herein in their entirety.

All combinations of embodiments of products or processes of the present invention, taught herein as being preferable, advantageous or otherwise generally applicable within the framework of the present invention, are to be interpreted as being within the scope of the present invention, except where such combinations of preferred features, disclosed in separate parts of the text hereinabove, are said therein to be mutually exclusive or are clearly contradictory / technically incompatible in context.

Worked examples provided within the present disclosure illustrate specific embodiments of the present invention but are not to be interpreted as defining or limiting the scope thereof.

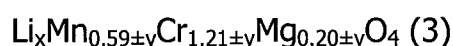
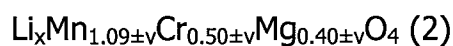
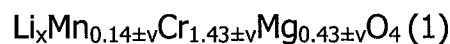
Claims

1. Mixed oxide LiM_2O_4 with reduced strain properties, where M can be one or more transition metals from the first row (Sc to Zn) and/or other elements
 5 selected from the group consisting of: Mg, Al, Si, Ga, Ge, Zr, Nb, La and Ta,
 wherein the "reduced strain properties" are characterized by a change in cell volume of less than or equal to 5% between the fully lithiated and delithiated state of the mixed oxide.

10 2. Mixed oxide according to claim 1, wherein M is a mixture of Mn, Mg and Cr.

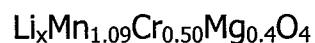
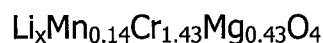
3. Mixed oxide according to claim 1 or 2, having any one of the following formulae (1), (2) or (3):

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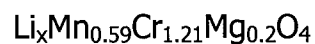


20 where v is less than or equal to 0.05.

4. A compound having one of the following formulae:



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5. Method of producing a mixed oxide as defined in any of claims 1 to 4 comprising the steps of:

(a) mixing a lithium source, a manganese source, a chromium source, and a magnesium source; and

5 (b) calcining the mixture obtained in step (a) in an oxygen-containing atmosphere, such as atmospheric air, at a temperature of between 700°C and 1100 °C for a time between 6 and 24 hours.

6. Method of producing a mixed oxide according to claim 5, wherein each of
10 the lithium source, manganese source, chromium source, and/or magnesium source are, independently of one another, metal sources in the form of carbonates, sulfates, nitrates, oxalates, chlorides, hydroxides and/or oxides.

7. Method of producing a mixed oxide according to claim 5, wherein the
15 lithium source, manganese source, chromium source, and/or magnesium source is (are) nitrate(s).

8. An all-solid-state lithium ion secondary battery comprising:

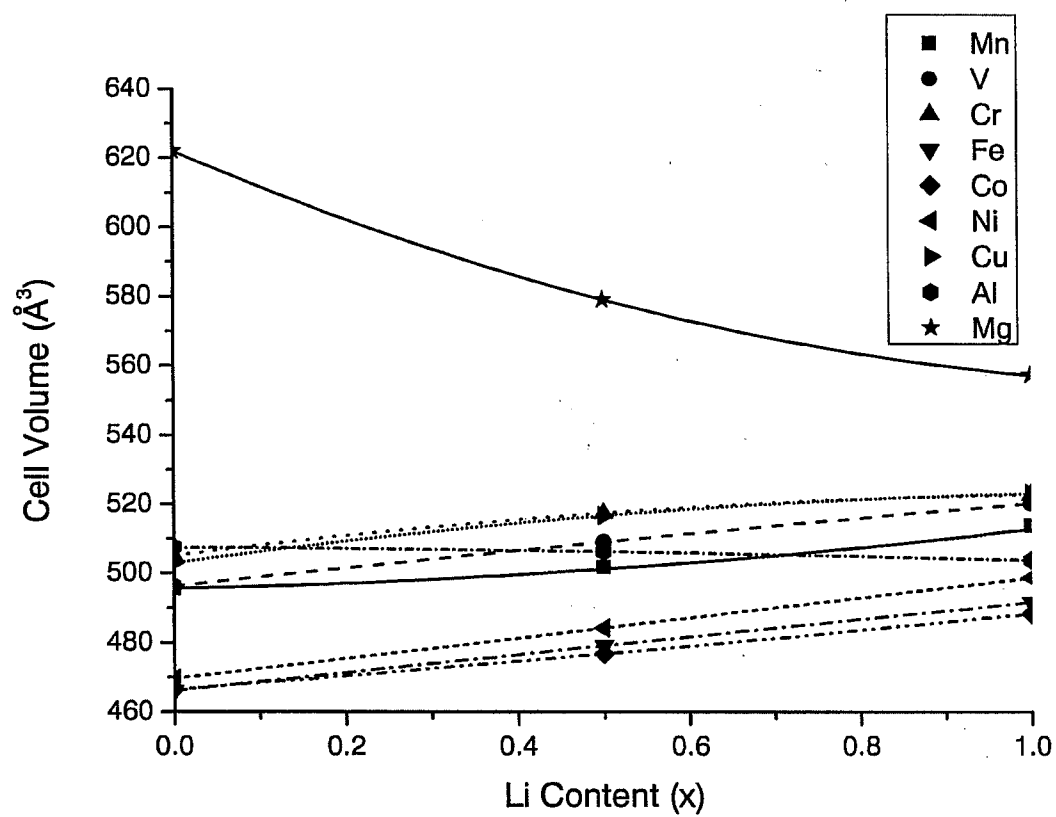
- a positive electrode containing a positive electrode active material
20 comprising a mixed oxide according to any of claims 1 to 4;

- a negative electrode containing a negative electrode active material capable of releasing and accepting lithium ions; and

- a solid electrolyte layer sandwiched between the positive electrode and the negative electrode.

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**Figure 1**

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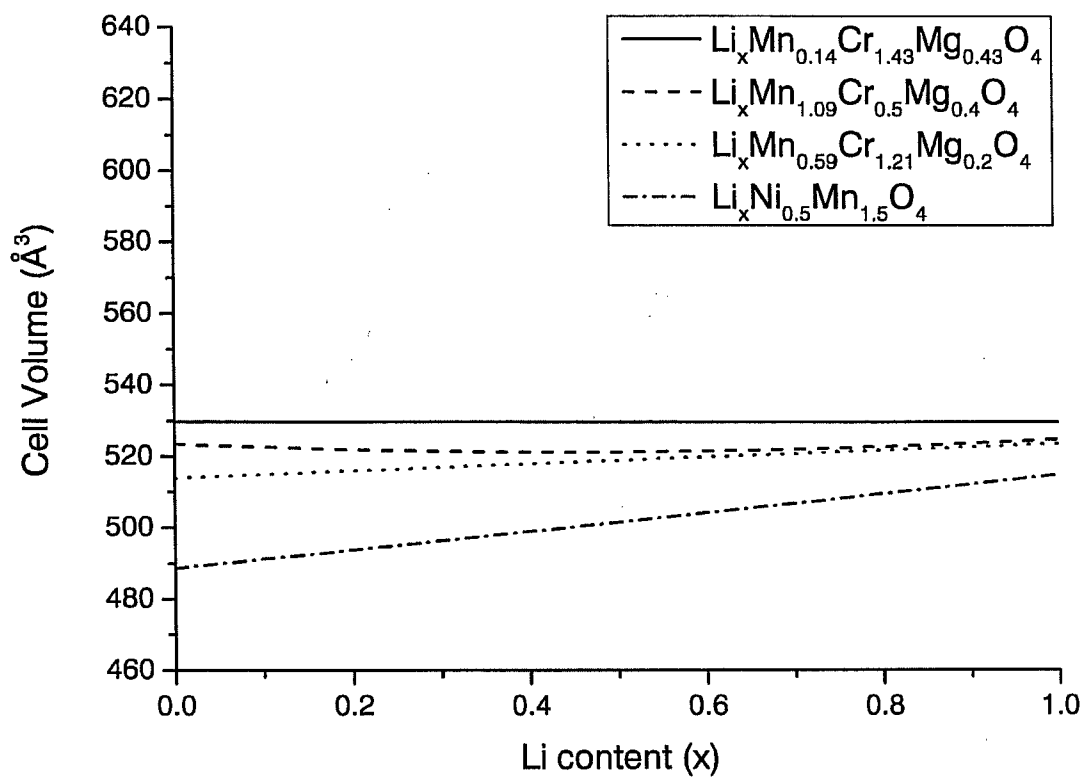
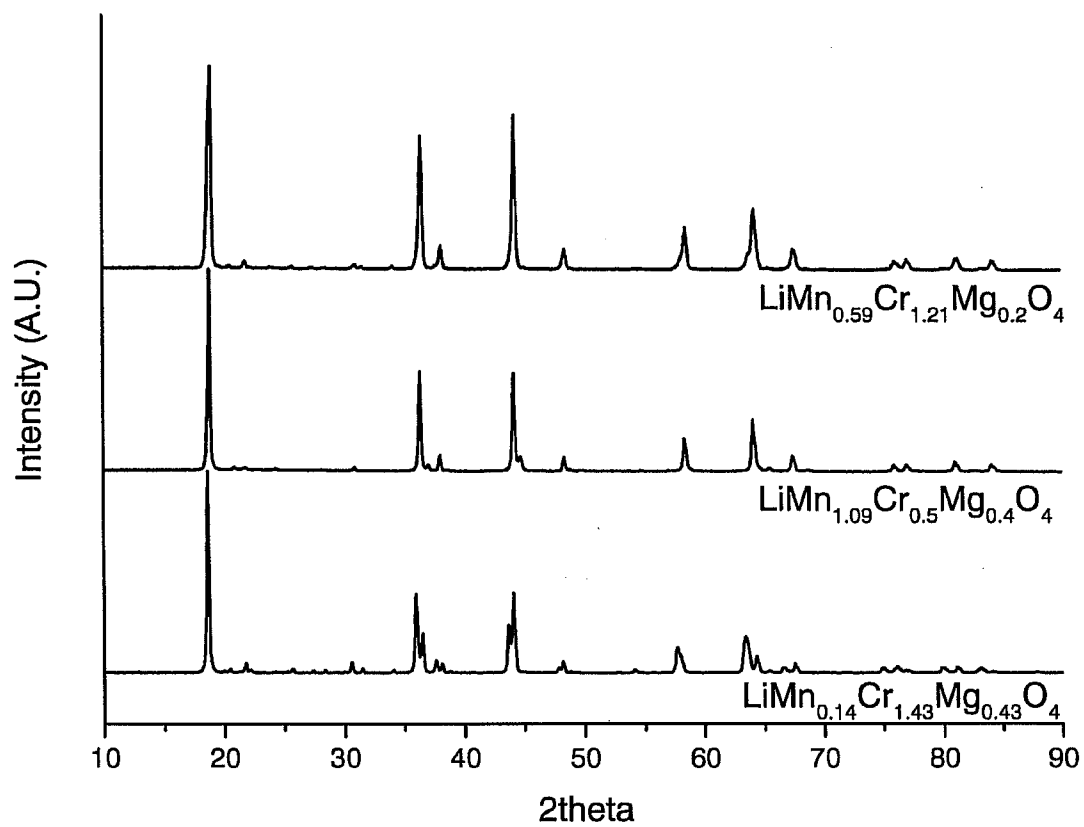
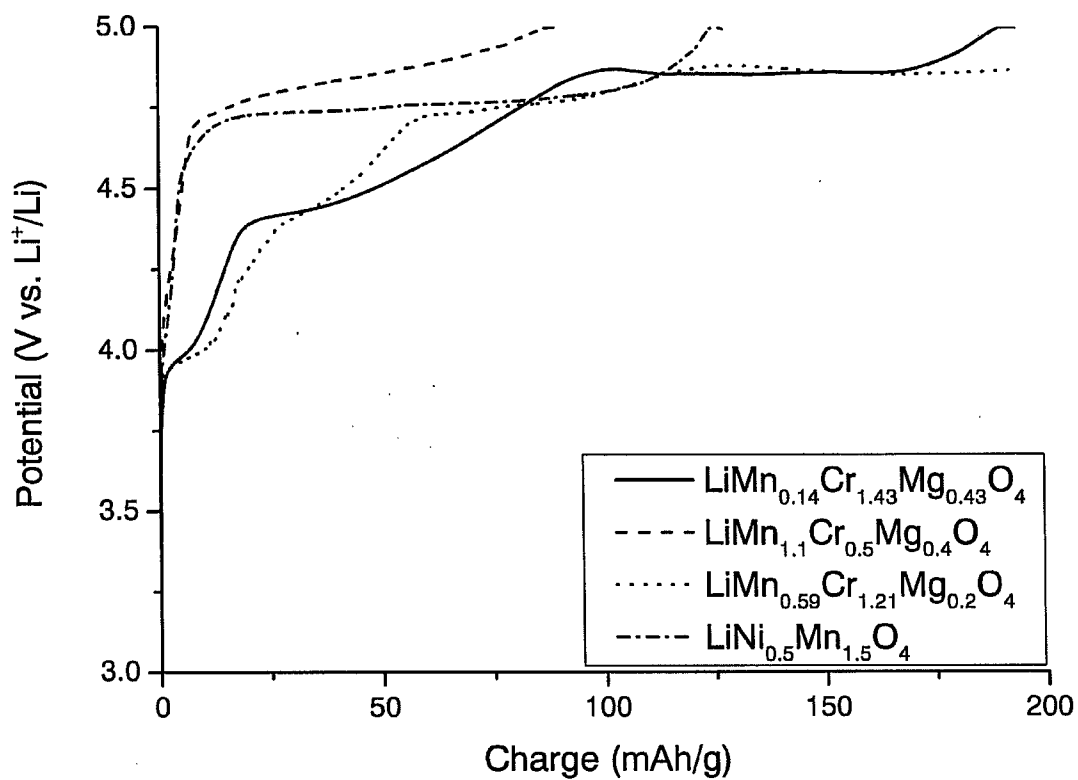


Figure 2

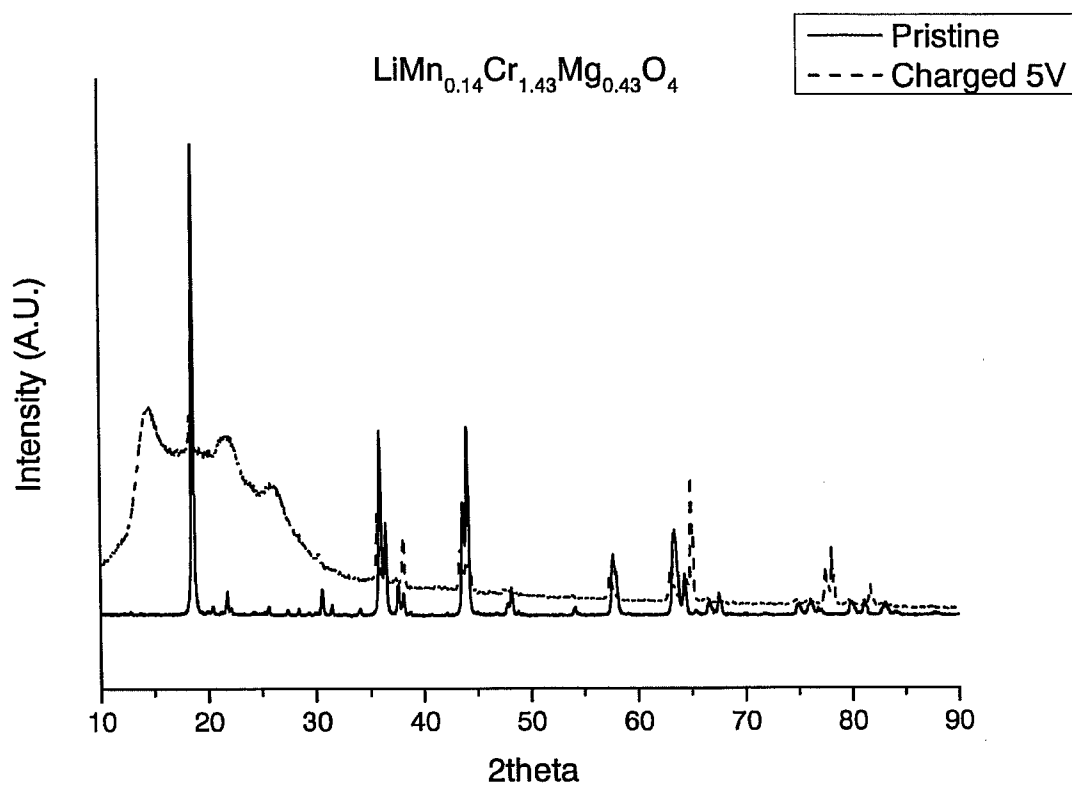
- 3/8 -

**Figure 3**

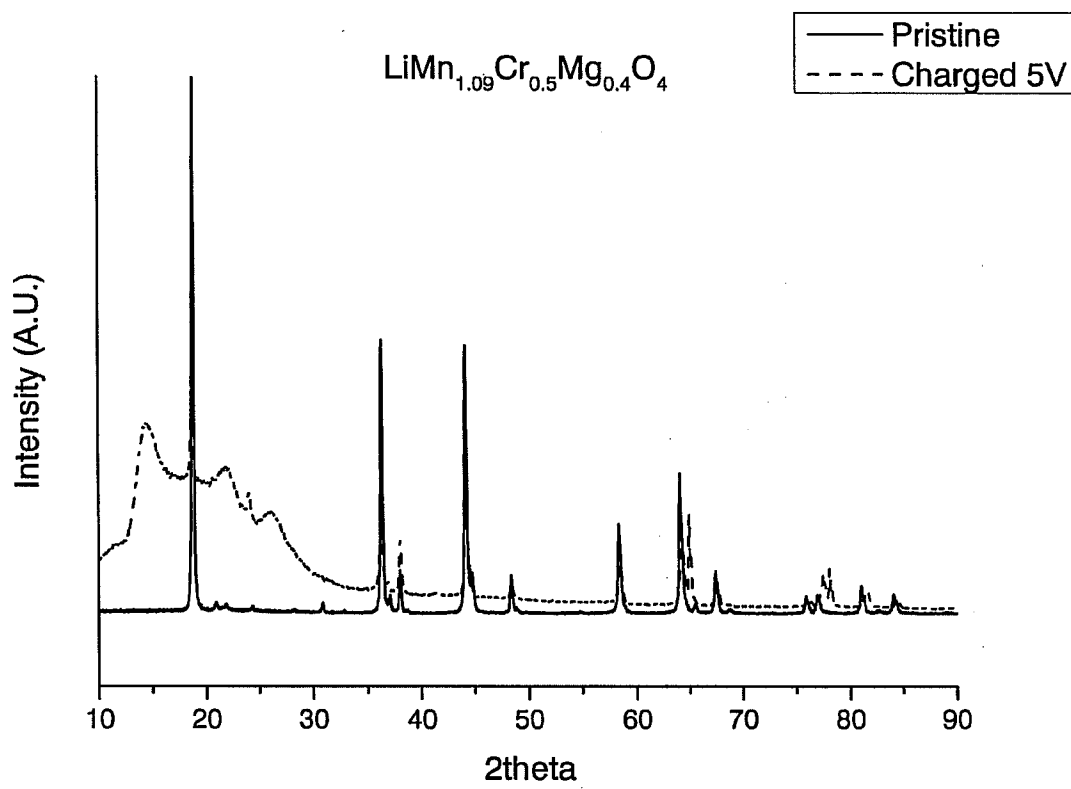
- 4/8 -

**Figure 4**

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**Figure 5a**

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**Figure 5b**

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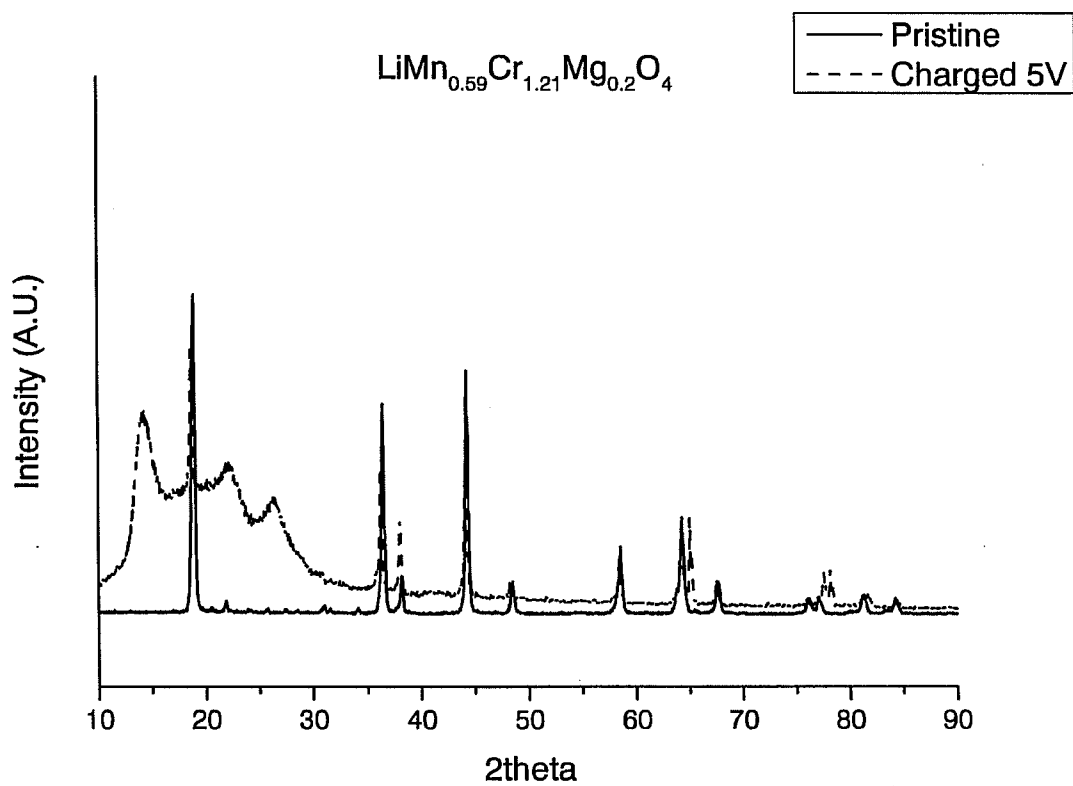


Figure 5c

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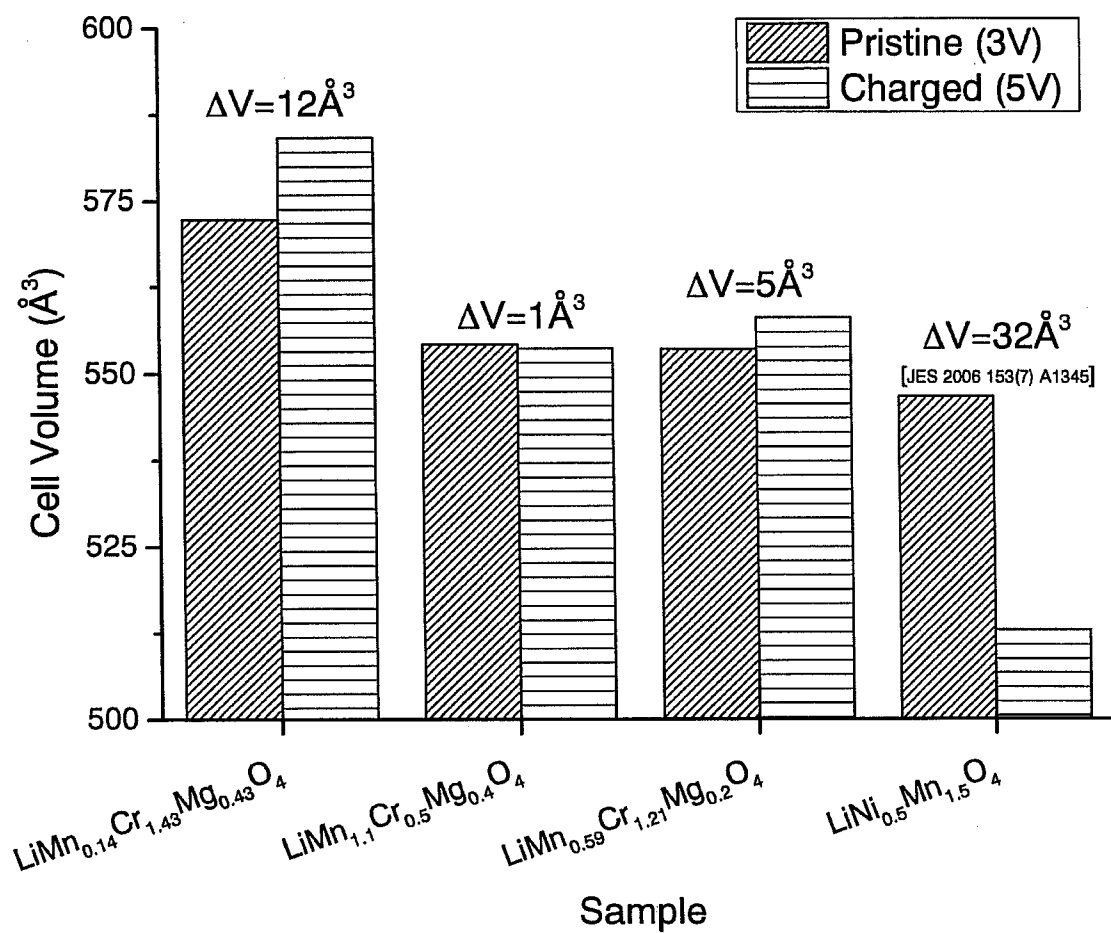


Figure 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/060881

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01G45/12 H01M4/505 H01M10/052 H01M10/0562
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)

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GUOHUA L ET AL: "THE SPINEL PHASES LIMUMN2-YO4(M=CO,CR,NI) AS THE CATHODE FOR RECHARGEABLE LITHIUM BATTERIES", JOURNAL OF THE ELECTROCHEMICAL SOCIETY, ELECTROCHEMICAL SOCIETY, MANCHESTER, NEW HAMPSHIRE; US, vol. 143, no. 1, 1 January 1996 (1996-01-01), pages 178-182, XP000556217, ISSN: 0013-4651 page 178 - page 182	1,8
A	----- -/--	2-7



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

14 January 2014

Date of mailing of the international search report

22/01/2014

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Authorized officer

Panitz, J

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/060881

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MUKERJEE S ET AL: "In situ synchrotron X-ray studies on copper-nickel 5 V Mn oxide spinel cathodes for Li-ion batteries", ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 49, no. 20, 30 August 2004 (2004-08-30), pages 3373-3382, XP004510938, ISSN: 0013-4686, DOI: 10.1016/J.ELECTACTA.2004.03.006 page 3379 - page 3381; figure 7 -----	1,8
X	BRAITHWAITE J S ET AL: "A COMPUTATIONAL STUDY OF THE HIGH VOLTAGE LIXCOYMN4-YO8 CATHODE MATERIAL", PHYSICAL CHEMISTRY CHEMICAL PHYSICS, ROYAL SOCIETY OF CHEMISTRY, CAMBRIDGE, GB, vol. 2, no. 17, 1 September 2000 (2000-09-01), pages 3841-3846, XP000936090, ISSN: 1463-9076, DOI: 10.1039/B003636F page 3841 - page 3845; figure 2; table 5 -----	1,8
X	ARILLO M A ET AL: "Electrochemical behaviour of $\text{LiCr}_{1-x}\text{Al}_x\text{TiO}_4$ ($0 \leq x \leq 0.4$)", SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY, AMSTERDAM; NL, NL, vol. 161, no. 1-2, 1 July 2003 (2003-07-01), pages 49-54, XP004448184, ISSN: 0167-2738, DOI: 10.1016/S0167-2738(03)00269-8 page 49 - page 54; figure 3 -----	1,8