The present invention includes compositions, surfaces and bulk modifications, and methods of making of (1—x)Li[NixLi(1/3-2x/3)Mn2/3-x/3]02 cathode materials by a simple combustion method, J Power Sources (2004); 129:288-295. Robertson, A. D., et al., “Overcapacity of Li[NixLi(1/3-2x/3)Mn(2/3-x/3)]02 electrodes,” Electrochemical Solid State Lett (2004), 7: A294-A298.


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Primary Examiner—Jing-Siu Choi
Assistance Examiner—Monique Peels
(74) Attorney, Agent, or Firm—Fish & Richardson P.C.

(57) ABSTRACT

The present invention includes compositions, surfaces and bulk modifications, and methods of making of (1—x)Li[NixLi(1/3-Mn2/3-x/3)]02 cathode materials having an O3 crystal structure with a x value between 0 and 1, and y value between 0 and 0.5, reducing the irreversible capacity loss in the first cycle by surface modification with oxides and bulk modification with cationic and anionic substitutions, and increasing the reversible capacity to close to the theoretical value of insertion/extraction of one lithium per transition metal ion (250-300 mAh/g).

34 Claims, 5 Drawing Sheets
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* cited by examiner
Figure 1

Figure 2
Figure 3

Figure 4
**Figure 5**

**Figure 6**
Figure 7
Figure 8

Figure 9
The present invention provides layered oxide cathode compositions as well as surface modification procedures for reducing the irreversible capacity loss and increasing the discharge capacity to about the theoretical value involving the reversible extraction of close to one lithium ion per formula unit. The surface modification suppresses undesired reactions of the cathode surface with the electrolyte, alters the solid-electrolyte interface (SEI) layer, and thereby lowers the irreversible capacity loss.

Layered \((1-x)Li[Li_{1/3}Mn_{2/3}]O_2, xLi[Li_{0.5-x}Ni_{0.5-x}]O_2\) cathodes belonging to a solid solution series between \(Li[Li_{1/3}Mn_{2/3}]O_2\) and \(Li[Li_{0.5-x}Ni_{0.5-x}]O_2\) with the value of \(x\) between 0 and 1 and the value of \(y\) between 0 and 0.5 have been synthesized and characterized by charge-discharge measurements in lithium cells before and after modifying their bulk and surface with cationic and anionic substitutions with metals and nonmetal ions like Al\(^{3+}\) and F\(^{-}\). The surface modified cathodes show significantly lower irreversible capacity loss (ICL) and higher discharge capacity with excellent cyclability compared to the unmodified counterparts. For example, \(Li[Li_{0.8}Mn_{0.2}Ni_{0.1}Co_{0.1}]O_2\) with \(x=0.4\) and \(y=1/6\) shows a remarkably high capacity of 285 mAh/g with an irreversible capacity loss of 41 mAh/g and good rate capability. This capacity value is much higher than that achieved with the previously known \(Li[Li_{0.7}Mn_{0.3}Ni_{0.1}Co_{0.1}]O_2\) with \(x=0.5\) and \(y=0\) after similar surface modification (<255 mAh/g).

The present invention provides a method of making a \((1-x)\)

\(Li[Li_{1/3}Mn_{2/3}]O_2, xLi[Li_{0.5-x}Ni_{0.5-x}]O_2\) cathode composition by mixing two or more co-precipitated transition metal hydroxides with a lithium hydroxide and firing the two or more co-precipitated transition metal hydroxides-lithium hydroxide mixture to form a \((1-x)\) \(Li[Li_{1/3}Mn_{2/3}]O_2, xLi[Li_{0.5-x}Ni_{0.5-x}]O_2\) material having an O3 crystal structure. The two or more co-precipitated transition metal hydroxides are formed by adding one or more transition metal acetate solutions to a basic solution.

The present invention also provides a cathode composition including \((1-x)\)

\(Li[Li_{1/3}Mn_{2/3}]O_2, xLi[Li_{0.5-x}Ni_{0.5-x}]O_2\) having an O3 crystal structure and in some instances, when incorporated in a lithium-ion battery, the capacity is between about 250 and 300 mAh/g and an irreversible capacity loss of between 30 and 50 mAh/g. The \((1-x)\) \(Li[Li_{1/3}Mn_{2/3}]O_2, xLi[Li_{0.5-x}Ni_{0.5-x}]O_2\) cathode composition has an x value between about 0.0 and about 1.0 and y value between 0 and 0.5, e.g., when \(x=0.5\) and \(y=0\), the resulting cathode composition is \(Li[Li_{0.5}Mn_{0.5}Ni_{0.25}Co_{0.25}]O_2\) when \(x=0.4\) and \(y=1/6\), the resulting cathode composition is \(Li[Li_{0.5}Mn_{0.5}Ni_{0.1}Co_{0.1}]O_2\) when \(x=0.7\) and \(y=1/6\), the resulting cathode composition is \(Li[Li_{0.5}Mn_{0.5}Ni_{0.1}Co_{0.1}]O_2\), when \(x=1.0\) and \(y=1/6\), the resulting cathode composition is \(Li[Mn_{0.5}Ni_{0.1}Co_{0.1}]O_2\), and when \(x=0.4\) and \(y=1/6\), the resulting composition is \(Li[Li_{0.4}Co_{0.1}]Ni_{0.1}Mn_{0.1}]O_2\).

For example, the present invention includes a method of making a lithium cathode by mixing a \((1-x)\) \(Li[Li_{1/3}Mn_{2/3}]O_2, xLi[Li_{0.5-x}Ni_{0.5-x}]O_2\) cathode composition with a conductive diluent and a binder and forming the mixture into a cathode shape. The cathode shape will depend on the final application or use of the cathode, e.g., generally cylindrical or generally disk shaped.

The binder includes powdered polytetrafluoroethylene or polyvinylidene fluoride. Suitable conductive diluent materials for this purpose include acetylene black, carbon black and/or graphite or a metallic powder such as powdered nickel, aluminum, titanium or stainless steel. For example, the binder may be powdered polytetrafluoroethylene at about 1 to about
10 weight percent of the cathode mixture, the conductive diluent comprises acetylene black at about 5 to about 25 weight percent of the cathode mixture, and the Li[(Li0.17Mn0.5Nio.25Co2y]O2 cathode composition may be about 70 to about 95 weight percent of the cathode mixture.

The present invention provides a method of modifying a layered oxide with a metal oxide by dispersing a (1-x)Li[(Li0.17Mn0.5Nio.25Co2y]O2 composition in a metal salt precursor solution. Ammonium hydroxide is added to the metal salt precursor solution to precipitate a metal hydroxide. The layered oxide containing the metal hydroxide is then heated to obtain a surface modified layered oxide. The metal salt precursor solution includes Al, Cr, Mn, Fe, Cu, Zn, Zr, Nb, Mo, W, Ga, Ca, and Cd and the mixture may be fired at a temperature of between about 800°C and about 1000°C. The present invention also includes the composition made by this process.

A method of fluoride modifying a layered oxide cathodes by combining a layered oxide cathodes with NH4HF2 at a low temperature of between 300 and 500°C is also provided.

In addition, the invention provides methods for bulk modifying a layered oxide cathode with the metal oxides by dispersing a (1-x)Li[(Li0.17Mn0.5Nio.25Co2y]O2 composition in a metal salt or metal alkoxide solution and adding ammonium hydroxide or water to precipitate the metal hydroxide or to hydrolyze the metal alkoxide to produce metal hydroxide. The product obtained is then heated at about 300°C to 700°C in air for about 4 hours, wherein the metal oxide content in the final product is between 2 and 10 weight percent. The surface modifying oxides include, for example, Al2O3, ZrO2, CeO2, SiO2, TiO2, and ZnO. The invention also provides methods for the surface modification with fluoride, which was accomplished by heating the already formed layered oxide cathodes with a fluorinating agent NH4HF2 at a low temperature of between 300 and 500°C.

In addition, the invention provides methods for bulk modification via cationic and anionic substitutions with ions like Al3+ and F-. While the Al3+ substitution was achieved by incorporating the aluminum ions into the mixed transition metal hydroxide precursors during the coprecipitation process before firing at 900°C, the fluorine substitution was achieved by firing the coprecipitated metal hydroxides with a mixture of lithium fluoride and lithium hydroxide at 900°C. For example, the present invention provides a method of making a bulk modified cathode composition by co- precipitating a metal hydroxide mixture comprising hydroxides of two or more transition metal ions and one or more metal ions and then forming a mixture of the co-precipitated metal hydroxide mixture and lithium hydroxide. The mixture is fired to form a cation substituted bulk modified cathode composition. The one or more metal ions may include Mg, Ti, V, Cr, Fe, Cu, Zn, Zr, Nb, Mo, W, Ga, Ca, and Cd and the mixture may be fired at a temperature of between about 800°C and about 1000°C. The present invention also includes the composition made by this process.

The present invention also provides a method of making a bulk modified cathode composition by co-precipitating a metal hydroxide mixture comprising hydroxides of two or more transition metal ions and forming a mixture comprising the metal hydroxide mixture, lithium hydroxide and an anionic substitution compound. The mixture is fired to form a bulk modified anion substituted cathode composition. The anionic substitution compound may be lithium fluoride, lithium chloride, lithium sulfide or a combination thereof depending on the substitution desired by the skilled artisan. The present invention also includes the composition made by this process.

**BRIEF DESCRIPTION OF THE DRAWINGS**

For a more complete understanding of the features and advantages of the present invention, reference is now made to the detailed description of the invention along with the accompanying figures and in which:

**FIG. 1** is an XRD pattern of samples having the O3 type structure of LiCoO2;

**FIGS. 2a and 2b** are TEM images of Al2O3-modified Li[(Li0.17Mn0.5Nio.25Co2y]O2 at different magnifications;

**FIG. 3** is a graph comparing the first charge-discharge profiles of samples before and after surface modification with Al2O3;

**FIG. 4** is a graph comparing the cyclability data of samples before and after surface modification with Al2O3;

**FIG. 5** is a graph comparing the rate capabilities of Li[(Li0.17Mn0.5Nio.25Co2y]O2 before and after surface modification with Al2O3;

**FIGS. 6a, 6b and 6c** are graphs comparing the first charge-discharge profiles of unmodified and surface modified samples;

**FIGS. 7a, 7b, and 7c** are graphs comparing the cyclabilities of the unmodified and surface modified samples;

**FIGS. 8a and 8b** are graphs comparing the first charge-discharge profiles of samples; and

**FIG. 9** is a graph comparing the cyclabilities of the Li[(Li0.17Mn0.5Nio.25Co2y]O2 and Li[(Li0.17Mn0.5Nio.25Co2y]O2±xFy cathodes.

**DETAILED DESCRIPTION OF THE INVENTION**

While the making and using of various embodiments of the present invention are discussed in detail below, it should be appreciated that the present invention provides many applicable inventive concepts that can be embodied in a wide variety of specific contexts. The specific embodiments discussed herein are merely illustrative of specific ways to make and use the invention and do not delimit the scope of the invention.

To facilitate the understanding of this invention, a number of terms are defined below. Terms defined herein have meanings as commonly understood by a person of ordinary skill in the areas relevant to the present invention. Terms such as "a", "an" and "the" are not intended to refer to only a singular entity, but include the general class of which a specific example may be used for illustration. The terminology herein is used to describe specific embodiments of the invention, but their usage does not delimit the invention, except as outlined in the claims.

As used herein the term "Ampere-hour (Ah)" refers to the units used in specifying the storage capacity of a battery. For example, a battery with 1 Ah capacity can supply a current of one ampere for one hour or 0.5 A for two hours, etc. 1 Ampere-hour (Ah) is the equivalent of 3600 coulombs of electrical charge.

As used herein the term "basic" refers to an aqueous solution containing more OH⁻ ions than H⁺ ions. Generally, the aqueous solution has a pH greater than about 7, e.g., lithium hydroxide, sodium hydroxide, potassium hydroxide, some more metal alkoxides are merely illustrative of specific ways to make and use the invention and do not delimit the scope of the invention.

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US 7,678,503 B2
rubidium hydroxide, cesium hydroxide, magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, and ammonium hydroxide.

As used herein the term “C Rate” refers to the charging or discharging rate of a cell or battery, expressed in terms of its total storage capacity in Ah or mAh. For example, a rate of 1 C means utilization of all of the stored energy in one hour; a 0.1 C means utilization of 10% of the energy in one hour and the full energy in 10 hours; and a 5 C means utilization of the full energy in 12 minutes.

As used herein the term metal oxides include precursors of the metal oxides such as nitrates, carbonates and acetates which can be converted to their corresponding metal oxides by heat treatment.

Surface modified layered $\text{Li}[\text{Li}_{0.3}\text{Mn}_{0.5}\text{Ni}_{0.2}\text{Co}_{0.15}]\text{O}_2$ cathodes belonging to a solid solution layer between layered $\text{Li}[\text{Li}_{0.3}\text{Mn}_{0.5}\text{O}_2]$ and $\text{Li}[\text{Ni}_{0.3}\text{Mn}_{0.5}\text{Co}_{0.15}]\text{O}_2$ exhibit a remarkably high reversible capacity of 285 mAh/g with excellent cyclability and low irreversible capacity loss. This capacity value of 285 mAh/g corresponds to a reversible extraction of 0.9 lithium ion per formula unit, and it is much higher than that found with any of the layered oxide compositions previously reported in the literature (e.g., <255 mAh/g) at similar C rates. The surface modification with $\text{Al}_2\text{O}_3$ suppresses the reaction between the cathode surface and the electrolyte, and thereby decreases the irreversible capacity loss and increases the reversible discharge capacity. Further optimization of the layered oxide cathode compositions as well as surface modification procedures can increase the capacity to the theoretical value involving the reversible extraction of one lithium ion per formula unit.

Lithium ion batteries have become attractive for portable electronic devices such as cell phones and laptop computers due to their high energy density. However, only 50% of the theoretical capacity of the currently used LiCoO$_2$ could be used in practical lithium ion cells (e.g., 140 mAh/g) due to the chemical and structural instabilities at deep charge with (1-$x$) <0.5 in $\text{Li}_{1-x}\text{CoO}_2$. Also, cobalt is relatively expensive and toxic. These difficulties have generated enormous interest in alternative cathode hosts. In this regard, solid solutions between $\text{Li}[\text{Li}_{0.3}\text{Mn}_{0.5}\text{O}_2]$ and $\text{Li}[\text{Mn}_{0.5-y}\text{Ni}_{0.5-y}\text{Co}_y\text{O}_2]$ have become appealing as some of them exhibit much higher capacity than the theoretical capacity values expected based on the reversible oxidation involving beyond the formal oxidation states of Mn$^{4+}$ and Ni$^{4+}$. The voltage plateau has been attributed to an irreversible loss of oxygen from the lattice based on in-situ X-ray diffraction studies. The oxygen loss leads to a lowering of the oxidation states of Mn and Ni correspondingly at the end of first discharge, which facilitates a higher reversible capacity with good cyclability in the subsequent cycles as the system operates with the chemically more stable Mn$^{3+}$-$4+$ and Ni$^{3+}$-$4+$ couples compared to the Co$^{3+}$-$4+$ couple. More recently, an ion exchange of Li$^+$ by H$^+$ in addition to the loss of oxygen has been suggested from thermogravimetric analysis and mass spectrometry.

In addition to the irreversible oxygen loss during the first charge, the (1-$x$)$\text{Li}[\text{Li}_{0.3}\text{Mn}_{0.5}\text{O}_2]$-$x\text{Li}[\text{Mn}_{0.5-y}\text{Ni}_{0.5-y}\text{Co}_y\text{O}_2]$ compositions exhibit an undesirable, irreversible capacity loss (ICL) of 40-100 mAh/g in the first cycle depending on the composition upon charging to 4.8 V. The high irreversible capacity loss could originate from a reaction of the cathode surface with the electrolyte, particularly with the high cutoff charge voltages of 4.8 V. One way to overcome this is to modify the cathode surface by coating with inert oxides and minimize the cathode-electrolyte interfacial reactions. For example, the surface modification (e.g., coating) of the LiCoO$_2$ cathode with oxides such as $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, $\text{MgO}$, $\text{SnO}_2$ and $\text{MgO}$ have been shown to improve the cyclability to higher cutoff charge voltages, offering an increase in reversible capacity from 140 to about 180 mAh/g. Similarly, the surface modification of $\text{Li}[\text{Li}_{0.3}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2]$ with Al(OH)$_3$ improves the rate capability.

The present invention provides a new series of cathodes (1-$x$)$\text{Li}[\text{Li}_{0.3}\text{Mn}_{0.5}\text{O}_2]$-$x\text{Li}[\text{Mn}_{0.5-y}\text{Ni}_{0.5-y}\text{Co}_y\text{O}_2]$ that belong to a solid solution between layered $\text{Li}[\text{Li}_{0.3}\text{Mn}_{0.5}\text{O}_2]$ and $\text{Li}[\text{Mn}_{0.5-y}\text{Ni}_{0.5-y}\text{Co}_y\text{O}_2]$, their surface modification with $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, $\text{CeO}_2$, $\text{SiO}_2$, $\text{ZnO}$, $\text{TiO}_2$ and $\text{SnO}_2$ and surface and bulk modification with anions like F$^-$ and cations like $\text{Al}^{13-}$, and a comparison of their electrochemical performances before and after surface or bulk modification. For a comparison, the electrochemical performance of the cobalt-free $\text{Li}[\text{Li}_{0.17}\text{Mn}_{0.50}\text{Ni}_{0.25}]\text{O}_2$ that belongs to a previously known solid solution series (1-$x$)$\text{Li}[\text{Li}_{0.3}\text{Mn}_{0.5}\text{O}_2]$-$x\text{Li}[\text{Mn}_{0.5-y}\text{Ni}_{0.5-y}\text{Co}_y\text{O}_2]$ is also presented before and after surface modification with $\text{Al}_2\text{O}_3$. The surface modified $\text{Li}[\text{Li}_{0.3}\text{Mn}_{0.5}\text{Ni}_{0.15}\text{Co}_{0.15}]\text{O}_2$ exhibits a high capacity of 285 mAh/g with excellent cyclability and a low irreversible capacity loss of 40 mAh/g.

$\text{Li}[\text{Li}_{0.3}\text{Mn}_{0.5}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ (x=0.4 and y=0.6) and $\text{Li}[\text{Li}_{0.3}\text{Mn}_{0.4}\text{Ni}_{0.22}\text{Co}_{0.22}]\text{O}_2$ (x=0.7 and y=0.6) in the series (1-$x$)$\text{Li}[\text{Li}_{0.3}\text{Mn}_{0.5}\text{O}_2]$-$x\text{Li}[\text{Mn}_{0.5-y}\text{Ni}_{0.5-y}\text{Co}_y\text{O}_2]$ as well as $\text{Li}[\text{Li}_{0.17}\text{Mn}_{0.50}\text{Ni}_{0.25}]\text{O}_2$ (x=0.5 and y=0.7) were synthesized by a co-precipitation method. Required amounts of the transition metal acetates were dissolved in deionized water and then added drop by drop into a 0.1 M KOH solution to form the coprecipitated hydroxides of Mn, Ni, and Co. After drying overnight at 100°C in an air-oven, the coprecipitated hydroxides were mixed with required amount of lithium hydroxide, fired in air at 900°C for 24 hours, and then quenched into liquid nitrogen. The surface modification of the synthesized layered oxides was carried out by dispersing the powders in an aluminum nitrate solution, followed by adding ammonium hydroxide to precipitate aluminum hydroxide and heating the products at about 300°C in air for 4 hours so that the Al$\text{O}_3$ content in the final product is 3 weight percent. All the samples were characterized by X-ray diffraction (XRD). Lithium content was determined by atomic absorption spectroscopy. Microstructural characterizations were carried out with a JEO/L 2010F high-resolution transmission electron microscope (TEM).

For example, cathodes for evaluating the electrochemical performances were prepared by mixing 75 weight percent active material with 20 weight percent acetylene black and 5 weight percent PTFE binder, rolling the mixture into thin sheets of about 0.1 mm thick, and cutting into circular electrodes of 0.64 cm$^2$ area. CR2032 coin cells were then assembled with the cathode thus fabricated, lithium anode, and 1M LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) electrolyte.
be present as an amorphous AlOOH, considering the low parameter values of the layered oxide compositions. Calculated based on the extraction of one lithium per LiMO2 formula voltage range of 2.0-4.8 V at C/20 rate.

Firing temperature of 300° C indicates a smooth, porous layer containing aluminum on the transition metal layer as has been suggested before.3s,11 Type structure of LiCo02.

Table 1 gives the lattice parameter values of the layered oxide compositions.

<table>
<thead>
<tr>
<th>Composition</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li[Li0.53Ni0.44Co0.03]O2</td>
<td>2.8518</td>
<td>14.2255</td>
<td>4.983</td>
</tr>
<tr>
<td>Li[Li0.53Ni0.44Co0.03]O2</td>
<td>2.8637</td>
<td>14.2503</td>
<td>4.976</td>
</tr>
<tr>
<td>Li[Li0.53Ni0.44Co0.03]O2</td>
<td>2.8671</td>
<td>14.2557</td>
<td>4.972</td>
</tr>
</tbody>
</table>

Rietveld refinement indicated a cation disorder of around 5%, which is consistent with the previous report for Li[Li0.17Mn0.58Ni0.13Co0.13]O2. The weak reflections around 20-300 are due to the superlattice ordering of Li+ and Mn2+ in the transition metal layer as has been suggested before.3s,11 The XRD patterns remain unchanged after modifying the surface with Al2O3 as seen in Fig. 16, indicating that the surface modification does not cause any undue bulk structural changes to the cathodes. No extra reflections corresponding to Al2O3 are seen, possibly due to the small quantity (e.g., about 3 weight percent) and amorphous nature.

Fig. 2 shows the TEM images of Al2O3 modified Li[Li0.17Mn0.58Ni0.13Co0.13]O2 at two magnifications. The image and energy dispersive spectroscopy (EDS) analysis indicates a smooth, porous layer containing aluminum on the cathode particle surface. For simplicity, the coating material can be presented as an amorphous AlOOH, considering the low firing temperature of 300° C.14

Fig. 3a, 3b and 3c are graphs that compare the cyclability data of all the three systems before and after surface modification with Al2O3 at C/20 rate, and the capacity fades per cycle are given in Table 2. While both Li[Li0.53Mn0.54Ni0.13Co0.13]O2 and Li[Li0.53Mn0.54Ni0.13Co0.13]O2 belonging to the newly developed cobalt-containing Li[Li1-x/3Mn2/3-x/3Ni1/3Co1-x/3O2 series show a significant improvement in capacity retention on surface modification, the cobalt-free Li[Li0.17Mn0.58Ni0.13Co0.13]O2 does not show any improvement. Additionally, there is little difference between the discharge and charge capacities after the first cycle as seen in Figs. 4a, 4b and 4c, indicating good electrochemical efficiency.

Fig. 5 compares the rate capability of Li[Li0.53Mn0.54Ni0.13Co0.13]O2 at C/20, C/5, C/2 and 2 C before and after surface modification with Al2O3. The surface modified cathode shows higher discharge capacity than the unmodified cathode at all rates. However, the difference between the discharge capacities of the surface modified and unmodified cathodes decreases as the C rate increase, indicating a slightly lower rate capability for the surface modified sample.

Surface modification of three materials in the system (1-x) Li[Li1-x/3Mn2/3]O2 + xLi[Mo0.54, Ni0.54, Co0.13]O2 with x=0.5 and y=0, x=0.4 and y=1/6, and x=0.4 and y=1/6 were also carried out with different oxides (Al2O3, CeO2, ZrO2, ZnO, SiO2) and fluorine. The surface modifications with Al2O3, CeO2, and ZnO were carried out similar to that presented before with

Table 2

<table>
<thead>
<tr>
<th>Composition</th>
<th>Theoretical capacity (mAh/g)*</th>
<th>First charge capacity (mAh/g)</th>
<th>First discharge capacity (mAh/g)</th>
<th>Irreversible capacity loss (mAh/g)</th>
<th>Capacity fade per cycle (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li[Li0.53Mn0.54Ni0.13Co0.13]O2</td>
<td>321</td>
<td>Unmodified</td>
<td>328</td>
<td>253</td>
<td>75</td>
</tr>
<tr>
<td>Li[Li0.53Mn0.54Ni0.13Co0.13]O2</td>
<td>304</td>
<td>Unmodified</td>
<td>290</td>
<td>227</td>
<td>63</td>
</tr>
<tr>
<td>Li[Li0.53Mn0.54Ni0.13Co0.13]O2</td>
<td>316</td>
<td>Unmodified</td>
<td>309</td>
<td>249</td>
<td>60</td>
</tr>
</tbody>
</table>

*Calculated based on the extraction of one lithium per LiMO2 formula.
Al₂O₃ by dispersing the cathode powder in the corresponding metal salt precursor solution, followed by adding ammonium hydroxide to precipitate the metal hydroxides. The surface modifications with ZrO₂ and SiO₂ were carried out by dispersing the cathode powder in the corresponding metal alkoxide solution, followed by adding water to hydrolyze the alkoxide and generate the metal hydroxides. In both the cases, the resulting product was heated at a temperature between 300°C and 700°C in air for 4 hours so that the metal oxide content in the final product is 3 weight percent. The surface modification with fluoride was carried out by heating the already formed layered oxide cathodes with NH₄HF₂ at a low temperature of between 300 and 500°C for about 4 hours. The first charge-discharge profiles are compared in Fig. 6. All the surface modifications reduce the irreversible capacity loss; among them, Al₂O₃ modification is the most effective one. For example, the discharge capacity increased from 253 to 285 mA h/g and the irreversible capacity loss decreased from 75 to 41 mA h/g for the sample with x=0.4 and y=1/3.

Figs. 6a, 6b and 6c are graphs comparing the first charge-discharge profiles of unmodified and surface modified samples belonging to the series (1-x)[Li₁₃Mn₂₈O₄]ₓLi[Li₀·₅₈Ni₀·₂₅]ₓ[Li₀·₁₇Mo₁₆N₈O₃7] and (1-x)[Li₁₃Mn₂₈O₄]ₓLi[Li₀·₅₈Ni₀·₂₅]ₓ[Li₀·₁₇Mo₁₆N₈O₃7] at 20°C rate and 2.0-4.8 V with (a) x=0.5 and y=0, (b) x=0.4 and y=1/3, and (c) x=0.4 and y=1/5.

The cyclabilities of the different modified samples are compared in the graphs of Figs. 7a, 7b and 7c. It gives a comparison of the cyclabilities of the unmodified and surface modified samples belonging to the series (1-x)[Li₁₃Mn₂₈O₄]ₓLi[Li₀·₅₈Ni₀·₂₅]ₓ[Li₀·₁₇Mo₁₆N₈O₃7] at 20°C rate and 2.0-4.8 V for x=0.5 and y=0 (Fig. 7a), x=0.5 and y=1/3 (Fig. 7b), and x=0.4 and y=1/5 (Fig. 7c). Samples modified with fluorine seem to have slightly better cycle performance, while the oxide modified samples have almost the same or worse cyclability than the unmodified sample. Again for the x=0.4 and y=1/6 sample modified with Al₂O₃, the discharge capacity is still as high as 268 mA h/g after 50 cycles.

The effects of partial substitution of Al³⁺ for Li⁺ in the transition metal layer and partial substitution of F⁻ for O²⁻ in Li₃Li₀·₁₇Ni₀·₂₅Mo₈O₃₇₅·₅₅O₃ have been investigated in detail. The fluorine substitution was accomplished by firing the coprecipitated transition metal hydroxides with a mixture of required amounts lithium fluoride and lithium hydroxide at 900°C for 24 hours and then quenching into liquid nitrogen. The aluminum substitution was accomplished by incorporating a required amount of Al³⁺ ions into the mixed transition metal ion solution before forming the coprecipitated hydroxides, followed by firing the coprecipitated hydroxides with lithium hydroxide at 900°C for 24 hours and then quenching into liquid nitrogen. It was found that cationic and anionic substitutions influence the performance of the cathodes dramatically.

Figs. 8a and 8b are graphs comparing the first charge-discharge profiles of Li₃Li₀·₁₇Al₈Mo₈O₃₇₅·₅₅O₃ and Li₃Li₀·₁₇Mo₈O₃₇₅·₅₅O₃ in Fig. 8a and Li₃Li₀·₁₇Al₈Mo₈O₃₇₅·₅₅O₃ in Fig. 8b. As shown in Fig. 8a, a small amount of substitution decreases the capacity. According to the cyclic voltammetry (CV) studies, Al and F substitutions strongly alter the chemical environment of Li₃Li₀·₁₇Mo₈O₃₇₅·₅₅O₃ and make it more difficult for the oxygen ion to be removed from the lattice.

Fig. 3 is a graph that compares the cyclabilities of the aluminum- and fluorine-substituted samples, Li₃Li₀·₁₇Al₈Mo₈O₃₇₅·₅₅O₃ and Li₃Li₀·₁₇Mo₈O₃₇₅·₅₅O₃, with and without fluoride substitutions, respectively. Although the substitutions lead to a decrease in capacity values, the fluorine substitution leads to a better cyclability. The decrease in capacity is due to a decrease in the ability of the samples to lose oxygen from the lattice during the first charge. It is interesting to note that an incorporation of a very small amount (<0.05) of foreign ions like Al³⁺ or F⁻ results in a significant change in the ability to lose oxygen from the lattice on charging.

Thus, cationic and anionic substitutions could be used effectively to control the irreversible loss of oxygen from the lattice and the electrochemical performance factors such as reversible capacity, cyclability, and irreversible capacity loss. It could also help to tune the chemical stability and safety. The surface modification to reduce the irreversible capacity loss could also be pursued with other materials like carbon, metal, and other oxides like SnO₂, CoO, NiO, and CuO. Combining the ion substitution and the surface modification may produce materials that have less oxygen loss, lower IRC, and high capacity.

The (1-x)Li₃Li₀·₁₇Mo₈O₃₇₅·₅₅O₃ cathode composition has an x value between about 0.0 and about 1.0 and a y value between 0 and 0.5. It is contemplated that any modification discussed in this invention can be employed in various embodiments without departing from the scope of the invention. Those skilled in the art will recognize, or be able to ascertain using no more than ordinary skill, that modifications can be made to the invention to further achieve the methods of the invention.

It is contemplated that any embodiment discussed in this specification can be implemented with respect to any method, kit, reagent, or composition of the invention, and vice versa. Furthermore, compositions of the invention can be used to achieve methods of the invention.
variation of error for the device, the method being employed to determine the value, or the variation that exists among the study subjects.

As used in this specification and claim(s), the words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "includes" and "include") or "containing" (and any form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

The term "or combinations thereof" as used herein refers to all permutations and combinations of the listed items preceding the term. For example, "A, B, C, or combinations thereof" is intended to include at least one of: A, B, C, AB, AC, BC, or ABC, and if order is important in a particular context, also BA, CA, CB, CBA, BCA, ACB, BAC, or CAB. Continuing with this example, expressly included are combinations that contain repeats of one or more item or term, such as BB, AAA, MB, BBC, AAAABC, CBBAAA, CABABB, and so forth. The skilled artisan will understand that typically there is no limit on the number of items or terms in any combination, unless otherwise apparent from the context.

All of the compositions and/or methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and/or methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the invention as defined by the appended claims.

REFERENCES


What is claimed is:

1. A method, comprising: adding two or more transition metal acetate solutions to a basic solution to form two or more co-precipitated transition metal hydroxides comprising two or more hydroxides of Mn, Ni or Co; mixing the two or more co-precipitated transition metal hydroxides with lithium hydroxide; and heating the two or more co-precipitated transition metal hydroxides-lithium hydroxide mixture to form a (1-x)Li[Li1/3Mn2/3]02.xLi[Li0.5-yNi0.5-yCo2y]02 material having an O3 crystal structure, wherein x is between 0.0 and 1.0 and y is from 0.0 to less than 0.5.
2. The method of claim 1, wherein the basic solution is selected from the group consisting of lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide, caesium hydroxide, magnesium hydroxide, nickel hydroxide, strontium hydroxide, barium hydroxide, ammonium hydroxide and combinations thereof.
3. The method of claim 1, further comprising drying the two or more co-precipitated transition metal hydroxides at about 90-120° C. for between 12 and 36 hours.
4. The method of claim 1, wherein the heating occurs at between 800-1000° C. for between 12 and 36 hours.
5. The method of claim 2, wherein the (1-x)Li[Li1/3Mn2/3]02.xLi[Li0.5-yNi0.5-yCo2y]02 material is selected from the group consisting of Li[Li1/3Mn0.58Ni0.25Co0.07]02, Li[Li0.2Mn0.54Ni0.13Co0.03]02, Li[Li1/3Mn0.44Ni0.25Co0.03]02, Li[Li1/3Mn0.33Ni0.25Co0.03]02 and Li[(Li0.5Mn0.25Co0.04)0.13]3.5O2.5 mixtures thereof.
6. The method of claim 1, further comprising incorporating the (1-x)Li[Li1/3Mn2/3]02.xLi[Li0.5-yNi0.5-yCo2y]02 material into a lithium-ion battery to produce a capacity of about 250 and 300 mAh/g and an irreversible capacity loss of between about 20 and 50 mAh/g.
7. The method of claim 1, wherein the (1-x)Li[Li1/3Mn2/3]02.xLi[Li0.5-yNi0.5-yCo2y]02 material is selected from the group consisting of Li[Li1/3Mn0.58Ni0.25Co0.07]02, Li[Li0.2Mn0.54Ni0.13Co0.03]02, Li[Li1/3Mn0.44Ni0.25Co0.03]02, Li[Li1/3Mn0.33Ni0.25Co0.03]02 and combinations thereof.
8. A cathode composition, comprising: (1-x)Li[Li1/3Mn2/3]02.xLi[Li0.5-yNi0.5-yCo2y]02 having an O3 crystal structure, wherein x is between 0.0 and 1.0, y is between 0.0 and 0.5, and the (1-x)Li[Li1/3Mn2/3]02.xLi[Li0.5-yNi0.5-yCo2y]02 has a capacity between about 250 and 300 mAh/g and an irreversible capacity loss of between about 20 and 50 mAh/g.
9. The cathode composition of claim 8, wherein the (1-x)Li[Li1/3Mn2/3]02.xLi[Li0.5-yNi0.5-yCo2y]02 material is incorporated into a lithium-ion battery.
10. The cathode composition of claim 8, wherein the (1-x)Li[Li1/3Mn2/3]02.xLi[Li0.5-yNi0.5-yCo2y]02 material is selected from the group consisting of Li[Li1/3Mn0.58Ni0.25Co0.07]02, Li[Li0.2Mn0.54Ni0.13Co0.03]02, Li[Li1/3Mn0.44Ni0.25Co0.03]02, Li[Li1/3Mn0.33Ni0.25Co0.03]02 and combinations thereof.
The method of claim 1, further comprising: mixing the Li(1-x)Li1/3Mn2/3O2-xLi1/3Co2/3O2 material with a conductive diluent and a binder to provide a mixture; and forming the mixture into a general cathode shape to provide a cathode.

The method of claim 11, wherein the binder comprises powdered polytetrafluoroethylene or polyvinylidene fluoride, and the conductive diluent is selected from the group consisting of acetylene black, carbon black, graphite, nickel powder, aluminum powder, titanium powder, stainless steel powder and combinations thereof.

13. The method of claim 11, wherein the binder comprises powdered polytetrafluoroethylene at about 1 to about 10 weight percent of the mixture, and the (1-x)Li1/3Mn2/3O2-xLi1/3Co2/3O2 material comprises about 70 to about 95 weight percent of the mixture.

A method, comprising: dispersing a (1-x)Li1/3Mn2/3O2-xLi1/3Co2/3O2 composition in a metal salt precursor solution to form a first combination, wherein x is between 0.0 and 1.0 and y is between 0.0 and 0.5; adding ammonium hydroxide to the first combination to precipitate a metal hydroxide, wherein a layered oxide containing the metal hydroxide is formed; and heating the layered oxide containing the metal hydroxide, wherein a surface modified layered oxide is formed having a capacity between about 250 and 300 mAh/g and an irreversible capacity loss of between about 20 and 50 mAh/g when incorporated in a lithium ion battery.

15. The method of claim 14, wherein the metal salt precursor solution comprises Al, Ce, Zn, Sn or combinations thereof at about 1 and 10 weight percent in the final product.

16. The method of claim 14, wherein the layered oxide containing the metal oxide is heated at a temperature between about 300° C. and about 700° C. for between about 1 and 6 hours.

17. A method, comprising: co-precipitating a metal hydroxide mixture comprising hydroxides of two or more transition metal ions and one or more metal ions; forming a mixture comprising the co-precipitated metal hydroxide mixture and lithium hydroxide; and heating the mixture at a temperature between about 800° C. and about 1000° C. to form a cationic substituted bulk modified cathode composition of (1-x)Li1/3Mn2/3O2-xLi1/3Co2/3O2, wherein x is between 0.0 and 1.0, and y is from 0.0 to less than 0.5.

18. The method of claim 17, wherein the one or more transition metal ions are selected from the group consisting of Mg, Ti, V, Cr, Fe, Cu, Zr, Nb, Mo, W, Ga, and Cd and combinations thereof.

19. The method of claim 17, further comprising: disposing the cationic substituted bulk modified cathode composition in a metal salt precursor solution to form a first combination; adding ammonium hydroxide to the first combination to precipitate a metal hydroxide, wherein a layered oxide containing the metal hydroxide is formed; and heating the layered oxide containing the metal hydroxide, wherein a surface modified layered oxide is formed.

20. A cathode composition formed by the method of claim 17.

21. The method of claim 17, further comprising an anionic substitution compound.

22. The method of claim 21, wherein the anionic substitution compound comprises lithium fluoride, lithium chloride, lithium sulfide or a combination thereof.

23. The method of claim 17, further comprising forming the cathode composition into a cathode.

24. The method of claim 19, wherein the metal salt precursor solution comprises a member selected from the group consisting of selected from Al, Ce, Zn, Zr, Si, Ti, Sn and combinations thereof.

25. The method of claim 24, wherein the surface modified layered oxide has a capacity between about 250 and 300 mAh/g and an irreversible capacity loss of between about 20 and 50 mAh/g when incorporated in a lithium ion battery.

26. The method of claim 24, wherein the layered oxide containing the metal oxide is heated at a temperature between about 300° C. and about 700° C. for between about 1 and 6 hours.

27. The method of claim 24, wherein the metal hydroxide is selected from the group consisting of aluminum hydroxide, cerium hydroxide, zirconium hydroxide, silicon hydroxide, titanium hydroxide and zinc hydroxide.

28. The method of claim 24, wherein the metal hydroxide is aluminum hydroxide.

29. The method of claim 1, further comprising: disposing the (1-x)Li1/3Mn2/3O2-xLi1/3Co2/3O2 material in a metal salt precursor solution to form a first combination; adding ammonium hydroxide to the first combination to precipitate a metal hydroxide, wherein a layered oxide containing the metal hydroxide is formed; and heating the layered oxide containing the metal hydroxide, wherein a surface modified layered oxide is formed.

30. The method of claim 29, wherein the surface modified layered oxide has a capacity between about 250 and 300 mAh/g and an irreversible capacity loss of between about 20 and 50 mAh/g when incorporated in a lithium ion battery.

31. The method of claim 29, wherein the layered oxide containing the metal oxide is heated at a temperature between about 300° C. and about 700° C. for between about 1 and 6 hours.

32. The method of claim 29, wherein the metal salt precursor solution comprises a member selected from the group consisting of selected from Al, Ce, Zn, Zr, Si, Ti, Sn and combinations thereof.

33. The method of claim 29, wherein the metal hydroxide is selected from the group consisting of aluminum hydroxide, cerium hydroxide, zirconium hydroxide, silicon hydroxide, titanium hydroxide and zinc hydroxide.

34. The method of claim 29, wherein the metal hydroxide is aluminum hydroxide.

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