The present invention includes compositions, surface and bulk modifications, and methods of making of (1—x)Li[NixLi(1/3-2x/3)Mn(2/3-x/3)]O2 compounds by a simple combustion method, with an effective use of surface oxides and behaviors of Li[NixLi(1/3-2x/3)Mn(2/3-x/3)]O2 solid mixture, thus reducing the irreversible capacity loss in the first cycle by surface modification with oxides and improving the capacity performance in thin-film LiCoO2 cathodes. The present invention is extended or adjusted under 35 U.S.C. 154(b) by 38 days.

Abstract

The present invention includes compositions, surface and bulk modifications, and methods of making of (1—x)Li[NixLi(1/3-2x/3)Mn(2/3-x/3)]O2 cathode materials having an O3 crystal structure with 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 behaviors of Li[NixLi(1/3-2x/3)Mn(2/3-x/3)]O2 solid mixture, thus reducing the irreversible capacity loss in the first cycle by surface modification with oxides and improving the capacity performance in thin-film LiCoO2 cathodes. The present invention is extended or adjusted under 35 U.S.C. 154(b) by 38 days.

Claims

34 Claims, 5 Drawing Sheets
OTHER PUBLICATIONS


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* cited by examiner
Figure 1

Figure 2
Figure 3

Figure 4
Figure 5

Figure 6
Figure 7
**Figure 8**

- Two graphs showing voltage (V) and capacity (mAh/g) as a function of cycle number.

**Figure 9**

- Graph showing capacity (mAh/g) as a function of cycle number for different doping concentrations and undoped samples.
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 undesirable 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[Li1/3Mn2/3]02+xLi[Mn0.5Ni0.5]O2 cathode materials belong to a solid solution series between Li[Li1/3Mn2/3]O2 and Li[Mn0.5Ni0.5]O2 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 Al3 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[Li0.6Mn0.8Ni0.15Co0.15]O2, when 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[Li0.7Mn0.3Ni0.25O2, when 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[Li1/3Mn2/3]O2+xLi[Mn0.5Ni0.5]O2 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[Li1/3Mn2/3]O2 with x=1.0 and y=−1/6, 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[Li1/3Mn2/3]O2+xLi[Mn0.5Ni0.5]O2 having an O3 crystal structure 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 about 30 and 50 mAh/g. The (1−x)Li[Li1/3Mn2/3]O2+xLi[Mn0.5Ni0.5]O2 cathode composition has an x value between about 0.0 and about 1.0 and a y value between 0 and 0.5, e.g., when x=0.5 and y=0, the resulting cathode composition is Li[Li0.5Mn0.5Ni0.15Co0.15]O2, when x=0.4 and y=−1/6, the resulting cathode composition is Li[Li0.5Mn0.5Ni0.15Co0.15]O2, when x=0.7 and y=−1/6, the resulting cathode composition is Li[Li0.5Mn0.5Ni0.15Co0.15]O2, when x=1.0 and y=−1/6, the resulting cathode composition is Li[Mn0.5Ni0.15Co0.15]O2, and when x=0.4 and y=−1/6, the resulting composition is Li[Li0.5Co0.48Ni1/3]O2.

For example, the present invention includes a method of making a lithium cathode by mixing a (1−x)Li[Li1/3Mn2/3]O2+xLi[Mn0.5Ni0.5]O2 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 diluents 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[Li1/3Mn2/3O2]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[Li1/3Mn2/3O2]O2+xLi[Li0.17-sMn0.54N1o.13C0o.13]O2 composition in a metal salt precursor solution. Anion 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, Ce, Zn or a combination thereof and the metal oxide comprises Al2O3, CeO2, ZnO or combinations thereof.

The present invention also provides a method of modifying a layered oxide cathode by combining a layered oxide cathode with NH4HF2 at a low temperature of between 300 and 500° C. The method involves the following steps:

1. Preparing a layered oxide cathode.
2. Dissolving a metal salt precursor solution in a metal alkoxide solution.
3. Dispersing a (1-x)Li[Li0.17-sMn0.54N1o.13C0o.13]O2 composition in the metal salt precursor solution. Ammonium hydroxide is added to the metal salt precursor solution to precipitate a metal hydroxide.
4. Heating the metal hydroxide to form a surface modified layered oxide.
5. The metal salt precursor solution includes Al, Ce, Zn or a combination thereof and the metal oxide comprises Al2O3, CeO2, ZnO or combinations thereof.

In addition, the invention provides methods for bulk modification of a layered oxide cathode by dispersing a (1-x)Li[Li1/3Mn2/3O2]O2+xLi[Li0.17-sMn0.54N1o.13C0o.13]O2 composition in a metal salt precursor solution. Anion hydroxide is added to the metal salt precursor solution to precipitate a metal hydroxide. The layered oxide comprising hydroxides of two or more transition metal ions and one or more metal ions is then heated to obtain a surface modified layered oxide. The metal salt precursor solution includes Al, Ce, Zn or a combination thereof and the metal oxide comprises Al2O3, CeO2, ZnO or combinations thereof.

A method of fluoride modifying a layered oxide cathodes by combining a layered oxide cathode with NH4HF2 at a low temperature of between 300 and 500° C. is also provided. In addition, the present invention provides a method of modifying a layered oxide cathode with a metal oxide by dispersing a (1-x)Li[Li1/3Mn2/3O2]O2+xLi[Li0.17-sMn0.54N1o.13C0o.13]O2 composition in a metal salt precursor solution. Ammonium hydroxide is added to the metal salt precursor solution to precipitate a metal hydroxide. Water is then added to the metal hydroxide solution, wherein the hydroxide solution is hydrolyzed and metal hydroxides are generated. The layered oxide containing the metal hydroxide is heated to form a surface modified layered oxide. The metal salt precursor solution includes Zr, Si, Ti or a combination thereof.

The present invention also provides a method of modifying a layered oxide cathode with a metal oxide by dispersing a (1-x)Li[Li1/3Mn2/3O2]O2+xLi[Li0.17-sMn0.54N1o.13C0o.13]O2 composition in a metal salt precursor solution. Anion 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, Ce, Zn or a combination thereof and the metal oxide comprises Al2O3, CeO2, ZnO or combinations thereof.

The present invention also provides a method of modifying a layered oxide cathode with a metal oxide by dispersing a (1-x)Li[Li1/3Mn2/3O2]O2+xLi[Li0.17-sMn0.54N1o.13C0o.13]O2 composition in a metal salt precursor solution. Anion 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, Ce, Zn or a combination thereof and the metal oxide comprises Al2O3, CeO2, ZnO or combinations thereof.

The present invention also provides a method of modifying a layered oxide cathode with a metal oxide by dispersing a (1-x)Li[Li1/3Mn2/3O2]O2+xLi[Li0.17-sMn0.54N1o.13C0o.13]O2 composition in a metal salt precursor solution. Anion 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, Ce, Zn or a combination thereof and the metal oxide comprises Al2O3, CeO2, ZnO or combinations thereof.

The present invention also provides a method of modifying a layered oxide cathode with a metal oxide by dispersing a (1-x)Li[Li1/3Mn2/3O2]O2+xLi[Li0.17-sMn0.54N1o.13C0o.13]O2 composition in a metal salt precursor solution. Anion 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, Ce, Zn or a combination thereof and the metal oxide comprises Al2O3, CeO2, ZnO or combinations thereof.

The present invention also provides a method of modifying a layered oxide cathode with a metal oxide by dispersing a (1-x)Li[Li1/3Mn2/3O2]O2+xLi[Li0.17-sMn0.54N1o.13C0o.13]O2 composition in a metal salt precursor solution. Anion 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, Ce, Zn or a combination thereof and the metal oxide comprises Al2O3, CeO2, ZnO or combinations thereof.

The present invention also provides a method of modifying a layered oxide cathode with a metal oxide by dispersing a (1-x)Li[Li1/3Mn2/3O2]O2+xLi[Li0.17-sMn0.54N1o.13C0o.13]O2 composition in a metal salt precursor solution. Anion 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, Ce, Zn or a combination thereof and the metal oxide comprises Al2O3, CeO2, ZnO or combinations thereof.

The present invention also provides a method of modifying a layered oxide cathode with a metal oxide by dispersing a (1-x)Li[Li1/3Mn2/3O2]O2+xLi[Li0.17-sMn0.54N1o.13C0o.13]O2 composition in a metal salt precursor solution. Anion 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, Ce, Zn or a combination thereof and the metal oxide comprises Al2O3, CeO2, ZnO or combinations thereof.

The present invention also provides a method of modifying a layered oxide cathode with a metal oxide by dispersing a (1-x)Li[Li1/3Mn2/3O2]O2+xLi[Li0.17-sMn0.54N1o.13C0o.13]O2 composition in a metal salt precursor solution. Anion 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, Ce, Zn or a combination thereof and the metal oxide comprises Al2O3, CeO2, ZnO or combinations thereof.
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 Li[Li1/3Mn2/3xLi1/3Mn0.5yNi0.5yCo2y1O2 cathodes belonging to a solid solution series between layered Li[Li1/3Mn2/3xLi1/3Mn0.5yNi0.5yCo2y1O2 and Li[Li0.2Mn0.54Ni0.13Co0.131O2 also 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 Al2O3 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 LiCoO2 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 Li1-xCoO2. Also, cobalt is relatively expensive and toxic. These difficulties have generated enormous interest in alternative cathode hosts. In this regard, solid solutions between layered Li[Li1/3Mn2/3xLi1/3Mn0.5yNi0.5yCo2y1O2 and LiMnO2 (M=Mn, Ni, Co; x,y=0.17) have become appealing as some of them exhibit much higher capacities with lower cost and better safety features compared to the currently used LiCoO2 cathode. For example, layered oxide compositions belonging to the series (1-x)Li[Li1/3Mn2/3xLi1/3Mn0.5yNi0.5yCo2y1O2, which is a solid solution between Li[Li1/3Mn2/3]0.5yNi0.5yCo2y1O2 and Li[Mn0.5yNi0.5yCo2y1O2, have been found to exhibit capacities as high as 250 mAh/g on cycling them to 4.8 V.

However, the discharge capacities of the (1-x)Li[Li1/3Mn2/3xLi1/3Mn0.5yNi0.5yCo2y1O2 cathodes are often much higher than the theoretical capacity values expected based on the initial oxidation states of manganese and nickel, and the first charge profile is accompanied by an irreversible voltage plateau for oxidation involving beyond the formal oxidation states of Mn4+ and Ni4+. The voltage plateau has been attributed to an irreversible loss of oxygen from the lattice based on in-situ X-ray diffraction studies.14 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 Mn3+4+ and Ni3+4+ couples compared to the Co3+4+ couple.15 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.12

In addition to the irreversible oxygen loss during the first charge, the (1-x)Li[Li1/3Mn2/3xLi1/3Mn0.5yNi0.5yCo2y1O2 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.3-5 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 LiCoO2 cathode with oxides such as Al2O3, ZrO2, MgO, and SnO2 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 Li[Li1/3Mn0.2Mn0.8O2 with Al(OH)3 improves the rate capability.18

The present invention provides a new series of cathodes (1-x)Li[Li1/3Mn2/3xLi1/3Mn0.5yNi0.5yCo2y1O2 that belong to a solid solution between layered Li[Li1/3Mn2/3xLi1/3Mn0.5yNi0.5yCo2y1O2 and Li[Mn0.5yNi0.5yCo2y1O2, their surface modification with Al2O3, ZrO2, CeO2, SiO2, ZnO, TiO2, and SnO2 and surface and bulk modification with anions like F- and cations like Al+3, and a comparison of their electrochemical performances before and after surface or bulk modification. For a comparison, the electrochemical performance of the cobalt-free Li[Li1/3Mn0.5yNi0.25O2 that belongs to a previously known solid solution series (1-x)Li[Li1/3Mn2/3xLi1/3Mn0.5yNi0.5yCo2y1O2 is also presented before and after surface modification with Al2O3. The surface modified Li[Li0.3Mn0.54Ni0.13Co0.131O2 exhibits a high capacity of 285 mAh/g with excellent cyclability and a low irreversible capacity loss of 40 mAh/g.

Li[Li2/3Mn0.54Ni0.13Co0.131O2 (x=0.4 and y=0.5) and Li[Li1/3Mn0.4yNi0.13Co0.131O2 (x=0.7 and y=0.6) in the series (1-x)Li[Li1/3Mn2/3xLi1/3Mn0.5yNi0.5yCo2y1O2 (x=0.5 and y=0.4) 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 Al2O3 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 characteristics were carried out with a JEOL 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 cm2 area. CR2032 coin cells were then assembled with the cathode thus fabricated, lithium anode, and 1 M LiPF6 in ethylene carbonate (EC) diethyl carbonate (DEC) electrolyte.
FIG. 7 compares the XRD patterns of LiLio.2Mn0.54Ni0.13Co0.13O2, LiLio.17Mn0.58Ni0.25Co0.25O2, and Al2O3 modified LiLio.2Mn0.54Ni0.13Co0.13O2. All the samples have the O3 type structure of LiCoO2 similar to that found previously for LiLio.17Mn0.25Ni0.25O2.59 and 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>LiLio.2Mn0.54Ni0.13Co0.13O2</td>
<td>2.8518</td>
<td>14.2255</td>
<td>4.983</td>
</tr>
<tr>
<td>LiLio.17Mn0.58Ni0.25Co0.25O2</td>
<td>2.8637</td>
<td>14.2503</td>
<td>4.976</td>
</tr>
<tr>
<td>LiLio.17Mn0.58Ni0.25Co0.25O2</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 LiLio.17Mn0.58Ni0.25O2. The very weak reflections around 20-30° are due to the superlattice ordering of Li+ and Mn+ 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. 1b, 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 LiLio.2Mn0.54Ni0.13Co0.13O2 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 could be present as an amorphous AlOOH, considering the low firing temperature of 300° C.14

FIGS. 3a, 3b and 3c are graphs that compare the charge-discharge profiles of LiLio.2Mn0.54Ni0.13Co0.13O2, LiLio.17Mn0.58Ni0.25Co0.25O2, and LiLio.17Mn0.58Ni0.25Co0.25O2 before and after surface modification with Al2O3 in the voltage range of 2.0-4.8 V at C/20 rate.

Table 2 compares the first charge and discharge capacities and the irreversible capacity loss values. All three systems exhibit lower irreversible loss and higher discharge capacities after surface modification with Al2O3 due to a suppression of the reaction between the cathode surface and the electrolyte and an optimization of the solid-electrolyte interface (SEI) layer. TABLE 2 illustrates the electrochemical cell data collected at C/20 rate and 2.0-4.8 V of the layered oxide cathodes before and after surface modification with Al2O3.

<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>LiLio.2Mn0.54Ni0.13Co0.13O2</td>
<td>321</td>
<td>Unmodified 328</td>
<td>253</td>
<td>75</td>
<td>0.53</td>
</tr>
<tr>
<td>LiLio.17Mn0.58Ni0.25Co0.25O2</td>
<td>304</td>
<td>Unmodified 290</td>
<td>227</td>
<td>63</td>
<td>0.42</td>
</tr>
<tr>
<td>LiLio.17Mn0.58Ni0.25Co0.25O2</td>
<td>316</td>
<td>Unmodified 309</td>
<td>249</td>
<td>60</td>
<td>0.79</td>
</tr>
</tbody>
</table>

*Calculated based on the extraction of one lithium per LiMO2 formula

For example, the irreversible capacity loss decreases from 75 to 41 mAh/g and the discharge capacity increases from 253 to 285 mAh/g after surface modification in the case of LiLio.2Mn0.54Ni0.13Co0.13O2. Similarly, irreversible capacity loss decreases from 63 to 38 mAh/g and the discharge capacity increases from 227 to 250 mAh/g in the case of LiLio.17Mn0.58Ni0.25Co0.25O2. In contrast, while the irreversible capacity loss decreases significantly from 60 to 30 mAh/g, the capacity increases only slightly from 249 to 254 mAh/g in the case of the cobalt-free LiLio.17Mn0.58Ni0.25O2 cathode. Thus the surface modification offers the advantage of increasing the discharge capacity significantly in the newly developed cobalt-containing LiLio.17Mn0.58Ni0.25Co0.25O2 series compared to the cobalt-free LiLio.17Mn0.58Ni0.25O2 series. Moreover, the capacity of 285 mAh/g observed with LiLio.2Mn0.54Ni0.13Co0.13O2 is significantly higher than the values reported previously in the literature for any layered oxide composition (<about 255 mAh/g). It corresponds to a reversible extraction of 0.9 lithium ion per LiMO2 formula unit (e.g., about 90% of theoretical capacity).

FIGS. 4a, 4b and 4c 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 LiLio.2Mn0.54Ni0.13Co0.13O2 and LiLio.17Mn0.58Ni0.25Co0.25O2 belonging to the newly developed LiLio.17Mn0.58Ni0.25Co0.25O2 series show a significant improvement in capacity retention on surface modification, the cobalt-free LiLio.17Mn0.58Ni0.25O2 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 coulombic efficiency.

FIG. 5 compares the rate capability of LiLio.2Mn0.54Ni0.13Co0.13O2 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) LiLio.2Mn0.58Ni0.25Co0.25O2 + LiLio.50Ni0.50Co0.25O2 with x=0.5 and y=0, x=0.4 and y=1/6, and x=0.4 and y=1/5 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
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 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 mAh/g and the irreversible capacity loss decreased from 75 to 41 mAh/g for the sample with x=0.4 and y=½.

FIGS. 6a, 6b and 6c are graphs comparing the first charge-discharge profiles of the unmodified and surface modified samples belonging to the series (1-x) Li[Li₁₃Mn₂₃O₂]ₓLi[Mn₀.₅₋₅ₓNi₀.₅₋₅ₓCo₂₀]O₂ at C/20 rate and 2.0-4.8V with (a) x=0.5 and y=0, (b) x=0.4 and y=½, and (c) x=0.4 and y=½.

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) Li[Li₁₃Mn₂₃O₂]ₓLi[Mn₀.₅₋₅ₓNi₀.₅₋₅ₓCo₂₀]O₂ at C/20 rate and 2.0-4.8V for x=0.5 and y=0 (FIG. 7a), x=0.5 and y=½ (FIG. 7b), and x=0.4 and y=½ (FIG. 7c). Samples modified with fluoride 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=½ sample modified with Al₂O₃, the discharge capacity is still as high as 268 mAh/g after 50 cycles.

The effects of partial substitution of Al³⁺ or Li⁺ in the transition metal layer and partial substitution of F⁻ for O²⁻ in Li[Li₁₃Mn₂₃O₂]ₓLi[Mn₀.₅₋₅ₓNi₀.₅₋₅ₓCo₂₀]O₂ (x=0.5 and y=0 sample) have also been investigated in detail. The fluorine substitution was accomplished by firing the co-precipitated 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 co-precipitated hydroxides, followed by firing the co-precipitated 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 Li[Li₁₃Mn₂₃O₂]ₓLi[Mn₀.₅₋₅ₓNi₀.₅₋₅ₓCo₂₀]O₂ in FIG. 8a and Li[Li₁₃Mn₂₃O₂]ₓLi[Mn₀.₅₋₅ₓNi₀.₅₋₅ₓCo₂₀]O₂ in FIG. 8b. As shown in FIG. 8, 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 Li[Li₁₃Mn₂₃O₂]ₓLi[Mn₀.₅₋₅ₓNi₀.₅₋₅ₓCo₂₀]O₂ and make it more difficult for the oxygen ion to be removed from the lattice.

FIG. 9 is a graph that compares the cyclabilities of the aluminum- and fluorine-substituted samples, Li[Li₁₃Mn₂₃O₂]ₓLi[Mn₀.₅₋₅ₓNi₀.₅₋₅ₓCo₂₀]O₂ and Li[Li₁₃Mn₂₃O₂]ₓLi[Mn₀.₅₋₅ₓNi₀.₅₋₅ₓCo₂₀]O₂. 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 Co₂O₃. Combining the ion substitution and the surface modification may produce materials that have less oxygen loss, lower IRC, and high capacity.

The (1-x) Li[Li₁₃Mn₂₃O₂]ₓLi[Mn₀.₅₋₅ₓNi₀.₅₋₅ₓCo₂₀]O₂ 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[Li₀.₅Mn₂₀Ni₁₃O₂]O₂, when x=0.7 and y=½, the resulting cathode composition is Li[Li₆, Mn₁, Ni₁, Co₂₀]O₂, when x=1.0 and y=½, the resulting cathode composition is Li[Li₁₃, Mn₁, Ni₁, Co₂₀]O₂ and when x=0.4 and y=½, the resulting composition is Li[Co₂₁Ni₁₂Co₂₁O₂]. In addition, the (1-x) Li[Li₁₃Mn₂₃O₂]ₓLi[Mn₀.₅₋₅ₓNi₀.₅₋₅ₓCo₂₀]O₂ cathode composition may be made from mixing two or more co-precipitated transition metal hydroxides dried at about 90-120°C for between 12 and 36 hours with lithium hydroxide. The (1-x) Li[Li₁₃Mn₂₃O₂]ₓLi[Mn₀.₅₋₅ₓNi₀.₅₋₅ₓCo₂₀]O₂ cathode composition may be fired at between 800-1000°C for 12 to 36 hours. In addition, the present invention may be doped with Mg, Ti, V, Cr, Fe, Cu, Zn, Nb, Mo, W, Ga, Ca, Sr, Si, and B or combinations thereof.

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.

It will be understood that particular embodiments described herein are shown by way of illustration and not as limitations of the invention. The principal features of 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 routine experimentation, numerous equivalents to the specific procedures described herein. Such equivalents are considered to be within the scope of this invention and are covered by the claims.

All publications and patent applications mentioned in this specification are indicative of the level of skill of those skilled in the art to which this invention pertains. All publications and patent applications are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated to be incorporated by reference.

The use of the word “a” or “an” when used in conjunction with the term “comprising” in the claims and/or the specification may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.” The use of the term “or” in the claims is used to mean “and/or” unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and “and/or.” Throughout this application, the term “about” is used to indicate that a value includes the inherent
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 "com-
prising" (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, unre-
cited 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"
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,

AABBC, and if order is important in a particular context, also

ABBBBC, 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 appar-
ent to those of skill in the art that variations may be applied to
the compositions and/or methods and 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.

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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 trans-

metal hydroxides comprising two or more hydrox-
ides 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]xO2,xLi][Mn1-yNiyCo2y]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 hydrox-
ide, cesium hydroxide, magnesium hydroxide, calcium hydrox-
ide, strontium hydroxide, barium hydroxide, ammon-
ium 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 12 to 36 hours.

5. The method of claim 2, wherein the (1-x) Li[[Li1/3Mn2/3]x
O2,xLi][Mn1-yNiyCo2y]02 material is selected from the
group consisting of Li[[Li1/3Mn2/3]xO2,xLi][Mn1-yNiyCo2y]02,
Li[[Li1/3Mn2/3]xO2,xLi][Mn1-yNiyCo2y]02
Li[[Li1/3Mn2/3]xO2,xLi][Mn1-yNiyCo2y]02
mixtures thereof.

6. The method of claim 1, further comprising incorporating the
(1-x) Li[[Li1/3Mn2/3]xO2,xLi][Mn1-yNiyCo2y]02 material into a lithium-ion battery to produce a capacity of
between 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]x
O2,xLi][Mn1-yNiyCo2y]02 material is selected from the
group consisting of Li[[Li1/3Mn2/3]xO2,xLi][Mn1-yNiyCo2y]02,
Li[[Li1/3Mn2/3]xO2,xLi][Mn1-yNiyCo2y]02,
Li[[Li1/3Mn2/3]xO2,xLi][Mn1-yNiyCo2y]02
mixtures thereof.

8. A cathode composition, comprising:
(1-x) Li[[Li1/3Mn2/3]xO2,xLi][Mn1-yNiyCo2y]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]xO2,xLi][Mn1-yNiyCo2y]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]xO2,xLi][Mn1-yNiyCo2y]02 is incor-
porated into a lithium-ion battery.
13. The method of claim 11, further comprising: mixing the \( \text{Li}(1-x)\text{Li}_1\text{Mn}_{2/3}\text{O}_2\cdot x\text{Li}[\text{Mn}_{0.5-y}\text{Ni}_{0.5-y}\text{Co}_{0.5-y}]\text{O}_2 \) material with a conductive diluent and a binder to provide a mixture; and forming the mixture into a cathode.

14. A method, comprising: dispersing a \((1-x)\text{Li}_1\text{Mn}_{2/3}\text{O}_2\cdot x\text{Li}[\text{Mn}_{0.5-y}\text{Ni}_{0.5-y}\text{Co}_{0.5-y}]\text{O}_2\) 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 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 \( (1-x)\text{Li}_1\text{Mn}_{2/3}\text{O}_2\cdot x\text{Li}[\text{Mn}_{0.5-y}\text{Ni}_{0.5-y}\text{Co}_{0.5-y}]\text{O}_2 \), 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, Zn, Zr, Nb, Mo, W, Ga, Cu, and Cd.

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; and 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 21, further comprising: disposing the \((1-x)\text{Li}_1\text{Mn}_{2/3}\text{O}_2\cdot x\text{Li}[\text{Mn}_{0.5-y}\text{Ni}_{0.5-y}\text{Co}_{0.5-y}]\text{O}_2 \) 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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