Title: CATHODE MATERIALS INCLUDING AN OXYGEN-GETTING COMPOUND AND AN ION- STORAGE COMPOUND

Abstract: A positive electroactive material is described, comprising: an oxygen-gettering compound capable of trapping oxygen and an ion-storage compound. In some embodiments, the ion-storage compound is capable of releasing reactive oxygen species, e.g., radical oxygen, when heated. The oxygen-gettering compound is capable of trapping the reactive oxygen species by either physical absorption or chemical reaction.
CATHODE MATERIALS INCLUDING AN OXYGEN-GETTERING COMPOUND AND AN ION-STORAGE COMPOUND

Incorporation by Reference

[0001] All patents, patent applications and publications cited herein are hereby incorporated by reference in their entirety in order to more fully describe the state of the art as known to those skilled therein as of the date of the invention described herein.

Related Application

[0002] The present application is related to United States Patent Application Serial No. 10/329,046, filed on December 23, 2002, now United States Patent No. 7,338,734, the content of which is hereby incorporated by reference herein in its entirety. The present application is also related to United States Patent Application Serial No. 12/868,530, filed on August 25, 2010, the content of which is hereby incorporated by reference herein in its entirety. Additionally, the present application is related to United States Provisional Patent Application Serial No. 61/511,280, filed on July 25, 2011, the content of which is hereby incorporated by reference herein in its entirety. Additionally, the present application is related to United States Provisional Patent Application Serial No. 61/524,532, filed on August 17, 2011, the content of which is hereby incorporated by reference herein in its entirety.

Background

[0003] Batteries produce energy from electrochemical reactions. Batteries typically include a positive electrode and a negative electrode; an ionic electrolyte solution that supports the movement of ions back and forth between the two electrodes; and a porous separator that ensures the two electrodes do not touch but allows ions to travel back and forth between the electrodes.

[0004] Contemporary portable electronic appliances rely almost exclusively on rechargeable lithium (Li)-ion batteries as the source of power. This has spurred a continuing effort to increase their energy storage capability, power capabilities, cycle life and safety characteristics, and decrease their cost. Lithium-ion battery or lithium ion cell refers to a rechargeable battery having a negative electrode capable of storing
a substantial amount of lithium at a lithium chemical potential above that of lithium metal. When a lithium-ion battery is charged, lithium ions travel from the positive electrode to the negative electrode. On discharge, these ions return to the positive electrode releasing energy in the process.

[0005] In a Li-ion battery, the cell includes lithium transition metal oxides for the positive electrode (or cathode), carbon/graphite for the negative electrode (or anode), and a lithium salt in an organic solvent for the electrolyte. In addition to lithium transition metal oxides, more recently, lithium metal phosphates have been used as a cathode electroactive material.

[0006] However, there are certain drawbacks associated with the current lithium ion positive electrode active materials. Specifically, lithium transition metal oxide materials, although having higher energy density, usually result in battery with the problem of thermal run away under high temperatures. In some cases, to improve the abuse tolerance performance, ceramic resistive layers are coated on the separator or anode. This adds additional cost to the cell. Thus, there remains a need for high energy density lithium ion battery material with improved thermal safety.

**Summary**

[0007] In one aspect, a positive electroactive material is described, including:
- an oxygen-gettering compound capable of trapping oxygen; and
- an ion-storage compound.

[0008] In any of the preceding embodiments, the oxygen-gettering compound is an ion-storage material.

[0009] In any of the preceding embodiments, the oxygen-gettering compound is orthorhombic alkali metal manganese oxide coated on the ion-storage compound.

[0010] In any of the preceding embodiments, the oxygen-gettering compound coating covers at least 50%, 60%, 70%, 80%, 90%, or 100% of the surface of the ion-storage compound.

[0011] In any of the preceding embodiments, the oxygen-gettering compound coating has at least 20%, 30%, 40%, 50%, 60%, 70%, or 80% porosity.

[0012] In any of the preceding embodiments, the oxygen-gettering compound has a formula of Li$_x$Na$_y$MnO$_4$, wherein $0 \leq x \leq 0.75$, $0 \leq y \leq 0.75$, and $0.2 \leq x + y \leq 0.75$.

[0013] In any of the preceding embodiments, the oxygen-gettering compound is Na$_{0.44}$MnO$_4$. 
In any of the preceding embodiments, the oxygen-gettering compound is Li$_{0.44}$MnO$_4$.

In any of the preceding embodiments, the oxygen-gettering compound includes one or more transition metal oxide, wherein the transition metal is selected from the group consisting of Fe, Mn, Co, Ni, Ti, V, and a combination thereof.

In any of the preceding embodiments, the oxygen-gettering compound is one or more compounds selected from the group consisting of FeO, MnO, CoO, NiO, Fe$_3$O$_4$, Mn$_3$O$_4$, Co$_3$O$_4$, Ni$_3$O$_4$, and vanadium oxide wherein the vanadium average valence is less than 5$^+$.

In any of the preceding embodiments, the oxygen-gettering compound is nanoscale alkali metal polyanion compound having a composition of $A_x(M_1-\delta_1M_2)\gamma(XD_4)_z$, $A_x(M_1-\delta_1M_2)\gamma(DXD_4)_z$, or $A_x(M_1-\delta_1M_2)\gamma(X_2D_7)_z$ and a specific surface area of at least 5 m$^2$/g, wherein A is at least one of an alkali metal or hydrogen, M' is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, boron, aluminum, silicon, vanadium, molybdenum and tungsten, M'' is one or more metal selected form the group consisting of Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, VIB metal and a combination thereof, D is at least one of oxygen, 10 nitrogen, carbon, or a halogen, $0 \leq \alpha \leq 0.1$, and x is equal to or greater than 0, y and z are greater than 0 and have values such that x, plus $y(1-a)$ times a formal valence or valences of M', plus ya times a formal valence or valence of M'', is equal to z times a formal valence of the XD$_4$, X$_2$D$_7$, or DXD$_4$ group.

In any of the preceding embodiments, the nanoscale alkali metal polyanion compound is Li$_{1.2}$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$.

In any of the preceding embodiments, the nanoscale alkali metal polyanion compound include one or more electroactive materials selected from the group consisting of

Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$,
Li$_1.2$Mn$_{0.4}$Co$_{0.8}$O$_{2.5}$P$_{0.4}$.
In any of the preceding embodiments, the nanoscale alkali metal polyanion compound is one or more compounds selected from the group consisting of L1C0PO₄, LiMnP0₄, Li₃V₂(P0₄)₃, L1VPO₄F, and mixed transition metal phosphate.

In any of the preceding embodiments, wherein the ion-storage compound is one or more compounds selected from the group consisting of lithium cobalt oxide and lithium nickel oxide.

In any of the preceding embodiments, the lithium cobalt oxide or lithium nickel oxide further comprises one or more transition metal selected from the group consisting of Group IIA, IIIB, IVA, VA, VIA, VIIA, VIIIB, VB, VIB metals and a combination thereof.

In any of the preceding embodiments, the lithium cobalt oxide further comprises a metal selected from the group consisting of Al, Mg, and a combination thereof.

In any of the preceding embodiments, the lithium nickel oxide further comprises a metal selected from the group consisting of Co, Mn, Al, Mg, and a combination thereof.

In any of the preceding embodiments, the lithium nickel oxide or the lithium nickel oxide has a nonuniform chemical composition across its particle radius.

In any of the preceding embodiments, a lithium ion battery is described, including a positive electrode comprising the positive electrode active material of any of the preceding embodiments.

As used herein, a "dopant metal" refers to a metal that can be doped into (or substituted for an element of) an electroactive material of a positive electrode, either
into the lattice sites of the electroactive material. In certain embodiment, the dopant metal is present at a small concentration (relative to that of the electroactive metal) or has a redox potential significantly different from the electroactive metal so that the dopant metal does not significantly contribute to the electric storage capacity in an electrochemical cell.

[0028] As used herein, a "olivine structure" refers to a compound composed of isolated tetrahedral A0\textsubscript{4} anionic groups and M1 and M2 cations surrounded by six oxygen ions. Generally, the olivine structure exhibits orthorhombic 2mmm crystal symmetry and has a plurality of planes defined by zigzag chains and linear chains. The M1 cations generally occupy the zigzag chains of octahedral sites and M2 cations generally occupy the linear chains of alternate planes of the octahedral sites. The lattices sites can be doped with other dopant metals and nevertheless maintain the olivine structure.

[0029] As used herein, an "olivinic phase" is any crystalline phase having the olivine structure. The olivinic phase can include one or more dopant metals substituted into the lattice structure of the olivine structure. For example, the olivinic phase can be based on lithium-iron-manganese-phosphate (LFMP) material having an olivine structure that is doped with one or more dopant metals in the lattice sites of the olivine structure.

[0030] As used herein, an "olivine compound" refers to a material having an olivine structure.

[0031] As used herein, a "stoichiometric olivine compound" refers to the amount of lithium and/or phosphate that is in the material relative to the other metals. For example, if the olivine compound is LiFePO\textsubscript{4}, the ratio of Li:Fe:P0\textsubscript{4} is 1:1:1 to form a stoichiometric olivine compound. If the olivine compound is Li-Fe-Mn-Co-Ni-V-P0\textsubscript{4}, the ratio of Li:Fe:Mn+Co+Ni+V: P0\textsubscript{4} is 1:1:1 to form a stoichiometric olivine compound.

[0032] As used herein, "excess lithium" or "lithium rich" refers to the amount of lithium in the overall composition in excess of that needed to form the stoichiometric olivine compound.

[0033] As used herein, "excess phosphate" or "phosphate-rich" refers to the amount of phosphate in the overall composition in excess of that needed to form the stoichiometric olivine compound.
As used herein, "solid solution" refers to a mixture of different atomic cations and anions that have arranged themselves into a single lattice structure, such as the olivine structure. For example, olivine compounds, such as LFMP and dopant metals, existing together as an olivinic phase can be referred to as a solid solution.

As used herein, the term "specific capacity" refers to the capacity per unit mass of the electroactive material in the positive electrode and has units of milliamps-hour/gram (mAh/g).

As used herein, the term "energy density" refers the amount of energy a battery has in relation to its size. Energy density is the total amount of energy (in Wh) a battery can store per amount of the electroactive material in the positive electrode for a specified rate of discharge.

**Brief Description of the Drawing**

A more complete appreciation of the present invention and many of its advantages will be understood by reference to the following detailed description when considered in connection with the following drawings, which are presented for the purpose of illustration only are not intended to limit the scope of the appended claims, and in which:

Figure 1 is a contour plot of specific energy of M1 (LiFeP0₄ Nanophosphate ®) blends with lithium nickel cobalt manganese oxide (NCM).

Figure 2 is a contour plot of specific energy of Mix (LiMn₀.₅Feo.₅P₀₄ Nanophosphate ®) blends with lithium nickel cobalt manganese oxide (NCM).

Figure 3 is a contour plot of DSC chart of M1 (LiFeP0₄ Nanophosphate ®) blends with lithium nickel cobalt manganese oxide (NCM).

Figure 4 is a contour plot of DSC chart of Mix (LiMn₀.₅Feo.₅P₀₄ Nanophosphate ®) blends with lithium nickel cobalt manganese oxide (NCM).

Figure 5 is a contour plot of DSC chart of M1 (LiFeP0₄ Nanophosphate ®) blends with a lithium metal oxide cathode material.

Figure 6 is a contour plot of DSC chart of Mix (LiMn₀.₅Feo.₅P₀₄ Nanophosphate ®) blends with a lithium metal oxide cathode material.
Detailed Description

[0044] Positive electrode active material with high energy density and improved thermal safety is described. The positive electrode active material includes an oxygen-gettering compound and an ion-storage compound.

[0045] One of the potential issues associated with high power and energy density ion-storage compound, e.g., lithium cobalt oxide or lithium nickel oxide, is its poor thermal stability. These compounds may be thermally unstable at high states of charge and/or at high temperatures, e.g., temperatures above 150 °C. These compounds may release oxygen species, e.g., radical oxygen which will react with organic electrolyte in a cell at elevated temperature and produce heat and gas. The heat and gas generated can lead to fire and explosion. The decomposition also is one cause of poor cycle life, particularly if the material is cycled to high states of charge.

[0046] The ion-storage compound may include lithium cobalt oxide or lithium nickel oxide. The lithium cobalt oxide or lithium nickel oxide may further includes one or more transition metal selected from the group consisting of Group IIA, IIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, VIB metals and a combination thereof. In some specific embodiments, the lithium cobalt oxide further comprises a metal selected from the group consisting of Al, Mg, and a combination thereof. In some specific embodiments, the lithium nickel oxide further comprises a metal selected from the group consisting of Co, Mn, Al, Mg, and a combination thereof.

[0047] As described herein, an oxygen-gettering compound is included in the electrode to trap oxygen species potentially released by the ion-storage compound. The oxygen-gettering compound can form a barrier which physically impedes the transport of oxygen to the electrolyte, thereby reducing the rate of reaction of oxygen with the electrolyte and/or the rate of oxygen release from the oxide structure. The oxygen-gettering compound may physically absorb the oxygen generated or chemically bind to the oxygen. In some instances, the amount of oxygen released by the ion-storage compound is reduced so that the heat and gas and other harmful effects due to the reaction between the oxygen and electrolyte can be ameliorated or eliminated. In other embodiments, the oxygen released by the ion-storage compound is trapped by the oxygen-gettering compound so that the speed by which the oxygen reacts with the electrolyte is reduced so that the heat and gas and other harmful effects due to the reaction between the oxygen and electrolyte can be ameliorated.
In some embodiments, the oxygen-gettering compound acts as a physical barrier to prevent the rapid release of the oxygen. In some embodiments, the oxygen-gettering compound traps or absorbs the oxygen through physical interactions. In some embodiments, the oxygen-gettering compound reacts with the oxygen chemically to absorb the released oxygen. The oxygen-gettering compound may also act with more than one mechanism to prevent or delay the release of oxygen. For instance, the oxygen-gettering compound may act as a transport barrier and also physically absorb oxygen. In other instances, the oxygen-gettering compound may act as a transport barrier and also chemically react with oxygen to form one or more stable compounds.

In some embodiments, the oxygen-gettering compound is capable of chemically reacting with the oxygen species, e.g., radical oxygen, so that the oxygen reaction with the electrolyte is reduced or completely eliminated. Such oxygen-gettering compound may contain transitional metal in a reduced oxidation state capable of reacting with oxygen.

In some embodiments, the oxygen-gettering compound includes one or more transition metal oxide, wherein the transition metal is selected from the group consisting of Fe, Mn, Co, Ni, Ti, V, and a combination thereof. The transitional metal may be in a reduced oxidation state which could be oxidized by oxygen, thus eliminating or reducing the oxygen generated by the ion-storage compound and resulting in a safer cell. Non-limiting examples of suitable transitional metal with proper oxidation state include Fe$^{2+}$, Mn$^{3+}$, Mn$^{2+}$, Mn$^{3+}$, Co$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Ni$^{3+}$, Ti$^{2+}$, V$^{2+}$, and V$^{3+}$. In some specific embodiments, the oxygen-gettering compound is one or more transitional metal oxides selected from the group consisting of FeO, MnO, CoO, NiO, Fe$_3$O$_4$, Mn$_3$O$_4$, Co$_3$O$_4$, Ni$_3$O$_4$, and vanadium oxide wherein the vanadium average valence is less than 5$^+$.

In some embodiments, the oxygen-gettering compound is nanoscale alkali metal polyanion compound having a composition of $A_x(M_1 M''_a)_{y}(XD_4)_{z}$, $A_x(M_1 M''_a)_{y}(DXD_4)_{z}$, or $A_x(M_1 M''_a)_{y}(X_2D_7)_{z}$, wherein A is at least one of an alkali metal or hydrogen, $M'$ is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, boron, aluminum, silicon, vanadium, molybdenum and tungsten, M$''$ is one or more metal selected form the group consisting of Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, VIB metal and a combination thereof, D is at least one of oxygen, 10 nitrogen, carbon, or a halogen, 0 ≤ a ≤ 0.1, and x is equal to or
greater than 0, y and z are greater than 0 and have values such that x₂, plus yₐ times a formal valence or valences of M, plus yₐ times a formal valence or valence of M⁺, is equal to z times a formal valence of the XD₄, X₂D₇, or DXD₄ group. In some specific embodiments, the nanoscale alkali metal polyanion compound is one or more compounds selected from the group consisting of Li₁C₀PO₄, Li₃MnPO₄, Li₃Y₂(PO₄)₃, Li₁VPO₄F, and mixed transition metal phosphate. In some specific embodiments, the nanoscale alkali metal polyanion compound is doped or undoped LiFePO₄.

In other embodiments, the oxygen-gettering compound the nanoscale alkali metal is one or more electroactive materials selected from the group consisting of

Lii₀₉₂Mno₄₀₀Feo₈₀Coo₈₀P0₄,  
Lii₀₉₂Mno₄₅₀Feo₅₅₀Coo₀₂₀P0₄,  
Lii₀₂₅Mno₅₀₀Feo₈₀Coo₈₀Nio₈₀Vo₈₀P0₄,  
Lii₀₅₀Mno₄₅₀Feo₅₀Coo₅₀Nio₅₀Vo₅₀P0₄,  
Lii₀₄₀Mno₄₀₀Feo₅₀Coo₅₀Nio₅₀Vo₅₀P0₄,  
Lii₀₃₀Mno₄₅₀Feo₅₀Coo₅₀Nio₅₀Vo₅₀P0₄,  
Lii₀₄₀Mno₄₅₀Feo₅₀Coo₅₀Nio₅₀Vo₅₀P0₄,  
Lii₀₃₀Mno₄₅₀Feo₅₀Coo₅₀Nio₅₀Vo₅₀P0₄,  
Lii₀ₓ₀Mno₄₅₀Feo₅₀Coo₅₀Nio₅₀Vo₅₀P0₄,  
Lii₀₄₀Mno₄₅₀Feo₅₀Coo₅₀Nio₅₀Vo₅₀P0₄,  
Lii₀₄₀Mno₄₅₀Feo₅₀Coo₅₀Nio₅₀Vo₅₀P0₄,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,  
Lii₀₇₀Mno₄ₕ₀Feo₇₀Coo₇₀Nio₇₀Vo₇₀P0₇₀,
and in turn reduce the speed of the possible detrimental reactions between the oxygen species and the electrolyte. As a result, the amount of heat generated due to these detrimental reactions is reduced and the safety profile of the cell is improved. In other embodiments, the oxygen-gettering compound in the coating is capable of reacting with oxygen and binds to the oxygen. In still other embodiments, the oxygen-gettering compound coating may have dual functions, i.e., trapping and delaying oxygen release; and chemically reacting with oxygen.

[0054] In some embodiments, the oxygen-gettering-compound coating has a thickness of from about 0.1 μη to about 10 μη, from about 0.5 μη to about 5 μη, or from about 1 μη to about 5 μη. In some embodiments, the oxygen-gettering-compound coating has a thickness of about 0.1 μη, about 0.5 μη, about 1 μη, about 1.5 μη, about 2 μη, about 3 μη, about 5 μη, or about 10 μη. In some embodiments, the oxygen-gettering-compound coating has a thickness from about 0.1 μη to about 2 μη.

[0055] In some embodiments, the oxygen-gettering compound coating covers at least 50%, 60%, 70%, 80%, 90%, or 100% of the surface of the ion-storage compound. In some embodiments, the oxygen-gettering compound coating has at least 20%, 30%, 40%, 50%, 60%, 70%, or 80% porosity.

[0056] Without wishing to bound by any particular theory, it is believed that the oxygen-gettering-compound coatings may serve as a physical barrier between the electrolyte and the oxygen released by the ion-storage compound (e.g., LiCoO₂ or LiNiO₂). Generally, the oxygen generated has to transport to the electrolyte before it can react with the electrolyte. In the instances where the oxide is covered with the gettering compound, the rate of oxygen transport may be slowed. Oxygen may transport through the coating either via solid-phase diffusion or through fluid-phase transport through cracks in the coating. By slowing the rate of transport, one slows the rate of reaction with the electrolyte. Additionally, increasing concentration of products should slow down rate of reaction. Thus, slowing the rate of transport may also increase the concentration of oxygen (the product of lithium metal oxide decomposition) adjacent to the lithium metal oxide electroactive material (reaction starting material), which may slow down the rate of the decomposition reaction.

[0057] Thus, the oxygen generated has to get through the gettering compound physical barrier and thus its release speed is reduced. As a result, the detrimental
reaction between the oxygen and the electrolyte is ameliorated. Still alternatively, the oxygen-gettering-compound may react chemically with the oxygen species and form a stable compound. As a result, the oxygen generated is reduced or eliminated and the detrimental reaction between the oxygen and the electrolyte is ameliorated or avoided.

[0058] It has been reported that lithium metal oxide can be coated with materials such as Al2O3, ZrO2, or MgO. While the Al2O3, ZrO2, or MgO coatings have been shown to improve the thermal stability and cycle life of LiCoO2 and LiNiO2, they have the disadvantage of being electrical insulators and electrochemically inactive. Coating the active electrode material with an insulator causes an increase in cell impedance, which is undesirable for high-power applications. Coating the active electrode material with an electrochemically inactive component adds dead weight to the cell, reducing the energy and power density.

[0059] Applicants have discovered that orthorhombic alkali metal manganese oxide can be used as the oxygen-gettering-compound coating. It is believed that orthorhombic alkali metal manganese oxide can be coated on the surface of the ion-storage compound and the coating is stable during cycling of the cell. That is, the orthorhombic alkali metal manganese oxide will maintain its crystallite structure during cycling. For instance, when the ion storage compound coated with orthorhombic alkali metal manganese oxide is used as a cathode active material in a lithium ion battery, lithium ion will exchange with the alkali metal in the coating during cycling, and yet the coating layer still maintains its orthorhombic crystalline structure. In some embodiments, the ion-storage compound is initially coated with orthorhombic sodium manganese oxide to use in a lithium ion cell. During cell cycling, a portion or all of the sodium is replaced by lithium while the orthorhombic crystallite structure of the coating layer is maintained. The orthorhombic crystallite structure of the coating is desirable since the crystalline structure is stable throughout the cell cycling. In sharp contrast, layered or spinel alkali metal manganese oxide coating material will gradually lose its crystalline structure upon lithium-alkali metal exchange during cell cycling, and eventually result in the loss of the coating layer.

Layered or spinel alkali metal manganese oxide coating material can suffer from metal dissolution which degrades cell cycle life and calendar life.

[0060] In some embodiments, the orthorhombic alkali metal manganese oxide has a formula of Li$_x$Na$_y$MnO$_{4-x}$, wherein 0 ≤ x ≤ 0.44, 0 ≤ y ≤ 0.44, and 0.2 ≤ x + y ≤ 0.75.
In some embodiments, the orthorhombic alkali metal manganese oxide is Na$_{0.44}$MnO$_4$ which can be coated onto the surface of the ion-storage compound. In other embodiments, the orthorhombic alkali metal manganese oxide is Li$_{0.44}$MnO$_4$. In still other embodiments, the orthorhombic alkali metal manganese oxide contains both Li and Na.

The orthorhombic alkali metal manganese oxide coating materials as described herein have the following advantages. The orthorhombic alkali metal manganese oxide is electronic- and ion-conductive. Thus, the resulting coated ion-storage compound still maintains good electronic conductivity and ion conductivity. Additionally, the orthorhombic alkali metal manganese oxide coating material may also act as a cathode active material and thus contribute to the overall energy density of the cell. Accordingly, a cell including orthorhombic alkali metal manganese oxide coated ion-storage compound as the cathode active material will have high power and energy density and low impedance.

**Method of preparing ion-storage compound coated with orthorhombic alkali metal manganese oxide**

The orthorhombic alkali metal manganese oxide can be synthesized first and then coated onto the ion-storage compound. In some embodiments, orthorhombic sodium manganese oxide is synthesized. In other embodiments, the precursors for the orthorhombic alkali metal manganese oxide can be mixed with particles of the ion-storage compound and the orthorhombic alkali metal manganese oxide coating on the ion-storage compound is formed *in situ*. The alkali metal precursor, e.g., sodium source such as Na$_2$CO$_3$, and a manganese precursor, e.g., MnCO$_3$, can be dissolved in a solvent, then mixed with ion-storage compound, e.g., LiCoO$_2$ or LiNiO$_2$. The ion-storage compound may be powders insoluble in the solvent. The solvent can be aqueous or non-aqueous. Non-limiting examples of the non-aqueous solvents include methanol, ethanol, isopropanol, and acetone. The resulting slurry can then be dried to leave a coating of the precursors on the surface of the ion-storage compound. This precursor-ion-storage compound mixture is then heated to high temperature for a time sufficient to produce the desired orthorhombic alkali metal manganese oxide phase on the particle of the ion-storage compound. In some embodiments, the mixture can be heated to about 500 °C, about 600 °C, about 700 °C, about 800 °C, or about 900 °C. Other suitable temperatures are contemplated. In some embodiments, the mixture can
be heated for about 30 min, 1 h, 2 h, or 3 h. Other suitable heating times are contemplated.

In other embodiments, the ion-storage compound is blended with the oxygen-gettering compound.

A coating of the oxygen-gettering compound may be synthesized via a solution-based chemical synthesis step on lithium metal oxide particles. Alternatively, the oxygen-gettering compound coating may be formed via mechanical milling of small getter particles onto larger lithium metal oxide particles.

In one aspect, a positive electroactive material comprising a mixture of an alkali transition metal polyanion compound as the oxygen-gettering compound and a lithium metal oxide as the ion-storage compound is described. The positive electrode material mixture as described herein has higher energy density than alkali transition metal polyanion compound and better thermal safety than lithium metal oxide.

Applicants have surprisingly found that an electroactive material formed by blending an alkali transition metal polyanion compound and a lithium metal oxide has improved energy density and better thermal safety. In some embodiments, the positive electroactive material is formed by blending a lithium transition metal phosphate compound and a lithium metal oxide. The resulting mixture has higher energy density than the lithium transition metal phosphate compound but can reduce or minimize the thermal run away issue of the lithium metal oxide or improved thermal safety.


In some embodiments, alkali transition metal polyanion compound and lithium metal oxide are mixed according to the ratios disclosed herein. In some embodiments, the two compounds can be mixed using a mill. In some specific embodiments, a planetary mixer is used to mix a slurry comprising alkali transition metal polyanion compound and lithium metal oxide. Other way of mixing powders known in the art are contemplated. In some specific embodiments, the alkali transition metal polyanion compound is subjected to a wet-mill, and then the resulting compounds are combined with lithium transition metal oxide such as NCM into a
mixer, e.g., a planetary mixer. In other embodiments, dry-mixing methods are used where the lithium metal oxide particles are coated with lithium transitional metal phosphate material coating.

[0069] The mixed positive electroactive material comprising alkali transition metal polyanion compound and lithium metal oxide has improved energy density and capacity. In some embodiments, the mixed positive electroactive material has a charge capacity of more than about 150 mAh/g, 155 mAh/g, 160 mAh/g, 165 mAh/g, 170 mAh/g, 175 mAh/g, or 180 mAh/g. In some embodiments, the mixed positive electroactive material has a specific energy of more than about 500 mWh/g, 550 mWh/g, or 600mWh/g. In some embodiments, the powder density using the mixed positive electroactive material disclosed herein is increased due to higher material density of oxide cathode material. In some embodiments, the powder density of the mixed positive electroactive material is about 4.5-4.8g/cc. In comparison, the powder density of lithium iron phosphate (LFP) is about 3.5-3.66g/cc and the powder density of lithium iron manganese phosphate (LFMP) is about 3.4-3.5g/cc.

[0070] The mixed positive electroactive material as disclosed herein has also improved safety and abuse tolerance compared with lithium transition meal oxide material. In some specific embodiments, the mixed positive electroactive materials do not show the exothermic peak around 260 °C as shown in a DSC spectrum. The absence of this peak can be expected to correspond to better safety profile under high temperature conditions. This is highly surprising since a component of the mixed positive electroactive material is lithium transition metal oxide material, which is known to have an exothermic peak around 260 °C in a DSC spectrum. Without wishing to be bound by any particular theory, the absence of this peak around 260 °C may be related to better thermal safety of the material.

[0071] The mixed positive electrode comprising lithium metal oxide material and lithium transitional metal phosphate material exhibits improved safety profile as shown by Figures 5 and 6. As shown in Figure 5, a lithium metal oxide cathode has a thermal peak shown on the DSC chart indicating an exothermic output between 250 to 300 °C. In comparison, in a LFP: oxide blend cathode, such thermal peak between 250 to 300 °C is no longer present. Similarly as shown in Figure 6, in a Mix: oxide blend cathode, such thermal peak between 250 to 300 °C is no longer present. The disappearance of this thermal peak indicates that the mix cathode materials have
a better safety as the cathode no longer has an exothermic reaction at the temperature range between about 250 to about 300 °C.

[0072] Without being bound to any particular theory, it is believed that the presence of the exothermic peak on the DSC chart for lithium metal oxide material is associate with the release of radical oxygen by the lithium metal oxide at high temperatures. These generated radical oxygen species are highly reactive and may oxidize other components and materials of the cell, e.g., the electrolyte. Suitable materials for use in an electrolyte may include various organic carbonates which may react with the radical oxygen species, resulting in exothermal reactions damaging the cell. Also without being bound to any particular theory, it is believed that the Fe in LFP or LFMP maybe be in its charged, delithiated state which is easily transformable to iron oxide, e.g. Fe$_2$O$_3$, by the radical oxygen. Such "trapping" of the radical oxygen by Fe may prevent the radical oxygen from reacting with the electrolyte and other component of the cell. This protective effect of the iron material is further improved due to the nanoscale of the lithium LFP or LFMP material. Due to its large specific surface area, the reaction rate of Fe with radical oxygen is greatly improved so that the oxygen is efficiently trapped by Fe to prevent any further oxidation effect of the radical oxygen. In some embodiments, the mix cathode material comprises at least about 10% of the doped, undoped, or mixed metal lithium iron phosphate material. In some embodiments, the mix cathode material comprises at least about 20% of the doped, undoped, or mixed metal lithium iron phosphate material. In some embodiments, the mix cathode material comprises at least about 30% of the doped, undoped, or mixed metal lithium iron phosphate material. In some embodiments, the mix cathode material comprises at least about 40% of the doped, undoped, or mixed metal lithium iron phosphate material. In some embodiments, the mix cathode material comprises at least about 50% of the doped, undoped, or mixed metal lithium iron phosphate material. In some embodiments, the mix cathode material comprises at least about 60% of the doped, undoped, or mixed metal lithium iron phosphate material. In some embodiments, the mix cathode material comprises at least about 70% of the doped, undoped, or mixed metal lithium iron phosphate material. In some embodiments, the mix cathode material comprises at least about 80% of the doped, undoped, or mixed metal lithium iron phosphate material.
**Alkali Transition Metal Poly-anion Compound as the oxygen-gettering compound**

[0073] In some embodiments, the oxygen-gettering compound is alkali transition metal poly-anion compound as disclosed in United States Patent No. 7,338,734 is used in the mixture with lithium transition metal oxide to produce the mixed positive electroactive material. In other embodiments, lithium transition metal poly-anion compound as disclosed in United States Patent Serial No. 12/868,530, filed on August 25, 2010, is used in the mixture with lithium transition metal oxide to produce the mixed positive electroactive material.

[0074] In some embodiments, the oxygen-gettering compound is alkali transition metal poly-anion compound with a formula $A_x(M'_1\cdots M''_x)_{y}(DXD)_z$, $A_x(M'_1\cdots M''_x)_{y}(X_2D)_z$, or $A_x(M'_1\cdots M''_x)_{y}(D_2D)_z$, has specific surface area of at least 10 m$^2$/g, wherein A is at least one of an alkali metal and hydrogen, M’ is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, molybdenum and tungsten, M” is any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of oxygen, nitrogen, carbon, or a halogen, 0≤a≤0.1, and x, y, and z have values such that x plus the quantity y(1-a) times a formal valence or valences of M’, plus the quantity ya times a formal valence or valence of M”, is equal to z times a formal valence of the XD, X$_2$D, or DXD group, x, y, and z are typically greater than 0. The conductivity of the compound can be at least about 10$^{-5}$ S/cm, at least about 10$^{-4}$ S/cm, and, in some cases, at least about 10$^{-3}$ S/cm. In some embodiments, A is lithium and x/(x+y+z) can range from about zero to about one third, or about zero to about two thirds. In one embodiment, X is phosphorus, while in other embodiments, M’ is iron. M” can be any of aluminum, titanium, zirconium, niobium, tantalum, tungsten, or magnesium. M” can be substantially in solid solution in the crystal structure of the compound. Typically, the compound has at least one of an olivine (e.g., AMP0$_4$), NASICON (e.g., A$_2$M$_2$(PO$_4$)$_3$), VOP0$_4$, LiFe(P$_2$O$_7$) or Fe$_4$(P$_2$O$_7$)$_3$ structure, or mixtures thereof.

[0075] In some embodiments, the alkali transition metal poly-anion compound is a compound with a formula $A_x(M'_1\cdots M''_x)_{y}(DXD)_z$, $A_x(M'_1\cdots M''_x)_{y}(D_2D)_z$, or $A_x(M'_1\cdots M''_x)_{y}(X_2D)_z$, has a conductivity at about 27$^\circ$ C of at least about 10$^{-8}$ S/cm, wherein A is at least one of an alkali metal and hydrogen, M’ is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, molybdenum and tungsten, M” is any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB
metal, D is at least one of oxygen, nitrogen, carbon, or a halogen, 0.0001<a ≤ 0.1, and x, y, and z have values such that x plus the quantity y(1-a) times a formal valence or valences of M', plus the quantity ya times a formal valence or valence of M", is equal to z times a formal valence of the XD₄, X₂D₇, or DXD₄ group. x, y, and z are typically greater than 0. The conductivity of the compound can be at least about 10⁻³ S/cm, at least about 10⁻⁴ S/cm, and, in some cases, at least about 10⁻⁵ S/cm. In some embodiments, A is lithium and x/(x+y+z) can range from about zero to about one third, or about zero to about two thirds. In one embodiment, X is phosphorus, while in other embodiments, M' is iron. M" can be any of aluminum, titanium, zirconium, niobium, tantalum, tungsten, or magnesium. M" can be substantially in solid solution in the crystal structure of the compound. Typically, the compound has at least one of an olivine (e.g., AMP0₄), NASICON (e.g., A₂M₂(P0₄)₃, VOP0₄, LiFe(P2O7) or Fe₄(P2O₇)₃ structure, or mixtures thereof. [0076] In some embodiments, the alkali transition metal polyanion compound is a lithium-transition metal-phosphate compound. The lithium-transition metal-phosphate compound may be optionally doped with a metal, metalloid, or halogen. In some embodiments, the positive electroactive material is an olivine structure compound LiMPO₄, where M is one or more of V, Cr, Mn, Fe, Co, and Ni, in which the compound is optionally doped at the Li, M or O-sites. Deficiencies at the Li-site are compensated by the addition of a metal or metalloid, and deficiencies at the O-site are compensated by the addition of a halogen. In some embodiments, the positive active material is a thermally stable, transition-metal-doped lithium transition metal phosphate having the olivine structure and having the formula (Liₓ₋ₓZₓ)MPO₄, or Li(Mi₋ₓZₓ)PO₄ where M is one or more of V, Cr, Mn, Fe, Co, and Ni, and Z is a non-alkali metal dopant such as one or more of Ti, Zr, Nb, Al, Ta, W or Mg, and x ranges from 0.005 to 0.05. In a typical battery, the electroactive material is (Liₓ₋ₓZₓ)MPO₄, where Z is Zr, Nb or Ti. [0077] In some cases, the alkali transition metal phosphate composition has an overall composition of (Al₋ₓM"ₐₙ₋ₓM"ₐₙ₋ₓ)ₓ(XD₄)₂, (Al₋ₓM"ₐₙ₋ₓM"ₐₙ₋ₓ)(DXD₄)₂, or (Al₋ₓM"ₐₙ₋ₓM"ₐₙ₋ₓ)ₓ(X₂D₇), and has a conductivity at 27°C of at least about 10⁻⁸ S/cm, wherein A is at least one of an alkali metal and hydrogen, M' is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, molybdenum, and tungsten, M" any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIII, IB, IIB, IIIB, IVB, VB, and VIB,
D is at least one of oxygen, nitrogen, carbon, or a halogen, 0.0002 < a < 0.1, and x, y, and z have values such that (1-a) x plus the quantity ax times the formal valence or valences of M" plus y times the formal valence or valences of M' is equal to z times the formal valence of the XD₄, X₂D₂ or DXD₄ group x, y, and z are typically greater than zero. The conductivity of the compound can be at least about 10⁻³ S/cm, at least about 10⁻² S/cm, and, in some cases, at least about 10⁻¹ S/cm. In some embodiments, A is lithium and x/(x+y+z) can range from about zero to about one third. In one embodiment, X is phosphorus, while in other embodiments, M' is iron. M" can be any of aluminum, titanium, zirconium, niobium, tantalum, tungsten, or magnesium. M" can be substantially in solid solution in the crystal structure of the compound.

Typically, the compound has at least one of an olivine, NASICON, VOP0₄, LiFe(P₂O₇) or Fe₄P₂O₇₃ structure, or mixtures thereof. In some embodiments, the compound is LiFeP0₄. In some embodiments, M" is at least partially in solid solution in the crystal structure of the compound at a concentration of at least 0.01 mole % relative to the concentration of M', the balance appearing as an additional phase, at least 0.02 mole % relative to the concentration of M', the balance appearing as an additional phase, and in yet other embodiments, at least 0.05 mole % relative to the concentration of M', the balance appearing as an additional phase and, in still other embodiments, at a concentration of at least 0.1 mole % relative to the concentration of M', the balance appearing as an additional phase.

[0078] Doped lithium iron phosphate compounds may be prepared from starting materials of lithium salts, iron compounds and phosphorous salts including, but not limited to, lithium carbonate, ammonium phosphate and iron oxalate, to which a low additional concentration of dopant metal such as Mg, Al, Ti, Fe, Mn, Zr, Nb, Ta and W have been added, typically as a metal oxide or metal alkoxide. The powder mixture is heated under a low oxygen environment at a temperature of 300 °C to 900 °C. These compounds exhibit increased electronic conductivity at and near room temperature, which is particularly advantageous for their use as lithium storage materials. Further details regarding the composition and preparation of these compounds are found in United States Published Application 2004/0005265 (corresponding to U.S. Patent Application No. 10/329,046, entitled "Conductive Lithium Storage Electrode"), which is incorporated herein in its entirety by reference.

[0079] In some embodiments, the lithium transition metal phosphates include those described in U.S. Patent Application No. 11/396,515, filed April 3, 2006.
entitled "Nanoscale Ion Storage Materials" which is incorporated herein in its entirety by reference. Examples include nanoscale ordered or partially disordered structures of the olivine \((A_xMP_0)_{\frac{4}{3}}\), NASICON \((A_x(M',M'')_2(P0_{\frac{4}{3}})_3)\), VOP0 \(_{\frac{4}{3}}\), LiVP0 \(_{\frac{4}{3}}\), LiFe\((P_{20})\) or \(Fe_d(P_{20})_3\) structure types, wherein \(A\) is an alkali ion, and \(M, M'\) and \(M''\) are metals.

[0080] In one or more embodiments, the lithium transition metal phosphate composition has the formula LiMP0 \(_{\frac{4}{3}}\) (i.e., an olivine structure type), where \(M\) is one or more transition metals. In some embodiments, \(M\) is one or more of \(V, Cr, Mn, Fe, Co\) and \(Ni\). In certain embodiments, the lithium transition metal phosphate composition is an ordered olivine \((Lii\_MX0)_{\frac{4}{3}}\), where \(M\) is at least one first row transition metal (e.g., one or more of \(V, Cr, Mn, Fe, Co\) and \(Ni\)), and \(x\) can range from zero to one, during lithium insertion and deinsertion reactions. In some embodiments, \(M\) is Fe. In the as-prepared state, \(x\) is typically about one. In particular embodiments, the special properties of the lithium transition metal phosphate may be augmented by doping with foreign ions, such as metals or anions. Such materials are expected to exhibit similar behavior to that demonstrated herein for \(Lii\_FeP0_{\frac{4}{3}}\) at the nanoscale, based on the scientific principles underlying such behavior. However, doping is not required for a material to exhibit special properties at the nanoscale.

[0081] In other embodiments, there is some substitution of \(Li\) onto the \(M\)-site. In one embodiment, there is about 5 or 10% substitution of \(Li\) onto the Fe site. The lithium transition metal phosphate material has an overall composition of \((Lii-xMi_{\frac{4}{3}})P0_{\frac{4}{3}}\), where \(M\) comprises at least one first row transition metal selected from the group consisting of \(Ti, V, Cr, Mn, Fe, Co\) and \(Ni\), where \(x\) is from 0 to 1 and \(z\) can be positive or negative. In some embodiments, \(M\) includes \(Fe\), and \(z\) is between about 0.15 and -0.15. The lithium transition metal phosphate material can exhibit a solid solution over a composition range of 0<x<0.30, for example 0<x<0.15. In some embodiments, the material exhibits a stable solid solution over a composition range of \(x\) between 0 and at least about 0.15. In some embodiments, the lithium transition metal phosphate material exhibits a stable solid solution over a composition range of \(x\) between 0 and at least about 0.07 or between 0 and at least about 0.05 at room temperature (22-25 °C). The lithium transition metal phosphate material can also exhibit a stable solid solution at low lithium content; e.g., where \(0.8<x<1\) or where \(0.9<x<1\), or where \(0.95<x<1\).
In some embodiments, the lithium transition metal phosphate has a lithium-rich transition metal phosphate phase and a lithium-poor transition metal phosphate phase. For example, in some embodiments, the lithium-rich transition metal phosphate phase has the composition \( \text{Li}_y\text{MP}_0 \), and the lithium-poor transition metal phosphate phase has the composition \( \text{Li}_{1-x}\text{MP}_0 \), and \( 0.02 < y < 0.2 \) and \( 0.3 > x > 0.02 \) at room temperature (22-25°C). In one or more embodiments, the material can exhibit a solid solution over a composition range of \( 0 < x < 0.15 \) and \( 0.02 < y < 0.10 \).

In some embodiments, the nanoscale lithium transition metal phosphate materials are also based on the alkali transition metal phosphates, such as those described in U.S. Patent Application No. 10/329,046. For example, in one embodiment, the electroactive material has an overall composition of \( \text{Li}_x\text{Fe}_{a-M} \text{Fe}^n \text{P}_0 \), and a conductivity at 27°C, of at least about \( 10^{-8} \) S/cm. However, in some cases, the conductivity is at least about at least about \( 10^{-7} \) S/cm, in other cases, at least about \( 10^{-6} \) S/cm, in yet other cases, at least about \( 10^{-5} \) S/cm, in still other cases, at least about \( 10^{-4} \) S/cm, in some cases, at least about \( 10^{-3} \) S/cm, and in other cases, at least about \( 10^{-2} \) S/cm.

In some embodiments, the lithium transition metal phosphate composition has an overall composition of \( \text{Li}_x\text{Fe}_{a-M} \text{Fe}^n \text{P}_0 \), the compound having a gravimetric capacity of at least about 80 mAh/g while the device is charging/discharging at a rate greater than about C rate. However, in some embodiments, the capacity is at least about 100 mAh/g, or in other embodiments, at least about 120 mAh/g, in some embodiments, at least about 150 mAh/g, and in still other embodiments, at least about 160 mAh/g.

In some embodiments, the lithium transition metal phosphate composition has an overall composition of \( \text{Li}_x\text{Fe}_{a-M} \text{P}_0 \).

In some embodiments, the lithium transition metal phosphate composition has an overall composition of \( \text{Li}_x\text{Fe}_{a-M} \text{Fe}^n \text{P}_0 \), and a conductivity at 27°C of at least about \( 10^{-8} \) S/cm. However, in some cases, the conductivity is at least about at least about \( 10^{-7} \) S/cm, in other cases, at least about \( 10^{-6} \) S/cm, in yet other cases, at least about \( 10^{-5} \) S/cm, in still other cases, at least about \( 10^{-4} \) S/cm, and in some cases, at least about \( 10^{-3} \) S/cm, and in further cases, at least about \( 10^{-2} \) S/cm.

In some embodiments, the lithium transition metal phosphate composition has an overall composition of \( \text{Li}_x\text{Fe}_{a-M} \text{Fe}^n \text{P}_0 \), the compound having a gravimetric...
capacity of at least about 80 mAh/g while the device is charging/discharging at greater than about C rate. However, in some embodiments, the capacity is at least about 100 mAh/g, or in other embodiments, at least about 120 mAh/g; in some embodiments, at least about 150 mAh/g and in still other embodiments, at least about 170 mAh/g. The present invention can, in some embodiments, also provide a capacity up to the theoretical gravimetric capacity of the compound.

[0088] In some embodiments, the nanoscale lithium transition metal phosphate is LiFePO$_4$.

[0089] In some embodiments, M" is at least partially in solid solution in the crystal structure of the compound at a concentration of at least 0.01 mole % relative to the concentration of M', the balance appearing as an additional phase, at least 0.02 mole % relative to the concentration of M', the balance appearing as an additional phase, and in yet other embodiments, at least 0.05 mole % relative to the concentration of M', the balance appearing as an additional phase and, in still other embodiments, at a concentration of at least 0.1 mole % relative to the concentration of M', the balance appearing as an additional phase.

[0090] In some embodiments, the lithium transition metal phosphate composition has a suitable electronic conductivity greater than about $10^8$ S/cm. The alkali transition metal phosphate composition can be a composition of Li$_x$(Mi$_a$M"$_b$)P$_4$ or L$_x$aM"$_b$M'P$_4$, and can crystallize in the ordered-olivine or triphylite structure, or a structure related to the ordered olivine or triphylite structure with small displacements of atoms without substantial changes in the coordination number of anions around cations, or cations around anions. In such compounds Li$^+$ substantially occupies the octahedral site typically designated as M1, and a substantially divalent cation M' substantially occupies the octahedrally-coordinated site typically designated as M2, as described in the olivine structure given in "Crystal Chemistry of Silicate Minerals of Geophysical Interest," by J. J. Papke and M. Cameron, *Reviews of Geophysics and Space Physics*, Vol. 14, No. 1, pages 37-80, 1976. In some embodiments, the exchange of Li and the metal M' between their respective sites in a perfectly ordered olivine structure is allowed so that M' may occupy either site. M' is typically one or more of the first-row transition metals, V, Cr, Mn, Fe, Co, or Ni. M" is typically a metal with formal valence greater than I+ as an ion in the crystal structure.

[0091] In some embodiments, M', M", x, and a are selected such that the electroactive material is a crystalline compound that has in solid solution charge
compensating vacancy defects to preserve overall charge neutrality in the compound. In the compositions of type Li\(_x\)(M\(_{1-a}\)M\(_a^+\))P\(_4\)O\(_8\) or Li\(_{x+y}\)M\(_a^+\)M'\(_a^+\)P\(_4\)O\(_8\), this condition can be achieved when a times the formal valence of M\(_a^+\) plus (1-a) times the formal valence of M' plus x is greater than 3+, necessitating an additional cation deficiency to maintain charge neutrality, such that the crystal composition is Li\(_x\)(M\(_{1-a}\)M\(_a^+\)M'\(_a^+\))P\(_4\)O\(_8\) or Li\(_{x+y}\)M\(_a^+\)M'\(_a^+\)vac\(_y\)P\(_4\)O\(_8\), where vac is a vacancy. In the language of defect chemistry, the dopant can be supervalent and can be added under conditions of temperature and oxygen activity that promote ionic compensation of the donor, resulting in nonstoichiometry. The vacancies can occupy either M1 or M2 sites. When x<1, the compound also has additional cation vacancies on the M1 site in a crystalline solid solution, said vacancies being compensated by increasing the oxidation state of M\(_a^+\) or M'. In order to increase the electronic conductivity usefully, a suitable concentration of said cation vacancies should be greater than or equal to 10\(^{18}\) per cubic centimeter.

[0092] In some cases, the lithium transition metal phosphate composition has an olivine structure and contains in crystalline solid solution, amongst the metals M' and M\(_a^+\), simultaneously the metal ions Fe\(^{2+}\) and Fe\(^{3+}\), Mn\(^{2+}\) and Mn\(^{3+}\), Co\(^{2+}\) and Co\(^{3+}\), Ni\(^{2+}\) and Ni\(^{3+}\), V\(^{2+}\) and V\(^{3+}\), or Cr\(^{2+}\) and Cr\(^{3+}\), with the ion of lesser concentration being at least 10 parts per million of the sum of the two ion concentrations.

[0093] In some embodiments, the alkali transition metal phosphate composition has an ordered olivine structure and A, M', M\(_a^+\), x, and a are selected such that there can be Li substituted onto M2 sites as an acceptor defect. In the compositions of type Li\(_x\)(M\(_{1-a}\)M\(_a^+\))P\(_4\)O\(_8\) or Li\(_{x+y}\)M\(_a^+\)M'\(_a^+\)P\(_4\)O\(_8\), typical corresponding crystal compositions are Li\(_x\)(M\(_{1-a}\)M\(_a^+\)Li\(_y\))P\(_4\)O\(_8\) or Li\(_{x+y}\)M\(_a^+\)M'\(_a^+\)Li\(_y\)P\(_4\)O\(_8\). In this instance, the subvalent Li substituted onto M2 sites for M' or M\(_a^+\) can act as an acceptor defect. In order to increase the electronic conductivity usefully, a suitable concentration of said Li on M2 sites should be greater than or equal to 10\(^{18}\) per cubic centimeter.

[0094] In some embodiments, the nanoscale lithium transition metal phosphate is a p-type semiconducting composition, for example Li\(_x\)(M\(_{1-a}\)M\(_a^+\))P\(_4\)O\(_8\), Li\(_x\)M\(_a^+\)M'\(_a^+\)P\(_4\)O\(_8\), Li\(_x\)(M\(_{1-a}\)M\(_a^+\)vac\(_y\))P\(_4\)O\(_8\), Li\(_{x+y}\)M\(_a^+\)M'\(_a^+\)vac\(_y\)P\(_4\)O\(_8\), Li\(_x\)(M\(_{1-a}\)M\(_a^+\)Li\(_y\))P\(_4\)O\(_8\) or Li\(_{x+y}\)M\(_a^+\)M'\(_a^+\)Li\(_y\)P\(_4\)O\(_8\). M' is a group IIA, IIIA, VIA, VA, VIA, VIIA, VIIIA, IB, IIB, IVB, VB, and VIB element of the Periodic Table (catalog number S-18806, published by the Sargent-Welch company in 1994). Magnesium is an example of a dopant from Group IIA, Y is an example of a dopant from Group IIIA, Ti and Zr are examples of
dopants from Group IVA, Nb and Ta are examples of dopants from Group VA, W is an example of a dopant from Group VIA, Fe is an example of a metal from Group VIIIA, and Al is an example of a dopant from Group IIIB.

In the lithium transition metal phosphate compositions described herein, x can have a value between zero and 1.1 in the initially prepared material. During its use as a lithium ion storage compound, x can vary between about zero and about 1.1. In the nanoscale materials described herein, a can have a value between about 0.0001 and 0.1. In some embodiments, out of the total amount a of $M^x_M$, at least 0.0001 is in solid solution in the crystalline structure of the compound.

In some embodiments, $M'$ is Fe and the solubility of $M''$ in the lattice can be improved if $M''$ has an ionic radius, in octahedral coordination, that is less than that of Fe$^{2+}$. Achieving solid solubility sufficient to increase the electronic conductivity above $10^8$ S/cm can require that processing conditions (for example, temperature, atmosphere, starting materials) allow $M''$ to be stabilized in a particular valence state that would provide an ionic radius less than that of Fe$^{2+}$. In some cases, for example, when solid solubility is achieved, the $M''$ ion may occupy the M1 site, or it may preferentially occupy the M2 site and cause Fe$^{2+}$ or Fe$^{3+}$, which would normally occupy the M2 site, to occupy the M1 site.

Generalizing the $M''$ solubility requirement to other olivines of composition $Li_xM''_{(1-x)}M'P0_4$, $M''$ typically has an ionic radius that is less than the average ionic radius of ions $M'$ at the Li concentration x at which the compound is first synthesized.

Electrochemical insertion and removal can later change the valence distribution amongst the $M'$ and $M''$ ions. In some cases, $M''$ can be in the desired valence state and concentration by adding, to the starting material, a salt of $M''$ having the desired final valence. However, the desired valence distribution amongst metals $M'$ and $M''$ can be obtained by synthesizing or heat treating under appropriate conditions of temperature and gas atmosphere. For example, if $M'$ is Fe, heat treatment should be conducted under temperature and atmosphere conditions that preserve a predominantly 2+ valence state, although some Fe$^{3+}$ is allowable and can even be beneficial for increasing conductivity.

In other cases, for example, for $Li_x(M_{1-a}M''_a)P0_4$ compositions, firing or heat treating at 600° C, can render the compositions conductive, even if $M''$, or $M'$, is a divalent cation, such as Mg$^{2+}$ or Mn$^{2+}$. In some cases, a $Li_3PO_4$ secondary phase can
be present. Thus, the olivine composition according to some embodiments of the
present invention may have a lithium deficiency that can result in a Li_{x-M''}M'P0_4
crystal composition.

[0100] The possible dopants M" are not limited to those Groups of the Periodic
Table that were previously identified, rather, M" can be any metal that satisfies the
above requirements of size and valence. Specifically, for compositions Li_{x-M'
-M''}M'P0_4, where M' is Fe, M" may be Mg^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, Ce^{3+}, Ti^{4+}, Zr^{4+}, Hf^{4+},
Nb^{5+}, Ta^{5+}, W^{4+}, W^{6+}, or combinations thereof.

[0101] The lithium transition-metal phosphate compounds (e.g., doped or
undoped LiFeP0_4) can be prepared with a markedly smaller particle size and much
larger specific surface area than previously known positive active materials, such as
LiCoO_2, LiNiO_2 or LiMn_2O_4 and, thus improved transport properties. Improved
transport properties reduce impedance and may contribute to low impedance growth.
In some embodiments the lithium transition-metal phosphate compounds consist of
powder or particulates with a specific surface area of greater than about 5 m^2/g,
greater than about 10 m^2/g, greater than about 15 m^2/g, greater than about 20 m^2/g,
greater than about 30 m^2/g, 35 m^2/g, 40 m^2/g, or 50 m^2/g. In comparison, lithium
transition metal oxide usually has specific surface areas of less than about 10 m^2/g.

[0102] It has been found that LiFeP0_4 having the olivine structure and made in
the form of very small, high specific surface area particles is exceptionally stable in
delithiated form even at elevated temperatures and in the presence of oxidizable
organic solvents, e.g., electrolytes, thus enabling a safer Li-ion battery having a very
high charge and discharge rate capability. In addition, the small-particle-size, high
specific-surface-area LiFeP0_4 material exhibits not only high thermal stability, low
reactivity and high charge and discharge rate capability, but it also exhibits excellent
retention of its lithium intercalation and deintercalation capacity during many
hundreds, or even thousands, of high-rate cycles.

[0103] In certain embodiments, lithium transition metal phosphate has the formula
LiMP0_4, where M is one or more transition metals. In some embodiments, the
nanoscale alkaline transition metal phosphate is doped at the Li site. In some
embodiments, the nanoscale alkaline transition metal phosphate is doped at the M site.
It has been unexpectedly discovered that these ion storage materials having
sufficiently small size scale and correspondingly high surface to volume ratio or
specific surface area provide fundamentally different physical properties compared to
their conventional coarse-grained counterparts. Despite having gross structural similarities such as crystal structure type and basic atomic arrangements, the nanoscale materials are compositionally and structurally distinct from, and provide different and improved electrochemical utility and performance compared to, the coarse-grained materials. The difference in relevant physical properties arises because the nanoscale materials are sufficiently small in at least one dimension (for instance, the diameter of an equi-axed particle, the diameter of a nanorod, or the thickness of a thin film) that they have different defect and thermodynamic properties. These nanoscale ion storage materials exhibit outstanding electrochemical performance for use in primary or secondary storage batteries, in particular providing a very high rate capability, while providing a large fraction of the intrinsic charge capacity and energy density of the material. In certain embodiments, the lithium transition metal phosphate has a BET (Brunauer-Emmett-Teller method) specific surface area of at least about 5 m²/g, at least about 10 m²/g, at least about 15 m²/g, at least about 20 m²/g, at least about 25 m²/g, at least about 30 m²/g, at least about 35 m²/g, at least about 40 m²/g, at least about 45 m²/g, or at least about 50 m²/g. In some instances, lithium transition metal phosphate includes approximately equi-axed particles having an "equivalent spherical particle size" (number-averaged mean particle diameter that would result in the measured surface area if the material were in the form of identically-sized spherical particles) of about 100 nm or less, for example, about 75 nm or less, about 70 nm or less, about 60 nm or less, about 50 nm or less, about 45 nm or less, about 40 nm or less, or about 35 nm or less. In certain embodiments, the material includes anisometric particles or a thin film or coating having a smallest cross-sectional dimension that is, on a number-averaged basis to provide a mean value, about 100 nm or less, for example, about 75 nm or less, about 70 nm or less, about 60 nm or less, about 50 nm or less, about 45 nm or less, about 40 nm or less, or about 35 nm or less. These dimensions can be measured using various methods, including direct measurement with an electron microscope of the transmission or secondary-electron type, or with atomic force microscopy. Such nanoscale ion storage materials are described in more detail in U.S. Application No. 10/329,046, supra.

[0104] In other embodiments, alkali transition metal polyanion compound with smaller specific surface areas can be used for the mixed positive electroactive material disclosed herein. In some specific embodiments, the alkali transition metal polyanion
compound is lithium transition metal phosphate with a BET (Brunauer-Emmett-Teller method) specific surface area of at least about 0.5 m²/g, at least about 1 m²/g, at least about 2 m²/g, at least about 3 m²/g, at least about 5 m²/g, at least about 7 m²/g, at least about 9 m²/g, or at least about 10 m²/g.

[0105] In certain embodiments, the lithium transition metal phosphate described herein are prepared from conventional materials by size-reduction processes (e.g., milling) to reduce the particle dimensions into the desired range. However, this can be a highly energy-intensive process. Thus, the materials also can be synthesized in the nanoscale state, by methods including, but not limited to, solid-state reactions between metal salts, wet-chemical methods, such as co-precipitation, spray-pyrolysis, mechanochemical reactions, or combinations thereof. Nanoscale materials with the desired particle sizes and specific surface areas are obtained by using homogeneous reactants, minimizing the reaction or crystallization temperature (in order to avoid particle coarsening), and avoiding formation of liquid phases in which the product is highly soluble (which also tends to lead to particle coarsening). Specific processing conditions can typically be established for a given process without undue experimentation by those skilled in the art. Further details regarding the composition and preparation of these compounds are found in United States Patent Application No. 11/396,515, supra.

[0106] In some embodiments, nanoscale lithium transition metal phosphate materials are prepared by non-equilibrium, moderate temperature techniques, such as wet-chemical or low temperature solid-state reactions or thermochemical methods. The materials thus prepared can acquire properties such as increased nonstoichiometry and disorder and increased solubility for dopants because they are synthesized in a metastable state or because kinetic pathways to the final product differ from those in conventional high temperature processes. Such disorder in the nanoscale form can also be preserved substantially under electrochemical use conditions and provide benefits as described herein.

[0107] In some embodiments, the lithium transition metal phosphate is doped LFMP material having at least one olivinic phase that comprises lithium (Li), iron (Fe), manganese (Mn), one or more dopants (D) and phosphate (PO₄), where the overall composition includes Fe+Mn+D=1.0, the ratio of the amount of Li : (Fe+Mn+D) ranges from about 1.0 to about 1.05, the ratio of the amount of PO₄ : (Fe+Mn+D) ranges from about 1.0 to about 1.025, D is one or more metals selected
from the group consisting of cobalt (Co), nickel (Ni), vanadium (V), niobium (Nb), and mixtures thereof, and Mn ranges from 0.350 to less than 0.600, or 0.400 to less than 0.600, or 0.400 to 0.550, or 0.450 to 0.550, or 0.450 to 0.500. In certain embodiments, D is one or more metals selected from the group consisting of cobalt (Co), vanadium (V), or mixtures thereof. In certain embodiments, the LFMP material can be further doped with fluorine (F).

[0108] In some embodiments, the composition comprises up to about 0.1 mol%, 0.5 mol%, 1 mol%, 1.5 mol%, 2 mol%, 2.5 mol%, 3 mol%, 3.5 mol%, 4 mol%, 4.5 mol%, 5 mol%, 6 mol%, 7, mol%, 8, mol%, 9 mol%, or 10 mol% of the one or more dopant metals. In certain embodiments, the composition comprises up to 0.1 mol%, 0.5 mol%, 1 mol%, 1.5 mol%, 2 mol%, 2.5 mol%, 3 mol%, 3.5 mol%, 4 mol%, 4.5 mol%, or 5 mol% of Co. In certain embodiments, the composition comprises up to 0.1 mol%, 0.5 mol%, 1 mol%, 1.5 mol%, 2 mol%, 2.5 mol%, 3 mol%, 3.5 mol%, 4 mol%, 4.5 mol%, or 5 mol% of Ni. In certain embodiments, the composition comprises up to 0.1 mol%, 0.5 mol%, 1 mol%, 1.5 mol%, 2 mol%, 2.5 mol%, 3 mol%, 3.5 mol%, 4 mol%, 4.5 mol%, or 5 mol% of V. In certain embodiments, the composition comprises up to 0.1 mol%, 0.5 mol%, 1 mol%, 1.5 mol%, 2 mol%, 2.5 mol%, 3 mol%, 3.5 mol%, 4 mol%, 4.5 mol%, or 5 mol% of F.

[0109] In one or more embodiments, lithium transition metal phosphate material comprises at least an olivinic phase that comprises lithium (Li), iron (Fe), manganese (Mn), one or more dopants (D) and phosphate (P0₄), where the overall composition has a ratio of Li : (Fe+Mn+D) ranging from about 1.000 to about 1.050, a ratio of (P0₄) : (Fe+Mn+D) ranging from about 1.000 to about 1.025, and D is one or more metals selected from the group consisting of cobalt (Co), nickel (Ni), vanadium (V), niobium (Nb), and mixtures thereof. In certain embodiments, D is one or more metals selected from the group consisting of cobalt (Co), vanadium (V), or mixtures thereof. In certain embodiments, the positive electrode material can be further doped with fluorine (F).

[0110] In one or more embodiments, lithium transition metal phosphate material is provided including a lithium and/or phosphate stoichiometric electroactive material, having one or more phases comprising lithium (Li), iron (Fe), manganese (Mn), one or more dopants (D) and phosphate (P0₄), where the overall composition has a ratio of Li : (Fe+Mn+D) that is about 1.000, a ratio of (P0₄) : (Fe+Mn+D) that is about 1.000, and D is one or more metals selected from the group consisting of cobalt (Co),
nickel (Ni), vanadium (V), niobium (Nb), or mixtures thereof. In certain embodiments, D is one or more metals selected from the group consisting of cobalt (Co), vanadium (V), or mixtures thereof. In certain embodiments, D is one or more metals selected from the group consisting of cobalt (Co), vanadium (V), niobium (Nb), or mixtures thereof. Without wishing to be bound by theory, the presence of Nb may increase the electrical conductivity of the electroactive material. In certain embodiments, the positive electrode material can be further doped with fluorine (F).

In one or more embodiments, lithium transition metal phosphate material including a lithium-rich and/or phosphate-rich electroactive material is provided. The electroactive material comprises at least an olivinic phase that includes lithium (Li), iron (Fe), manganese (Mn), one or more dopants (D) and phosphate (PO₄), where the overall composition has a ratio of Li : (Fe+Mn+D) ranging from about greater than 1.000 to about 1.050, a ratio of (PO₄) : (Fe+Mn+D) ranging from about greater than 1.000 to about 1.025, and D is one or more metals selected from the group consisting of cobalt (Co), nickel (Ni), vanadium (V), niobium (Nb), and mixtures thereof. In certain embodiments, D is one or more metals selected from the group consisting of cobalt (Co), vanadium (V), or mixtures thereof. In certain embodiments, the positive electrode material can be further doped with fluorine (F).

The excess lithium and excess phosphate in the overall composition need not provide a non-stoichiometric olivine compound in a single olivinic structure or single olivinic phase. Rather, the excess lithium and/or phosphate may be present, for example, as secondary phases and the like in conjunction with an olivinic phase.

Typically, the dopants, such as Co, Ni, V, Nb, and/or F, are doped into and reside on the lattice sites of the olivinic structure to form an olivinic phase. However, small amounts of dopant-rich secondary phases may be tolerated before degradation of the Li-ion battery cell performance is exhibited.

Some suitable exemplary lithium transition metal phosphate material that may provide improved energy density and power density include, but are not limited to:

\[ \text{Lii.}_{0.25}\text{Mno.}_{0.4}\text{Feo.}_{0.58}\text{Coo.}_{0.2}\text{O}(\text{PO}_4)_{1\text{i.000}} \]
\[ \text{Lii.025Mno.450Feo.530Coo.020(P04)1i.00O} \]
\[ \text{Lii.025Mno.500Feo.480Coo.010NiO.010(P04)i.000} \]
\[ \text{Lii.050Mno.450Feo.500Coo.010NiO.010Vio.010(P04)1i.25} \]
\[ \text{Lii.040Mno.400Feo.560Coo.010NiO.010Vo.020(P04)i.0i5} \]
One general expectation is that since the redox potential of Mn in the olivine structure (about 4.0 V vs. Li) is approximately 0.5 V higher than that of Fe (3.5 V vs. Li), Mn-rich Li-Fe-Mn phosphate (LFMP) materials should achieve improved properties, such as energy density and specific capacity. In fact, others have focused on such Mn-rich phosphate materials. However, surprisingly and contrary to conventional wisdom, improved properties of compounds can be obtained, such as energy density and specific capacity, of positive electrode LFMP material having lower levels of Mn, and, for example, where the molar amount of Mn in the LFMP is less than 60%, 55%, 50%, 45%, or 40%.

Moreover, without wishing to be bound by theory, most dopant metals have stable oxidation states that may be changed only at potentials that are significantly different from the redox potentials of Fe and/or Mn. Therefore, these dopant metals are not expected to directly contribute to the electric storage capacity of the material. For example, since the redox potentials of Co and Ni are about at least 0.5 V higher than that of manganese and at least 1.0 V higher than that of iron, such dopant metals would not normally contribute significant electric storage capacity to a battery cell operating at or near the redox plateau for Fe$^{2+} \rightarrow$ Fe$^{3+}$.

In certain embodiments, the lithium transition metal phosphate including a doped olivine electroactive compound can be prepared from starting materials of lithium salts, iron compounds and phosphorous salts including, but not limited to, lithium carbonate, iron oxalate or carbonate, manganese carbonate, and ammonium...
phosphate to which a low additional concentration of dopant metal such as Co, Ni, V, and/or F have been added, such as using cobalt oxalate, nickel oxalate, vanadium oxide, and/or ammonia fluoride. In other embodiments, lithium transition metal phosphate is prepared from a lithium source, e.g., a lithium salt, and a transition metal oxide. Additional dopant metal(s) can be added as well. The dried powder mixture is heated under a low oxygen, e.g., inert, environment at a temperature of 300 °C to 900 °C, and for example at a temperature of about 600-700°C. Further details regarding the composition and preparation of these compounds are found in United States Published Application 2004/0005265, US 2009/01238134, and US 2009/0186277, all of which are incorporated by reference herein in their entirety.

Additionally, control of the primary olivine crystallite size to < 100 nm dimensions may be beneficial in enhancing both lithium transport kinetics and conductivity of the LFMP materials. Further details regarding the composition and preparation of such analogous compounds (lithium-iron phosphate materials) are found in United States Published Application 2004/0005265, now U.S. Patent No. 7,338,734, which is incorporated herein in its entirety by reference.

Doping with hypervalent transition metals such as Nb or V may further contribute to the advantageous application of the resulting olivine materials for rechargeable lithium ion battery applications. The advantageous role of the dopant may be several fold and include the increased electronic conductivity of the olivine powder and may limit the sintering of the olivine nanophosphate particles to allow full utilization of the lithium capacity during fast charge/discharge of the battery. Other non-limiting examples of lithium transition metal polyanion compounds include L1C0PO4, LiMnPO4, Li3V2(P04)3, LiVP3F and mixed transition metal phosphate.

Lithium Transition Metal Oxide Compound as Ion-storage Compound

In some embodiments, lithium transition metal oxide for the mixed positive electroactive material is lithium nickel cobalt aluminum oxide (NCA), lithium nickel cobalt manganese oxide (NCM), lithium nickel cobalt magnesium oxide, spinel lithium manganese oxide (LMO), or LLC (Layered oxide cathode). Other non-limiting examples of lithium transition metal oxide include LCO (lithium cobalt oxide); high voltage, spinel Ni, Mn oxide; layered Mn oxide, and other lithium transition metal oxides known in the art can also be used in the mixture of the positive electroactive material as disclosed herein. In some embodiments, the lithium transition metal oxides disclosed in U.S. Patent No. 7,041,239 (the content of which is
hereby incorporated by reference herein in its entirety) are used in the mixture of the positive electroactive material as disclosed herein. In some embodiments, the oxygen atom in lithium transition metal oxide is substituted by an another atom such as F, Cl, or Br. In some embodiments, the concentration of nickel, cobalt, manganese, aluminum, and/or magnesium changes across the radius of the particle.

Assembly of Electrode and Battery

[0121] On an electrode level, the active material and a conductive additive are combined to provide an electrode layer that permits rapid lithium diffusion throughout the layer. A conductive additive such as carbon or a metallic phase is included in order to improve its electrochemical stability, reversible storage capacity, or rate capability. Exemplary conductive additives include graphite, carbon black, acetylene black, vapor grown fiber carbon ("VGCF") and fullerenic carbon nanotubes. Conductive diluents are present in a range of about 1%-5% by weight of the total solid composition of the positive electrode.

[0122] The positive electrode (cathode) is manufactured by applying a semi-liquid paste containing the mix cathode active material and conductive additive homogeneously dispersed in a solution of a polymer binder in an appropriate casting solvent to both sides of a current collector foil or grid and drying the applied positive electrode composition. A metallic substrate such as aluminum foil or expanded metal grid is used as the current collector. To improve the adhesion of the active layer to the current collector, an adhesion layer, e.g., thin carbon polymer intercoating, may be applied. Exemplary adhesion layers include, without limitation, those described in U.S. Patent Application No. 11/5 15,633, entitled "Nanocomposite Electrodes and Related Devices," filed September 5, 2006, which is incorporated herein in its entirety by reference. The dried layers are calendared to provide layers of uniform thickness and density. The binder used in the electrode may be any suitable binder used as binders for non-aqueous electrolyte cells. Exemplary materials include a polyvinylidene fluoride (PVDF)-based polymers, such as poly(vinylidene fluoride) (PVDF) and its co- and terpolymers with hexafluoroethylene, tetrafluoroethylene, chlorotrifluoroethylene, poly(vinyl fluoride), polytetrafluoroethylene (PTFE), ethylene-tetrafluoroethylene copolymers (ETFE), polybutadiene, cyanoethyl cellulose, carboxymethyl cellulose and its blends with styrene-butadiene rubber,
polyacrylonitrile, ethylene propylene diene terpolymers (EPDM), styrene-butadiene rubbers (SBR), polyimides, ethylene-vinyl acetate copolymers.

[0123] A positive electrode can have a thickness of less than 150 μη, e.g., between about 50 μη to 125 μη, or between about 80μη to 100 μη on each side of the current collector, and a pore volume fraction between about 30 and 70 vol. %. The active material is typically loaded at about 10-20 mg/cm², and typically about 11-15 mg/cm². Other numerical ranges of thickness and material loadings are contemplated. In general, a thicker electrode layer (and higher active material loading) provides greater total capacity for the battery. However, thicker layers also increase the electrode impedance. The present inventors have surprisingly discovered that high capacity, thick layers may be used in a low impedance (high rate) cell. Use of a high specific surface area active material, while maintaining adequate pore volume, provides the desired capacity without increasing impedance to unacceptably high levels.

[0124] In another embodiment, the electroactive material of the positive electrode includes a material that, while of high electronic conductivity, does not vary its conductivity by more than a factor of five, or factor of two, over the entire charge cycle. This feature of the Li-ion cell is contrasted with conventional electroactive positive electrode materials such as LiCoO₂, LiNiO₂ or LiMn₂O₄ for which conductivity increases dramatically once delithiation during charging occurs. The dramatic increase in conductivity of the electroactive material of the positive electrode contributes to a decrease in impedance. In contrast, an electroactive material of the present cells exhibit only moderate increases in conductivity, so that its contribution to impedance is more moderate.

[0125] The selection criteria for an anode are at two levels, the particle level and the electrode level. At the particle level, the particle size and the Li diffusion coefficient of the particle are selection criteria. In one embodiment, the negative active material is a carbonaceous material. The carbonaceous material may be non-graphitic or graphitic. A small-particle-size, graphitized natural or synthetic carbon can serve as the negative active material. Although non-graphitic carbon materials or graphite carbon materials may be employed, graphitic materials, such as natural graphite, spheroidal natural graphite, mesocarbon microbeads and carbon fibers, such as mesophase carbon fibers, are preferably used. The carbonaceous material has a
numerical particle size (measured by a laser scattering method) that is smaller than about 25 \( \mu \text{m} \), or smaller than about 15 \( \mu \text{m} \), or smaller than about 10 \( \mu \text{m} \), or even less than or equal to about 6 \( \mu \text{m} \). The smaller particle size reduces lithium diffusion distances and increases rate capability of the anode, which is a factor in preventing lithium plating at the anode. In those instances where the particle is not spherical, the length scale parallel to the direction of lithium diffusion is the figure of merit. Larger particle sized materials may be used if the lithium diffusion coefficient is high. The diffusion coefficient of MCMB is \( \sim 10^{-10} \text{ cm}^2/\text{s} \). Artificial graphite has a diffusion coefficient of \( \sim 10^{-8} \text{ cm}^2/\text{s} \). As a result larger particle size artificial graphite could be used, approximately equal to 15 microns times the square root of the ratio of the respective diffusivities (H. Yang et al, *Journal of Electrochemical Society*, 151 (8) A1247-A1250 (2004)).

[0126] In some embodiments, the anode materials include high capacity silicon tin alloy, other metal compound anode, lithium metal and lithium metal alloy, and lithium titanium oxide (LTO). In other embodiments, anode materials include high capacity of Silicon alloy, tin alloy, SiO nano compound, and other metal compound for higher capacity. Also, other oxide can be used such as LTO(lithium titanium oxide). Other suitable anode materials known in the art are contemplated.

[0127] In one or more embodiments, the anode is an alloy or compound of lithium with another metal or metalloid including Al, Si, Sn, Sb, B, Ag, Bi, Cd, Ga, Ge, In, Pb, or Zn. Other anode materials include those disclosed in U.S. Patent Publication No. 2006/0292444, the content of which is hereby incorporated by reference herein in its entirety.

[0128] In some embodiments, the negative active material consists of powder or particulates with a specific surface area measured using the nitrogen adsorption Brunauer-Emmett-Teller (BET) method to be greater than about 0.1 \( \text{m}^2/\text{g} \), 0.5 \( \text{m}^2/\text{g} \), 1.0 \( \text{m}^2/\text{g} \), 1.5 \( \text{m}^2/\text{g} \), 2 \( \text{m}^2/\text{g} \), 4 \( \text{m}^2/\text{g} \), 6 \( \text{m}^2/\text{g} \), 8 \( \text{m}^2/\text{g} \), 10 \( \text{m}^2/\text{g} \), 12 \( \text{m}^2/\text{g} \), 14 \( \text{m}^2/\text{g} \), or 16 \( \text{m}^2/\text{g} \). Other specific surface areas for the negative active material are contemplated.

[0129] On an electrode level, the active material and a conductive additive are combined to provide an electrode layer that permits rapid lithium diffusion throughout the layer. A conductive additive such as carbon or a metallic phase may also be included in the negative electrode. Exemplary conductive additives include graphite, carbon black, acetylene black, vapor grown fiber carbon ("VGCF") and fullerenic
carbon nanotubes. Conductive diluents are present in a range of about 0%-5% by weight of the total solid composition of the negative electrode.

[0130] The negative electrode (anode) of the battery is manufactured by preparing a paste containing the negative active material, such as graphitic or non-graphitic carbon, and a conductive carbon additive homogeneously suspended in a solution of a polymer binder in a suitable casting solvent. The paste is applied as a uniform-thickness layer to a current collector and the casting solvent is removed by drying. A metallic substrate such as copper foil or grid is used as the negative current collector. To improve the adhesion of the active material to the collector, an adhesion promoter, e.g., oxalic acid, may be added to the slurry before casting. The binder used in the negative electrode may be any suitable binder used as binders for non-aqueous electrolyte cells. Exemplary materials include a polyvinylidene fluoride (PVDF)-based polymers, such as poly(vinylidene fluoride) (PVDF) and its co- and terpolymers with hexafluoroethylene, tetrafluoroethylene, chlorotrifluoroethylene, poly(vinyl fluoride), polytetrafluoroethylene (PTFE), ethylene-tetrafluoroethylene copolymers (ETFE), polybutadiene, cyanoethyl cellulose, carboxymethyl cellulose and its blends with styrene-butadiene rubber, polyacrylonitrile, ethylene propylene diene terpolymers (EPDM), styrene-butadiene rubbers (SBR), polyimides, ethylene-vinyl acetate copolymers.

[0131] At the electrode level, the negative electrode can have a thickness of less than about 200 μm, about 150 μm, about 100 μm, or about 75 μm, e.g., between about 20 μm to about 65 μm, or between about 40μm to about 55 μm on both sides of the current collector, and a pore volume fraction between about 20 and about 40 vol.%. The active material is typically loaded at about 1-20 mg/cm², or about 4-5 mg/cm². In general, a thicker electrode layer (and higher active material loading) provides greater total capacity for the battery. However, thicker layers also increase the electrode impedance by reducing the ease of lithium diffusion into the anode. The present inventors have surprisingly discovered that high capacity, thick layers may be used in a low impedance cell through selection of active materials as indicated above and maintaining adequate pore volume.

[0132] A nonaqueous electrolyte is used and includes an appropriate lithium salt. Non-limiting examples of the salts include LiPF₆, LiBF₄, LiAsF₆, or lithium bis(trifluoromethylsulphonimide) (LiTFMSI), lithium bis(oxalatoborate) (LiBOB), or
lithium bis(pentafluoroethylsulfonyl)imide (LiBETI) dissolved in a nonaqueous solvent. Other suitable salts known in the art are contemplated. One or more functional additives, such as, for example, C0_2, vinylene carbonate, ethylene sulfite, ethylene thiocarbonate, dimethyl dicarbonate, spirodicarbonate and propane sulfone, can be included to modify the solid-electrolyte interface/interphase (SEI) that forms on the electrodes, particularly negative carbon electrodes. The electrolyte may be infused into a porous separator that spaces apart the positive and negative electrodes. In one or more embodiments, a microporous electronically insulating separator is used.  

Numerous organic solvents have been proposed as the components of Li-ion battery electrolytes, notably a family of cyclic carbonate esters such as ethylene carbonate (EC), Fluoroethylene Carbonate (FEC), propylene carbonate (PC), butylene carbonate (BC), and vinylene carbonate (VC), and their chlorinated or fluorinated derivatives, and a family of acyclic dialkyl carbonate esters, such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC), dipropyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, dibutyl carbonate, butylmethyl carbonate, butylethyl carbonate and butylpropyl carbonate. Other solvents proposed as components of Li-ion battery electrolyte solutions include methyl acetate (MA), ethyl acetate (EA), methyl formate (MF), propyl acetate (PA), methyl butyrate (MB), ethyl butyrate (EB), γ-butyrolactone (γ-BL), dimethoxyethane, tetrahydrofuran, 2-methyl tetrahydrofuran, 1,3-dioxolane, 4-methyl-1,3-dioxolane, diethyl ether, sulfolane, methylsulfolane, acetonitrile, propiononitrile, ethyl acetate, methyl propionate, ethyl propionate and the like. These nonaqueous solvents are typically used as multicomponent mixtures. Other solvents suitable for use as electrolytes known in the art are contemplated.  

In certain embodiments, a cell exhibiting low impedance growth employs an electrolyte having the following composition: about 0.8 M to about 1.5 M LiPF_6 in an organic solvent made up of about 30 wt% to about 70 wt% ethylene carbonate, about 0 wt% to about 20 wt% propylene carbonate, about 0 wt% to about 60 wt% dimethyl carbonate, about 0 wt% to about 60 wt% ethyl methyl carbonate, about 0 wt% to about 60 wt% diethyl carbonate, and about 0 wt% to about 5 wt% vinylene carbonate. The sum of the weight percents of ethylene carbonate and propylene carbonate is between about 30 wt% and about 70 wt% of the total organic solvent, and propylene carbonate represents about 30 wt% or less of this sum. In particular
embodiments, the cell exhibiting low impedance growth and employing this electrolyte composition includes a cathode active material having an olivine structure and a formula LiMPO$_4$, where M is one or more transition metals, and the material is doped or undoped at the lithium or M site. In at least some instances, the cell includes a carbonaceous anode active material, for example, a graphitic material such as mesocarbon microbeads (MCMB).

[0135] In some embodiments, a cell exhibiting low impedance growth employs an electrolyte having the following composition: about 0.8 M to about 1.5 M LiPF$_6$ in an organic solvent made up of about 30 wt% to about 70 wt% ethylene carbonate, about 0 wt% to about 20 wt% propylene carbonate, about 0 wt% to about 60 wt% dimethyl carbonate, and about 0 wt% to about 60 wt% ethyl methyl carbonate. The sum of the weight percents of ethylene carbonate and propylene carbonate is between about 30 wt% and about 70 wt% of the total organic solvent, and propylene carbonate represents about 30 wt% or less of this sum. In particular embodiments, the cell exhibiting low impedance growth and employing this electrolyte composition includes a cathode material having an olivine structure and a formula LiMPO$_4$, where M is one or more transition metals, and the material is doped or undoped at the lithium or M site. In at least some instances, the cell includes a carbonaceous anode material, for example, a graphitic material such as mesocarbon microbeads (MCMB).

[0136] In certain embodiments, a cell exhibiting low impedance growth employs an electrolyte having the following composition: about 0.8 M to about 1.5 M LiPF$_6$ in an organic solvent made up of about 30 wt% to about 70 wt% ethylene carbonate, about 0 wt% to about 20 wt% propylene carbonate, and about 0 wt% to about 70 wt% dimethyl carbonate and/or diethyl carbonate and/or ethyl methyl carbonate. The sum of the weight percents of ethylene carbonate and propylene carbonate is between about 30 wt% and about 70 wt% of the total organic solvent, and propylene carbonate represents about 30 wt% or less of this sum. In particular embodiments, the cell exhibiting low impedance growth and employing this electrolyte composition includes a cathode material having an olivine structure and a formula LiMPO$_4$, where M is one or more transition metals, and the material is doped or undoped at the lithium or M site. In at least some instances, the cell includes a carbonaceous anode material, for example, a graphitic material such as mesocarbon microbeads (MCMB).

[0137] In certain embodiments, a cell exhibiting low impedance growth employs an electrolyte having the following composition: about 1.0 M to about 1.3 M LiPF$_6$ in
an organic solvent made up of about 30 wt% to about 50 wt% ethylene carbonate, about 10 wt% to about 20 wt% propylene carbonate, about 20 wt% to about 35 wt% dimethyl carbonate, about 20 wt% to about 30 wt% ethyl methyl carbonate, and about 1 wt% to about 3 wt% vinylene carbonate. In particular embodiments, the cell exhibiting low impedance growth and employing this electrolyte composition includes a cathode material having an olivine structure and a formula Li$_2$MPO$_4$, where M is one or more transition metals, and the material is doped or undoped at the lithium or M site. In at least some instances, the cell includes a carbonaceous anode material, for example, a graphitic material such as mesocarbon microbeads (MCMB).

[0138] A solid or gel electrolyte may also be employed. The electrolyte may be an inorganic solid electrolyte, e.g., LiN or Lil, or a high molecular weight solid electrolyte, such as a gel, provided that the materials exhibits lithium conductivity. Exemplary high molecular weight compounds include poly(ethylene oxide), poly(methacrylate) ester based compounds, or an acrylate-based polymer, and the like.

[0139] As the lithium salt, at least one compound from among LiClO$_4$, LiPF$_6$, LiBF$_4$, LiSO$_3$CF$_3$, LiN(S0$_2$CF$_3$)$_2$, LiN(S0$_2$CF$_2$CF$_3$)$_2$, LiAsF$_6$, lithium bis(trifluoromethylsulfonimide) (LiTFMSI), lithium bis(oxalatoborate) (LiBOB), lithium bis(pentafluoroethylsulfonyl)imide (LiBETI) and the like are used. In some embodiments, the lithium salt is at a concentration from about 0.5 to about 1.5 M, for example, in certain embodiments from about 1.0 to about 1.3 M.

[0140] In certain embodiments, the above described positive electrode is brought into intimate contact with the negative electrode through the separator layers, which are then spirally wound a number of times around a small-diameter mandrel to form the jelly-roll electrode-separator assembly. Next, the jelly-roll structure is inserted into a battery can, for example, made of nickel-plated steel or aluminum, current collector tabs are spot-welded to the battery can and can header, which is preferably equipped with a variety of safety features, such as positive-temperature coefficient elements, pressure burst disks, etc. Alternatively, uncoated regions can be created along the edge of the electrode, thereby exposing bare metal foil. One or preferably more metal foil strips or tabs, between about 0.4cm and about 0.8cm wide, can be attached to these bare regions using an ultrasonic welder. These tabs can then be attached to the can or header using an ultrasonic or spot (resistance) welder. The nonaqueous electrolyte, for example, including a solution of a lithium salt in a mixture of carbonate esters, is injected into the battery can, the can header is sealed to
the battery can using a crimp seal or laser weld. An alternative cell design is
described in U.S. Patent No. 7927732, filed on September 5, 2006, entitled "Battery
Cell Design and Method of Its Construction," which is incorporated in its entirety by
reference herein. Other non-limiting examples of cell types include pouch sealing
type prismatic and Aluminum can or the other metal can type prismatic cells. In some
specific embodiments, the cell is a pouch material sealing type of pouch cells.

[0141] According to one or more embodiments, a Li-ion battery contains an
optionally doped lithium transition metal phosphate positive electrode, a highly
microporous electronically insulating separator layer, a graphitized-carbon negative
electrode, and a multicomponent liquid organic electrolyte solution in which a lithium
salt is dissolved at a concentration from about 0.5 to about 1.5 M. Both the positive
and negative electrodes have high surface area and high pore volume. In order to
reduce the chance of lithium plating at the anode, the lithium capacity of the negative
electrode is higher than that of the positive electrode. The battery is capable of being
charged and discharged at a very high rate, due to having the above described relative
electrode resistances, which is accomplished by the selection of appropriate active
materials, e.g., composition, particle size, porosity, surface area, pore volume, etc.,
and by the addition of appropriate amounts of conductive diluents such as carbon to
the positive or negative electrode. The types, amounts, and methods of adding such
conductive diluents are readily determined by methods well-known to those skilled in
the art.

[0142] In other embodiments, a process for the synthesis of a lithium electroactive
metal phosphate includes the milling and heating a mixture of materials including a
lithium source, an iron phosphate and one or more additional dopant metal sources
under a reducing atmosphere. Exemplary starting materials include, but are not
limited to, lithium carbonate, ferric phosphate, and vanadium oxide. The mixtures are
heated at atmospheric pressures under a reducing atmosphere to temperatures of
approximately 550-700°C, followed by cooling to room temperature, typically under
inert atmospheres. Further details regarding the composition and preparation of these
compounds are found in United States Patent No. 7,282,301, which is incorporated
herein in its entirety by reference.

[0143] In other embodiments, a process for the synthesis of a lithium electroactive
metal phosphate includes the a water-based milling process, wherein starting
materials, such as lithium carbonate, hydrated iron phosphate, hydrated manganese
phosphate, lithium dihydrogen phosphate, hydrated cobalt oxalate, hydrated nickel oxalate, and ammonium metavanadate are mixed with water soluble vinyl based copolymers or sugar precursors for milling and subsequent drying. After drying, the power can be heated under desired temperature ramp-up conditions up to about 700 °C, followed by cooling to room temperature.

[0144] The positive electrode (cathode) is manufactured by applying a semi-liquid paste containing the cathode active compound and conductive additive homogeneously dispersed in a solution of a polymer binder in an appropriate casting solvent to both sides of a current collector foil or grid and drying the applied positive electrode composition. A metallic substrate such as aluminum foil or expanded metal grid is used as the current collector. To improve the adhesion of the active layer to the current collector, an adhesion layer, e.g., thin carbon polymer intercoating, may be applied. The dried layers are calendared to provide layers of uniform thickness and density. The binder used in the electrode may be any suitable binder used as binders for non-aqueous electrolyte cells.

[0145] The positive electrode active material can be incorporated into any battery shape. In fact, various different shapes and sizes, such as cylindrical (jelly roll), square, rectangular (prismatic) coin, button or the like may be used.

Prophetic Example 1: Producing LiCoO\(_2\) or LiNiO\(_2\) coated with Na\(_{0.44}\)MnO\(_2\)

[0146] The precursors, consisting of a sodium source such as Na\(_3\)C\(_0\)_3 and a manganese source such as MnC\(_0\)_3, are dissolved in the stoichiometric ratio in water, then mixed with LiCoO\(_2\) or LiNiO\(_2\), which are insoluble powders. The resulting slurry is dried to leave a coating of the precursors on the surface of the lithium metal oxide. This precursor mix is then heated to about 800 °C for a time sufficient to produce the desired orthorhombic Na\(_{0.44}\)MnO\(_2\) phase on the particle of LiCoO\(_2\) or LiNiO\(_2\).

Example 1: Producing Mixed Positive Electroactive Material

[0147] Lithium iron phosphate (LFP) material as disclosed in U.S. Patent No. 7,338,734) or lithium iron manganese phosphate (LFMP) as described in United States Patent Serial No. 12/868,530, were used as the alkali transition metal polyanion compound for the oxide blend cathode. Lithium iron phosphate (Nano phosphate
powder) or lithium iron manganese phosphate powders were mixed together with lithium transition metal oxide cathode powders such as lithium nickel aluminum oxide (NCA), lithium nickel cobalt, manganese oxide (NCM), spinel lithium manganese oxide (LMO), and LLC (Layered oxide cathode) for use in the cathode. Graphite based anode was prepared and polyolefim type separator or ceramic-coated separator can be used to assemble the cell. Typical liquid electrolyte as described herein were used. After the battery is assembled, the cell was run from 2.4V to 4.2V range for cycling and operation.

DSC spectrum protocol: 10 min rest, followed by 3 cycles (C/10 charge to 4.3V, CV hold at 4.3V to C/50, 10 min rest, C/10 discharge to 2.0V, 10 min rest), followed by C/10 charge to 4.3V, CV hold at 4.3V to C/50, followed by 5 hr rest. For CC charge and CC discharge, data was recorded every 10 min or every 0.05V (voltage difference) (Maximum step time allowed for CC charge = 20 hr). For CV hold, data was recorded every 10 min or every C/25 (current difference) (Maximum step time allowed for CV hold = 5 hr). For 10 min rest, data was recorded every 2 min or every 0.05V. For 5 hr rest, data was recorded every 10 min or every 0.05V. Final capacity in (mAh/g) was calculated using the last charge capacity divided by the sample's active area mass.

The mixed positive electroactive materials exhibited high energy density and better abuse tolerance performances. Higher energy density was obtained with better cell safety (see the coin cell data for the cell energy in Figures 1, 2, and 3, and Tables 1 and 2). Blend cathode of oxide NCM active material shows higher energy than 100% LFP (M1, Mix) cathode cells.

As shown by the DSC data, (Figures 3 and 4), 100% LFP or LFMP cathode do not show the exothermic peak around 260 °C. Surprisingly, 50%> blended NCM cathode also does not show this peak even though 100% NCM clearly show this peak around 260 °C. This indicates a improved safety of the cell.

Additionally, as shown in the Figures, there was a smooth discharge voltage profile when using LFMP material in the mixed positive electrode material (See the voltage profile in Figure 2: Purple line). In comparison, LFP oxide blend has a bump in the voltage profile (See purple line in Figure 1).

Table 1. Capacity and efficiency of M1 (LiFeP0₄ Nanophosphate) blends with NCM (oxide cathode).

<table>
<thead>
<tr>
<th>Cathode</th>
<th>FCC (mAh/g)</th>
<th>Reversible (mAh/g)</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1 100%</td>
<td>152</td>
<td>150</td>
<td>0.984</td>
</tr>
</tbody>
</table>
Table 2. Capacity and efficiency of M1 (LiMn$_{0.5}$Fe$_{0.5}$PO$_4$ Nanophosphate®) blends with NCM (oxide cathode).

<table>
<thead>
<tr>
<th>Cathode</th>
<th>FCC (mAH/g)</th>
<th>Reversible (mAh/g)</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix 50%, NCM 50%</td>
<td>170</td>
<td>155</td>
<td>0.901</td>
</tr>
<tr>
<td>Mix 30%, NCM 70%</td>
<td>177</td>
<td>157</td>
<td>0.892</td>
</tr>
<tr>
<td>NCM 100%</td>
<td>186</td>
<td>162</td>
<td>0.868</td>
</tr>
</tbody>
</table>

[0152] Upon review of the description and embodiments described above, those skilled in the art will understand that modifications and equivalent substitutions may be performed in carrying out the invention without departing from the essence of the invention. Thus, the invention is not meant to be limiting by the embodiments described explicitly above.
Claims

1. A positive electroactive material, comprising:
   an oxygen-gettering compound capable of trapping oxygen; and
   an ion-storage compound.

2. The positive electroactive material of claim 1, wherein the oxygen-gettering compound is an ion-storage material.

3. The positive electroactive material of claim 2, wherein the oxygen-gettering compound is orthorhombic alkali metal manganese oxide coated on the ion-storage compound.

4. The positive electroactive material of claim 3, wherein the oxygen-gettering compound coating covers at least 50%, 60%, 70%, 80%, 90%, or 100% of the surface of the ion-storage compound.

5. The positive electroactive material of claim 3, wherein the oxygen-gettering compound coating has at least 20%, 30%, 40%, 50%, 60%, 70%, or 80% porosity.

6. The positive electroactive material of claim 3, wherein the oxygen-gettering compound has a formula of $\text{Li}_x\text{Na}_y\text{Mn}_4\text{O}_{12}$, wherein $0 \leq x \leq 0.75$, $0 \leq y \leq 0.75$, and $0.2 \leq x + y \leq 0.75$.

7. The positive electroactive material of claim 6, wherein the oxygen-gettering compound is $\text{Na}_0.4\text{Mn}_0.4$.

8. The positive electroactive material of claim 6, wherein the oxygen-gettering compound is $\text{Li}_0.4\text{Mn}_0.4$.

9. The positive electroactive material of claim 1, wherein the oxygen-gettering compound comprises one or more transition metal oxide, wherein the transition metal is selected from the group consisting of Fe, Mn, Co, Ni, Ti, V, and a combination thereof.

10. The positive electroactive material of claim 9, wherein the oxygen-gettering compound is one or more compounds selected from the group consisting of FeO,
MnO, CoO, NiO, Fe₃O₄, Mn₃O₄, Co₃O₄, Ni₃O₄, and vanadium oxide wherein the
vanadium average valence is less than 5⁺.

11. The positive electroactive material of claim 2, wherein the oxygen-gettering
compound is nanoscale alkali metal polyanion compound having a composition of
Aₓ(M¹ₓM²ₓ)ₙ(XD₄)ₙ, Aₓ(M¹ₓM²ₓ)ₙ(2DXD₄)ₙ, or Aₓ(M¹ₓM²ₓ)ₙ(X₂D₇)ₙ and a
specific surface area of at least 5 m²/g, wherein A is at least one of an alkali metal or
hydrogen, M¹ is a first-row transition metal, X is at least one of phosphorus, sulfur,
arrows, boron, aluminum, silicon, vanadium, molybdenum and tungsten, M² is one or
more metal selected form the group consisting of Group IIA, IIIA, IVA, VA, VIA,
VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, VIB metal and a combination thereof. D is at
least one of oxygen, 10 nitrogen, carbon, or a halogen, 0 ≤ a ≤ 0.1, and x is equal to or
greater than 0, y and z are greater than 0 and have values such that x, plus y(l-a) times
a formal valence or valences of M¹, plus ya times a formal valence or valence of M²,
is equal to z times a formal valence of the XD₄, X₂D₇, or DXD₄ group.

12. The positive electrode active material of claim 11, wherein the nanoscale
alkali metal polyanion compound is LiFePO₄.

13. The positive electrode active material of claim 11, wherein the nanoscale
alkali metal polyanion compound comprises one or more electroactive materials
selected from the group consisting of

Lii.o₂5Mn.0₄₀₀₅Feo.₅₈oCoo.₀₂₀₂₀P₀₄₄,
Lii.o₂5Mno.₄₅₀₀₅Feo.₅₉oCoo.₀₂₀₂₀P₀₄₄,
Lii.o₂5Mno.₅₀₀Feo.₄₈oCoo.₀₂₀₀₁oNio.₀ioP₀₄₄,
Lii.₀₅₀Mno.₄₅₀Feo.₅₀₀Coo.₀ioNio.₀ioVo.₀io(P₀₄₄)io.₀₂₅₄,
Lii.₀₄₀Mno.₄₀₀Feo.₅₆oCoo.₀ioNio.₀ioVo.₀io(P₀₄₄)io.₀₁₅₄,
Lii.₀₄₀Mno.₄₅₀Feo.₅₁₀Coo.₀ioNio.₀ioVo.₀io(P₀₄₄)io.₀₁₅₄,
Lii.₀₂₀Mno.₄₅₀Feo.₅₂₀Coo.₀ioNio.₀ioVo.₀io(P₀₄₄)io.₀₁₅₄,
Lii.₀₄₀Mno.₄₅₀Feo.₅₁₀Coo.₀ioNio.₀ioVo.₀io(P₀₄₄)io.₀₁₅₄,
Lii.₀₁₀Mno.₅₀₀Feo.₅₁₀Coo.₀ioNio.₀ioVo.₀io(P₀₄₄)io.₀₁₅₄,
14. The positive electrode active material of claim 11, wherein the nanoscale alkali metal polyanion compound is one or more compounds selected from the group consisting of LiCoPO$_4$, LiMnPC, Li$_3$V$_2$(PO$_4$)$_3$, LiVPO$_4$F, and mixed transition metal phosphate.

15. The positive electrode active material of claim 1, wherein the ion-storage compound is one or more compounds selected from the group consisting of lithium cobalt oxide and lithium nickel oxide.

16. The positive electrode active material of claim 15, wherein the lithium cobalt oxide or lithium nickel oxide further comprises one or more transition metal selected from the group consisting of Group IIA, IIB, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, VIB metals and a combination thereof.

17. The positive electrode active material of claim 15, wherein the lithium cobalt oxide further comprises a metal selected from the group consisting of Al, Mg, and a combination thereof.

18. The positive electrode active material of claim 15, wherein the lithium nickel oxide further comprises a metal selected from the group consisting of Co, Mn, Al, Mg, and a combination thereof.

19. The positive electrode active material of claim 15, wherein the lithium nickel oxide or the lithium nickel oxide has a nonuniform chemical composition across its particle radius.

20. A lithium ion battery comprising a positive electrode comprising the positive electrode active material of claim 1.
Figure 2

Energy, 0.5C

Potential (V) vs. Sp. Energy (mWh/g)

- M1x 100%, NCM 0%
- M1x 50%, NCM 50%
- M1 0%, NCM 100%
Figure 3

Heat Capacity Comparison of Cathode Material

- NCM oxide 100%
- LFP:NCM Oxide 50:50
- LFP 100%

Temperature (°C) vs Heat Flow (mW)
FIG. 5

HEAT CAPACITY COMPARISON OF CATHODE MATERIALS

- - - - 100% OXIDE
- - - - LFP: OXIDE BLEND
- - - - 100% LFP

HEAT FLOW (mW)

TEMPERATURE (°C)

0  50  100  150  200  250  300  350  400
HEAT CAPACITY COMPARISON OF CATHODE MATERIALS

--- 100% OXIDE
-- M1x: OXIDE BLEND
- 100% M1x

FIG. 6
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

**IPC(8) - H01 M 4/50 (2012.01)**  
**USPC - 429/224**  

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)  
**USPC - 429/224**  
**IPC(8) - H01 M 4/50 (2012.01)**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
**USPC: 429/231 :1. 231.95, 218.1, 219, 222, 223, 224, 231.6: 231.3, 221: 252/182.1**  
**IPC(8): H01 M 4/50 (2012.01)**  see keywords below

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatBase, Google Patents, Google Scholar. Search terms used: positive electroactive material oxygen gettering ion storage orthorhombic alkali metal manganese oxide lithium cobalt nickel transition polyaniion iron phosphate secondary phase olivine nanoscale nanoparticle trapping oxygen physical absorption chemical reaction precursor nonuniform co

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>Y</td>
<td>US 2008/0070122 A1 (Park et al.), 20 March 2008 (20.03.2008), entire document, especially para [0005], [0006], [0010], [0011], [0013], [0024], [0029]-[0031], [0039], claim 1</td>
<td>2-8, 10-14, 19</td>
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<tr>
<td>Y</td>
<td>US 2004/0005265 A1 (Chiang et al.) 08 January 2004 (08.01.2004), para [0010], [0167], [0064], [0048]</td>
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<td>US 2005/0191554 A1 (Soga) 01 September 2005 (01.09.2005), para [0051], [0462], [0467]</td>
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</table>

Further documents are listed in the continuation of Box C.

**Date of the actual completion of the international search**  
28 November 2012 (28.11.2012)

**Date of mailing of the international search report**  
24 DEC 2012

Name and mailing address of the ISA/US  
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents  
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Facsimile No. 571-273-3204

Form PCT/ISA/2.10 (second sheet) (July 2009)