LMO CATHODE COMPOSITION

The present invention relates to a set of electroactive lithium-rich manganese cathode compositions having a rock salt structure. More specifically the present invention relates to a set of high capacity lithium-rich manganese oxide cathode compositions which can be used as a bulk composition or composite cathode composition in an electrochemical cell.

The performance and cost of lithium ion batteries primarily relies on the composition of the positive electrode (cathode). Currently available lithium-based cathode compositions are graded mainly on their energy density, electrochemical performance and the price of raw materials required to formulate the composition. Manganese would be an ideal sole-transition metal centre for a lithium-based cathode composition, as the abundance of manganese in the Earth's crust is far greater than cobalt and nickel. Although much higher capacities and energy densities can currently be achieved with compositions comprising nickel, cobalt and aluminium, the cost of these metals is far greater. In addition, these nickel, cobalt and aluminium-based composition still suffer with problems of the voltage profile evolving on cycling, costly (because of the inclusion of cobalt and nickel) and show significant stability issues, such as gas loss during cycling. There is a need for a simple, robust and cost-effective lithium-rich composition which delivers parity or better in terms of energy density and performance.

Summary

In a first aspect, the present ~~invention~~disclosure ~~provides~~ refers to a cathode composition for a lithium-ion battery of the general formula: $Li_{1+x}Mn_{1-x}O_2$; wherein the composition is in the form of a single phase having a rock salt crystal structure such that an x-ray diffraction pattern of the composition using a Cu Kα radiation source has an absence of peaks below a 2θ value of 35; and the value of x is greater than 0, and equal to or less than 0.3.

Conventional ordered or layered lithium and manganese-rich compositions ($Li_{1+x}Tm_{1-x}O_2$ where Tm is predominately Mn) have lithium ions sitting in both the alkali and transition metal sites. In addition to the above, x-ray diffraction pattern of these conventional compositions will have a peak at a 2θ value of 18. However, in the present ~~invention~~disclosure the x-ray diffraction pattern of the cathode composition has an absence of a peak at a 2θ value of 18. In other words, the single phase crystal structure of the present ~~invention~~disclosure is absent of any spinel or layered structures, and is considered purely as a single phase rock salt crystal structure.

The single phase crystal structure does not exhibit either a R3(bar)m and/or a C2/m space group. Where lithium and cobalt ions fully occupy alternating layers within the structure.

It has been found that a cathode composition with an improved stability and capacity performance can be achieved by the lithium-rich manganese oxide compositions as defined above. The cathode compositions of the present ~~invention~~disclosure also exhibit improved electrochemical cycling when compared to the traditional layered lithium manganese oxide structures of the prior art.

In particular, the compositions are provided as a single phase rock salt crystal structure (i.e. face centred cubic lattice with the Fm3(bar)m space group). The specifically identified compounds can be manufactured reproducibly at a high rate using conventional ball-milling techniques by mixing $LiMnO_2$ and Li_2MnO_3 precursors in different proportions. In addition, other conventional techniques can be used to manufacture a thin film of the cathode composition, such as PVD techniques including, but not limited to sputtering and sublimation/evaporation of target material.

In specific examples, the value of x may be equal to or greater than 0.1. The value of x may be equal to or greater than 0.17. The value of x may be equal to or greater than 0.2. The value of x may be equal to or greater than 0.2 and equal to or less than 0.3. The value of x may be equal to or greater than 0.1 and equal to or less than 0.2. The value of x may be equal to 0.2.

In a particular example, x is equal to 0.2. This particular composition is thus $Li_{1.2}Mn_{0.8}O_2$. This particular composition has demonstrated an improved capacity for charge, and stability over a number of cycles.

The composition may be expressed as the general formula: $(a)LiMnO_2 \bullet (1\text{-}a)Li_2MnO3$; wherein two precursors are provided in proportions defined by a, and a has a value in the range greater than 0 and less than 1; and the precursors are mixed by a ball milling process to provide a bulk composition with a rock salt structure. In examples a has a value in the range greater than 0.05 and less than 0.95.

In specific examples, the value of a may be equal or greater than 0.15 and equal to or less than 0.7. The value of a may be equal to or greater than 0.15 and equal to or less than 0.4. As shown in the Examples of the present ~~invention~~disclosure below, the cathode composition may be selected from one of 0.7LiMnO2·0.3Li2MnO3; 0.6LiMnO2·0.4Li2MnO3; 0.5LiMnO2·0.5Li2MnO3; 0.4LiMnO2·0.6Li2MnO3; 0.3LiMnO2·0.7Li2MnO3; 0.2LiMnO2·0.8Li2MnO3; 0.15LiMnO2·0.85Li2MnO3; $0.4LiMnO_2 \cdot 0.6Li_2MnO_3$.

In a second ~~aspect~~example, the present ~~invention~~disclosure provides a cathode (or more generally an electrode). The cathode can be made with the cathode composition as a thin film as part of a PVD technique, or alternatively the cathode can be made using the cathode composition as cathode active in a composite electrode.

In a second aspect, the present disclosure refers to an electrode comprising the cathode composition as disclosed herein.

In examples, a composite cathode may be made from a cathode composition of the present ~~invention~~disclosure comprising 3 fractions. The first is the cathode composition of the present ~~invention~~disclosure as previously described (in a variety of mass percentages from 60-98%, however, typically 70, 75, 80, 90 and 95%). The second fraction of the composite cathode comprises electroactive additives such as carbon, for example, Super P and Carbon black, which comprises 60-90 % of the mass fraction remaining excluding the first fraction. The third fraction is typically a polymeric binder such as PVDF, PTFE, NaCMC and NaAlginate. In some case additional fractions maybe included and the overall percentages may change. The overall electrochemical performance of the composite cathode can be improved by the introduction of electroactive additives, and the structural properties of the resulting composite cathode can also be improved by adding material that improves cohesion of the cathode composition and adhesion of the material to particular substrates.

In a third ~~aspect~~example, the present ~~invention~~disclosure provides an electrochemical cell comprising a cathode with a cathode composition according to the description above, an electrolyte and an anode. The electrolyte may, for example, take the form of a liquid or solid, such as a gel or a ceramic.

In a third aspect, the present disclosure refers to an electrochemical cell comprising a cathode as disclosed herein, an electrolyte, and an anode.

In order that the present invention may be more readily understood, an embodiment of the invention will now be described, by way of example, with reference to the accompanying Figures, in which: