LMO CATHODE COMPOSITIONS

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 bulk or composite cathode material 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 material 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; 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. This is compared to an ideal $LiCoO_2$ R3/m type structure, 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 cathode comprising cathode material of the present ~~invention~~disclosure comprises 3 fractions. The first is the compound 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 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 cathode can be improved by the introduction of electroactive additives, and the structural properties of the resulting 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, the present ~~invention~~disclosure ~~provides~~ refers to an electrochemical cell comprising a cathode ~~according to the description above~~as disclosed herein, 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 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:

Figure 1 shows powder X-ray Diffraction patterns of various Li-Mn-O compounds that exist, with their space groups and lattice parameters;

Figure 2 shows powder X-ray Diffraction patterns of the synthesised materials $Li_{1.2}Mn_{0.8}O_2$ (or $0.4LiMnO_2 \cdot 0.6Li_2MnO_3$) compound in Example 1;

Figures 3a and b shows first cycle galvanostatic load curves for the first cycle of $Li_{1.2}Mn_{0.8}O_2$ and $Li_{1.1}Mn_{0.9}O_2$ at 45ºC at C/10 respectively, and Figures 3c and d show