

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.

In a first aspect, the present invention provides a cathode composition for a lithium-ion battery of the general formula: $\text{Li}_{1+x}\text{Mn}_{1-x}\text{O}_2$; 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 K α 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 ($\text{Li}_{1+x}\text{Tm}_{1-x}\text{O}_2$ 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 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 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 $R\bar{3}m$ 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 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 $Fm\bar{3}m$ 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: $(a)LiMnO_2 \bullet (1-a)Li_2MnO_3$; 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 below, the cathode composition may be selected from one of $0.7\text{LiMnO}_2 \cdot 0.3\text{Li}_2\text{MnO}_3$; $0.6\text{LiMnO}_2 \cdot 0.4\text{Li}_2\text{MnO}_3$; $0.5\text{LiMnO}_2 \cdot 0.5\text{Li}_2\text{MnO}_3$; $0.4\text{LiMnO}_2 \cdot 0.6\text{Li}_2\text{MnO}_3$; $0.3\text{LiMnO}_2 \cdot 0.7\text{Li}_2\text{MnO}_3$; $0.2\text{LiMnO}_2 \cdot 0.8\text{Li}_2\text{MnO}_3$; $0.15\text{LiMnO}_2 \cdot 0.85\text{Li}_2\text{MnO}_3$; $0.4\text{LiMnO}_2 \cdot 0.6\text{Li}_2\text{MnO}_3$.

In a second aspect, the present invention 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 examples, a composite cathode may be made from a cathode composition of the present invention comprising 3 fractions. The first is the cathode composition of the present invention 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, the present invention 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 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 cathode compositions $\text{Li}_{1.2}\text{Mn}_{0.8}\text{O}_2$ (or $0.4\text{LiMnO}_2 \cdot 0.6\text{Li}_2\text{MnO}_3$) compound in Example 1;

Figures 3a and b shows first cycle galvanostatic load curves for the first cycle of $\text{Li}_{1.2}\text{Mn}_{0.8}\text{O}_2$ and $\text{Li}_{1.1}\text{Mn}_{0.9}\text{O}_2$ at 45°C at C/10 respectively, and Figures 3c and d show evolution of the charge and discharge capacity as a function of cycle for $\text{Li}_{1.2}\text{Mn}_{0.8}\text{O}_2$ and $\text{Li}_{1.1}\text{Mn}_{0.9}\text{O}_2$ respectively;

Figure 4 shows preparation of $\text{Li}_{1.2}\text{Mn}_{0.8}\text{O}_2$ with a conventional planetary ball mill at 400 rpm with ZrO_2 balls (upper line) compared to the high energy ball mill with 700 rpm and WC balls (lower line);

Figure 5 shows preparation of $\text{Li}_{1.2}\text{Mn}_{0.8}\text{O}_2$ with starting materials Li_2MnO_3 , Li_2O_2 and Mn_2O_3 (upper line) compared to starting materials Li_2MnO_3 and LiMnO_2 (lower line);

Figure 6 shows Electrochemical data of $\text{Li}_{1.2}\text{Mn}_{0.8}\text{O}_2$ prepared from Li_2MnO_3 , Li_2O_2 and Mn_2O_3 with C/10 charge, and C/5 discharge; and

Figure 7 shows X-ray diffraction patterns of the precursors (lower line), ball milled for 40 min (second to lower line), ball milled for 5 h (second to higher line) and ball milled for 10h (higher line).

The present invention will now be illustrated with reference to the following examples.

Example 1 – Synthesis of the Lithium Rich Manganese Oxide Cathode Compositions

Material comprising LiMnO_2 and Li_2MnO_3 precursors were mixed in different molar proportions in accordance with Table 1 using WC jars and balls. All materials were handled at all times under inert atmosphere (in an Argon filled glovebox) and never exposed to ambient atmosphere, ie protected against moisture and oxygen at all times. A planetary ball milling (Fritsch Planetary Micro Mill PULVERISETTE 7 premium line which can deliver energy

which are approximately 150 % above that which can be achieved through conventional milling) was employed and the milling was performed at a speed rate of 700 rpm for 10 minutes, following 30 minutes break. Phase purity was assessed after repeating this milling and resting cycle for at least 30 times, i.e. for a total milling time of at least 5 hours. However, it is possible that less milling times are necessary to achieve phase purity. The phase transformation is assessed by X-ray diffraction. If the phase transformation is not complete, the same program is repeated, and so on.

LiMnO ₂	Li ₂ MnO ₃	Resulting Composition	Stoichiometry
0.7	0.3	0.7LiMnO ₂ ·0.3Li ₂ MnO ₃	Li _{1.1} Mn _{0.9} O ₂
0.6	0.4	0.6LiMnO ₂ ·0.4Li ₂ MnO ₃	Li _{1.13} Mn _{0.87} O ₂
0.5	0.5	0.5LiMnO ₂ ·0.5Li ₂ MnO ₃	Li _{1.17} Mn _{0.83} O ₂
0.4	0.6	0.4LiMnO ₂ ·0.6Li ₂ MnO ₃	Li _{1.2} Mn _{0.8} O ₂
0.3	0.7	0.3LiMnO ₂ ·0.7Li ₂ MnO ₃	Li _{1.23} Mn _{0.77} O ₂
0.2	0.8	0.2LiMnO ₂ ·0.8Li ₂ MnO ₃	Li _{1.27} Mn _{0.73} O ₂
0.15	0.85	0.15LiMnO ₂ ·0.85Li ₂ MnO ₃	Li _{1.28} Mn _{0.72} O ₂

Alternate starting materials can be used here including but not limited to Mn₂O₃, MnO₂, Li₂O, Li₂O₂, Mn₂O₄, LiMn₂O₄. An addition route for the preparation of Li_{1.2}Mn_{0.8}O₂ was tried with Li₂O, Mn₂O₃ and MnO₂ which resulted in the same phase as shown in Figure 2.

Alternatively a conventional planetary ball mill was used, the Retsch PM 100 mill. Here both mills were used to prepare Li_{1.2}Mn_{0.8}O₂ at a milling speed of 400 rpm with ZrO₂ balls. Here it can be clearly understood that the lower density of the milling media and the rotation rate will result in significantly lower energy collisions. The conditions employed by both mills were successful in obtaining the disordered rock salt phase (Fig 4) with a composition of Li_{1.2}Mn_{0.8}O₂ indicating that preparation at high energies is not the only route to cathode composition production.

Alternatively, mechanofusion or conventional Physical Vapour Deposition techniques can be considered to prepare these cathode compositions.

Example 2 – Structural Analysis and Characterisation of the Lithium Rich Manganese Oxide Cathode Compositions

The materials according to Example 1 were examined with Powder X-Ray Diffraction (PXRD) which was carried out utilising a Panalytical Aeris benchtop XRD with a Cu K α Radiation. The range of measurement was 10-90 ° 2 theta.

Figure 2 shows a representative Powder X-ray Diffraction pattern of the synthesised compositions. These are characteristic of a cation disordered rock salt structure. All of the patterns appear to show the broad major peaks consistent with a face centred cubic lattice with the Fm3(bar)m space group, as shown in Figure 2. It should be noted that broad peaks are displayed due to the ball milling process which without wishing to be bound by theory results in a cathode composition with a small crystallite size. There is no evidence for the presence of the layered precursors which had a layered LiMnO₂ or Li₂MnO₃ structures with the space group R3(bar)m or C2/m, which would indicate that the ball-milling synthesis has converted the material of the precursors into the cathode composition of the present inventions. No presence of extra peaks due to impurities was observed. The example XRD in Figure 2 shown for Li_{1.2}Mn_{0.8}O₂ was indicative of all samples with a slight shifting of the peak positions in accordance with changes to the bulk lattice parameters as a result of the changing composition. It should also be noted that no crystalline phases for other common Li_pMn_rO_q (database patterns shown in Figure 1 for comparison) can be seen in the final product. Figure 7 also shows how the reaction proceeds as the initial precursors are slowly removed on continual milling as the disordered rock salt phase becomes the dominant feature.

Example 3 – Electrochemical Analysis of the Lithium Rich Manganese Oxide Cathode Compositions

The cathode compositions according to Example 1 were characterised electrochemically through galvanostatic cycling performed with a BioLogic BCS series potentiostats. All the samples were assembled as powdered cathodes into Swagelok type cells with a metallic lithium counter/ reference electrode and cycled between 2 and 4.8 V vs. Li⁺/Li at a current rate of C/10 as defined by a capacity of 300 mAh/g. The electrolyte employed was LP40 (a 1M solution of LiPF₆ in 1:1 w/w ratio of EC;DEC).

Figures 3a-d shows the potential curves during the charge and subsequent discharge of the first cycle for compositions $0.7\text{LiMnO}_2 \cdot 0.3\text{Li}_2\text{MnO}_3$ and $0.4\text{LiMnO}_2 \cdot 0.6\text{Li}_2\text{MnO}_3$ according to Example 1. Both samples present high discharge capacities above 200 mAh/g at C/10. The values of the first discharge capacities for all materials which have been prepared are detailed in the Table below.

The $0.4\text{LiMnO}_2 \cdot 0.6\text{Li}_2\text{MnO}_3$ cathode composition exhibits a sloping region at the beginning of charge, until ca. 4 V vs Li⁺/Li and a high potential plateau centred at around 4.2 V vs Li⁺/Li that appears to be irreversible on the first discharge. This general feature could be considered consistent for all the prepared materials with Li > 1.1 per formula unit with the length of the plateau correlating to the amount of lithium in the material: the more lithium is present the longer the plateau.

The $0.7\text{LiMnO}_2 \cdot 0.3\text{Li}_2\text{MnO}_3$ composition exhibits a different first charge. A long sloping region is observed up to the high potential cut-off of 4.8 V vs Li⁺/Li. No potential plateau is observed, less irreversibility on discharge is seen and therefore a higher first cycle coulombic efficiency.

	Phase purity	First charge capacity (mAh/g)	First discharge capacity (mAh/g)	Coulombic efficiency at the first cycle
$0.7\text{LiMnO}_2 \cdot 0.3\text{Li}_2\text{MnO}_3$	No crystalline phase detectable except rock-salt structure (Fm3(bar)m)	230	209	90.8%
$0.6\text{LiMnO}_2 \cdot 0.4\text{Li}_2\text{MnO}_3$	No crystalline phase detectable except rock-salt structure (Fm3(bar)m)	279.5	249.6	89.3%
$0.5\text{LiMnO}_2 \cdot 0.5\text{Li}_2\text{MnO}_3$	No crystalline phase detectable except rock-salt structure (Fm3(bar)m)	281	250	88.9%
$0.4\text{LiMnO}_2 \cdot 0.6\text{Li}_2\text{MnO}_3$	No crystalline phase detectable except rock-salt structure (Fm3(bar)m)	315.9	245.3	77.7%
$0.3\text{LiMnO}_2 \cdot 0.7\text{Li}_2\text{MnO}_3$	No crystalline phase detectable except rock-salt structure (Fm3(bar)m)	317.8	264	83.1%

0.2LiMnO ₂ ·0.8Li ₂ MnO ₃	No crystalline phase detectable except rock-salt structure (Fm3(bar)m)	346.2	239.6	69.2
0.15LiMnO ₂ ·0.85Li ₂ MnO ₃	No crystalline phase detectable except rock-salt structure (Fm3(bar)m)	376.9	242.9	64.4%