Quality control of $Li_{1+\delta}Mn_{2-\delta}O_4$ spinels with their impurity phases by Jaeger and Vetter titration

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Abstract

Powders of lithium manganese oxide phases are synthesised and characterised for possible application in a Li-ion battery. A modified phase diagram on the basis of the manganese oxidation state and content is used to interpret the results. X-ray diffraction, flame atomic absorption spectroscopy, and Jaeger and Vetter titration are performed in order to classify the synthesised powders. The experiments reveal powders of $Li_{1+\delta}Mn_{2-\delta}O_4$ ($0 < \delta < 0.2$, i.e. $0 < Li/Mn < 0.65$), with a spinel structure. At higher Li/Mn ratios mixtures of $Li_{1.2}Mn_{1.8}O_4$ and Li_2MnO_3 are formed. Spinels with small δ-values are favoured since they are more stable than the pure $LiMn_2O_4$, but they have still acceptable capacity. Also, aluminium-doped spinel materials with the composition $Li_{1+\delta}Al_nMn_{2-\delta-n}O_4$ ($0 < n < 0.3$, $\delta = 0.0645$) are synthesised and characterised. However, no improvement in terms of capacity is found. © 1997 Elsevier Science S.A.

Keywords: Lithium manganese oxides; Spinels; Quality control

1. Introduction

Lithium manganese oxide spinels can be synthesised in a number of stable stoichiometries. Among them, $LiMn_2O_4$ is the best known. On extraction of lithium, either chemically [1] or electrochemically [2], the host spinel lattice remains intact. In addition to this well-known stoichiometry of $LiMn_2O_4$, spinels with stoichiometry of $Li_{1+\delta}Mn_{2-\delta}O_4$ have been reported [3,4] with δ ranging from 0 to 1/3, hereafter called δ-spinels. Consequently, the manganese in the latter spinels has a higher oxidation state than in $LiMn_2O_4$, with the highest (4+) found for $Li_{4/3}Mn_{5/3}O_4(Li_4Mn_5O_{12})$. Since only Mn^{3+} is able to contribute to the lithium extraction, the increase in Mn^{4+} is highly undesirable with respect to battery operation. Often, powders of δ-spinels were detected as single phase [3], but impurities such as Li_2MnO_3 or α-Mn_2O_3 could be present [5]. Both impurities are known to be inert towards lithium extraction and/or insertion.

We studied the consequences for the relative capacity of powders with various compositions, single phased or dual phased. In addition, examples are given for aluminium-doped spinels $Li_{1+\delta}Al_nMn_{2-\delta-n}O_4$, with n up to 0.3.

2. Experimental

Mixtures of manganese acetate tetrahydrate ($Mn(CH_3COO)_2 \cdot 4H_2O$) and an appropriate amount of lithium hydroxide monohydrate ($LiOH \cdot H_2O$) were used to form the lithium manganese compounds [5]. Calcination was performed at 600 °C. Aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) was used in order to form the doped materials. The materials were characterized by X-ray diffraction (XRD) and flame atomic adsorption spectroscopy (AAS). Furthermore, the powders were analysed by the Jaeger and Vetter titration method: about 30 mg of powder is dissolved in 20 ml 1 M iron(II) sulfate containing 1 M sulfuric acid. The remaining Fe^{2+} is titrated with potassium permanganate ($KMnO_4$) to the equivalence point. After saturating the remaining solution with sodium pyrophosphate, the titration is resumed with $KMnO_4$ to determine the total amount of manganese present. In order to measure the utilisation of the materials, test cells were prepared with the following sequence

$$Li(foil)/PC, DME, LiClO_4/(aLi_{1+\delta}Al_nMn_{2-\delta-n}O_4 \\ + bLi_2MnO_3) \quad (1)$$
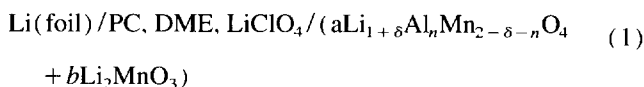
with $0.8 < a < 1$, $0 < b < 0.2$, $0 < n < 0.3$, and $0 < \delta < 0.2$.

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3. Results and discussions

The lattice parameters as derived by XRD of powders with $0.5 < Li/Mn < 0.65$ agree quite well with the reported values [3]. However, the lattice parameters of powders with $0.65 < Li/Mn < 0.8$ are too large, indicating the presence of $Li_{1+\delta}Mn_{2-\delta}O_4$ with lower δ values than expected by means of the Li/Mn input concentrations. This deviation arises from the formation of the impurity phase Li_2MnO_3, which is seen in the XRD patterns. It is concluded that at 600 °C and a ratio above $Li/Mn = 2/3$, formation of the impurity of Li_2MnO_3 favours the reaction, and, hence, the materials that can be expected are $Li_{1.2}Mn_{1.8}O_4$ compensated by Li_2MnO_3 on the basis of the input Li/Mn ratio. This is also seen by the neutron diffraction method [6], and will be shown by infra red spectroscopy in a forthcoming paper [7].

The calculations of the theoretical capacities are given in Fig. 1. It appears that the formation of the single phase δ-spinels $Li_{1+\delta}Mn_{2-\delta}O_4$ results in a dramatic reduction of the relative capacity, even at small excess lithium (line A in Fig. 1). However, it is often reported that small amounts of excess lithium contribute to the stabilisation of the spinel material towards the electrolyte during operation of the cell. Therefore, in order to prevent the formation of high δ-values in the δ-spinel, it would be reasonable to start with an Li/Mn precursor composition slightly higher than 0.5. Fig. 1 also contains theoretical lines for $Li_xMn_2O_4$ (line B), $LiMn_2O_4 + \alpha$-Mn_2O_3 (line C), $LiMn_2O_4 + Li_2MnO_3$ (line D), $Li_{1.2}Mn_{1.8}O_4 + Li_2MnO_3$ (line E), and $Li_{1-\delta}Mn_{2-2\delta}O_4$ (line F). The utilisation of the synthesised lithium manganese oxide compounds as a function of the Li/Mn ratio is also given in Fig. 1. It is seen that the maximum capacity observed is found at an Li/Mn ratio of 0.5. A clear decrease is observed when going to higher Li/Mn ratios, which was expected according to the theoretical values as shown in the figure. According to the theoretical line of the δ-spinel, it appears that up to $Li/Mn = 2/3$ the utilisation agrees to about 80% of the theoretical value (the dotted line). However, above $Li/Mn = 2/3$ the utilisation in terms of relative capacity towards the expected value increases, indicating that the powders contain Li_2MnO_3. Hence, in terms of capacity it seems
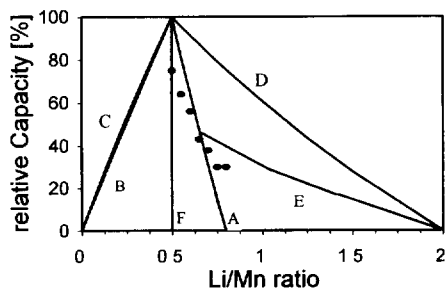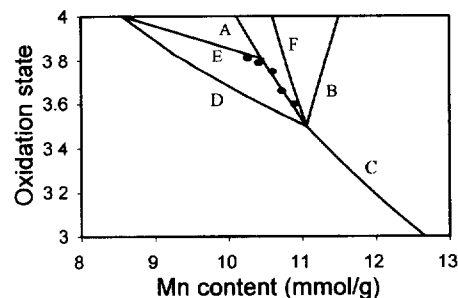

Fig. 2 Manganese oxidation state vs. manganese content in various Li–Mn–O compounds: (A) $Li_{1+\delta}Mn_{2-\delta}O_4$; (B) $Li_xMn_2O_4$, (C) $LiMn_2O_4 + \alpha$-Mn_2O_3; (D) $LiMn_2O_4 + Li_2MnO_3$; (E) $Li_{1.2}Mn_{1.8}O_4 + Li_2MnO_3$, and (F) $Li_{1-\delta}Mn_{2-2\delta}O_4$. The bold symbols represent measured data

better to form Li_2MnO_3 in addition to $LiMn_2O_4$ rather than to form the δ-spinel $Li_{1+\delta}Mn_{2-\delta}O_4$.

Assuming the stoichiometry of $Li_{1+\delta}Mn_{2-\delta}O_4$, the actual composition of the powder can be determined by the oxidation state versus manganese content measurements, and the input Li/Mn ratio. From the theoretical plot of the manganese oxidation state versus the manganese content (see Fig. 2) it is possible to assign the composition of the material as prepared. The figure can be seen as a modified phase diagram, as all compositions can be assinged indistinguishly. The same compositions of the lithium manganese oxide compounds are taken to construct this figure as was done for Fig. 1. Again, it is seen that at $Li/Mn = 2/3$, i.e. $\delta = 0.2$, the experimental results deviate from the theoretical line of the δ-spinel, due to formation of Li_2MnO_3.

The aluminium-doped materials contain excess lithium with a lithium to metal ratio of $Li/(Al + Mn) = 0.55$. Therefore, these materials can be written as $Li_{1+\delta}Al_nMn_{2-\delta-n}O_4$, with $\delta = 0.0645$. The aluminium-doped spinels show a decrease in capacity, due to substitution of Mn^{3+} by Al^{3+}. Fig. 3 shows the results of both the theoretical as well as the observed manganese oxidation state and manganese content. A reasonable agreement is observed. It should be borne in mind that if $n = 0$, the compound is the δ-spinel $Li_{1.065}Mn_{1.935}O_4$. The actual utilisation, calculated as the relative capacity with respect to pure $LiMn_2O_4$, is shown in Fig. 4, together with the theoretical capacity. The maximum utilisation is limited by the number of Mn^{3+} present, decreas-

Fig. 1. Relative capacity vs. Li/Mn input ratio in various Li–Mn–O compounds: (A) $Li_{1+\delta}Mn_{2-\delta}O_4$; (B) $Li_xMn_2O_4$. (C) $LiMn_2O_4 + \alpha$-Mn_2O_3, (D) $LiMn_2O_4 + Li_2MnO_3$; (E) $Li_{1.2}Mn_{1.8}O_4 + Li_2MnO_3$, and (F) $Li_{1-\delta}Mn_{2-2\delta}O_4$. The bold symbols show measured data, and the dotted line represent 80% of the theoretical value.
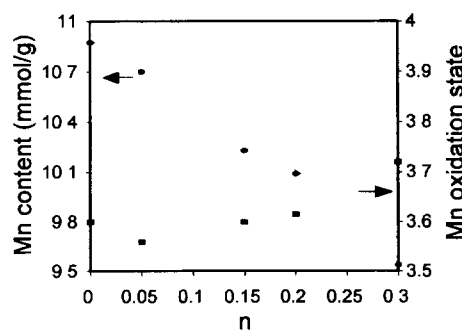

Fig 3. Measured and theoretical manganese content and manganese oxidation state vs. n in $Li_{1+\delta}Al_nMn_{2-\delta-n}O_4$. The dotted lines represent the theoretical values.
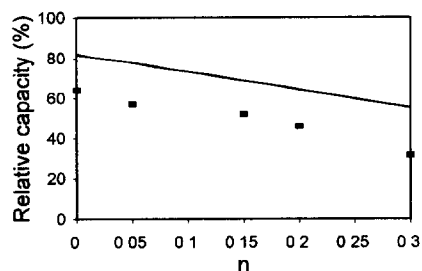
Fig. 4. Measured and theoretical relative capacity (to $LiMn_2O_4$) of $Li_{1+\delta}$ $Al_nMn_{2-\delta-n}O_4$. The closed and dotted lines represent 100 and 80%, respectively.

ing with equal amounts on substitution by Al^{3+}. It can be seen that the data extrapolate to the same relative capacity as observed for the δ-spinels in the absence of aluminium. As for the pure δ-spinel, the maximum capacity is about 80% of the theoretical value.

4. Conclusions

Powders of lithium manganese oxide reveal $Li_{1+\delta}$ $Mn_{2-\delta}O_4$ ($0 < \delta < 0.2$, i.e. $0 < Li/Mn < 2/3$) with a spinel structure. At higher Li/Mn ratios mixtures of $Li_{1.2}Mn_{1.8}O_4$ and Li_2MnO_3 are formed. A modified phase diagram on the basis of the manganese oxidation state and manganese content in combination with the Jaeger and Vetter titration can be used to characterise these phases and classify them on the basis of capacity for battery application. Spinels with small

δ-values are favoured as they are more stable and have still acceptable capacity Doping the spinel materials with aluminium does not improve the capacity.

Acknowledgements

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