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Activation of LiMnBO glass as cathode material for lithium-ion batteries

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A method capable of transforming LiMnBO glass (such as $0.5LiMnO_2$–$0.5B_2O_3$) by appropriate heating into an electrochemically active cathode material is presented. The pristine lithium manganese borate glass prepared by quenching of the melt in air has almost no electrochemical activity within the potential range from 2.5 to 4.5 V *vs.* Li/Li^+. The oxidation of Mn^{2+} to Mn^{3+} and Mn^{4+} was found to occur around the glass transition temperature (T_g). Single-phase $LiMn_2O_4$ can be formed by prolonged heating of the glass powders in air to temperatures around T_g. A composite cathode material in which the electrochemically active substance is dispersed on the surface of a fast-ion-conducting matrix was prepared and found to exhibit a cathodic capacity remarkably higher than that of the pristine glass. Good cycling performance between potentials of 2.5 and 4.5 V *vs.* Li/Li^+ has also been observed.

Introduction

The cathode materials for lithium-ion batteries investigated so far are essentially crystalline.[1] However, several significant advantages inherent in glasses suggest that we consider them as candidate materials for lithium battery electrodes. These advantages include their isotropic structure, absence of composition limitations, low densities leading to larger electrochemically active surface areas, high diffusion coefficients of the mobile ions, and a larger number of sites available to the intercalated ions. Uchiyama *et al.*[2] had already studied vanadium–molybdenum oxides in the form of P_2O_5 glasses, and observed higher charge densities. Superior capacity retention could also be seen. These improvements have been attributed to the greater structural flexibility resulting from variable metal–oxygen bond lengths.

It is the purpose of this paper to introduce a method capable of transforming LiMnBO glass by appropriate heating into an electrochemically active cathode material.

Experimental

Reagent grade $LiNO_3$, MnO_2, and B_2O_3 were mixed in a molar ratio of Li : Mn : B = 1 : 1 : 2, ground, and heated for 5 h to 350 °C in an electronically controlled furnace. After renewed grinding the mixture was placed into an alumina crucible, melted at about 1100 °C, and maintained in the molten state for a given period of time. The melt was then quenched between a brass plate and a brass disk pressed against the brass plate, and then formed into disk-shaped samples 1.5 to 2.0 mm in thickness. The samples had a brown color. Part of the samples was ground to powder for crystallisation and electrochemical studies. The glassy state of the quenched samples and the crystallinity of heat-treated glasses were confirmed by X-ray diffraction analysis using a Rigaku X-ray diffractometer with Cu $K_{\alpha 1}$ radiation monochromated by a graphite single crystal. Differential thermal analysis (DTA) equipment (Setaram TGA-92) was employed to follow the crystallisation process.

The electrochemical properties of pristine and annealed samples were investigated by cyclic voltammetry and galvanostatic cycling. The electrochemical cells consisted of a composite cathode, lithium metal anode, and 1 M $LiPF_6$ in a 1 : 1 (by volume) mixture of ethylene carbonate (EC) and dimethoxyethane (DME) as an electrolyte. Celgard 2400 membranes were used as separators in the cells. The composite cathodes were prepared from a mixture (in weight percent) of 74% active material, 22% carbon black and 4% PTFE binder. The cells were assembled in an argon-filled dry box.

Results and discussion

1 The electrochemical performance of pristine glass

Fig. 1 shows the charge/discharge profiles recorded with a cell where pristine $0.5LiMnO_2$–$0.5B_2O_3$ glass was the active cathode material. With a current density of 0.02 mA cm^{-2} and a voltage window of 2.5–4.5 V *vs.* Li/Li^+, plateaux are not seen in the charge/discharge curves, and with values of 10–20 mA h g^{-1}, the cathodic capacities are very low. It appears that lithium ions cannot be intercalated into or deintercalated from the glass matrix host structure within this voltage window. A plateau seen in the charge/discharge curves at 1.0 V *vs.* Li/Li^+ is disregarded, since our interest is that of examining the material as a cathode material, and we do not

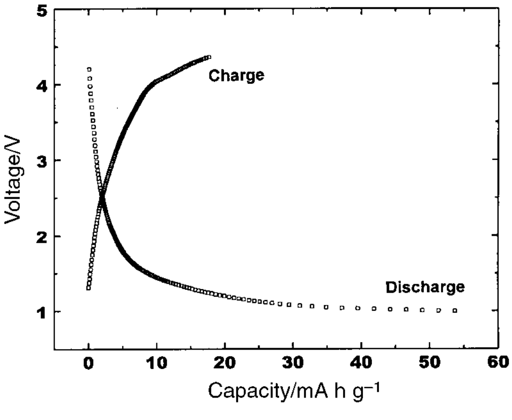

Fig. 1 Typical charge/discharge profiles for pristine $0.5LiMnO_2$–$0.5B_2O_3$ glass; $I = 0.02$ mA cm^{-2}.

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consider the stability of the electrolyte outside the above window.

Why should the pristine LiMnBO glasses exhibit such a poor electrochemical activity as a cathode within the above window? In studies of the mechanism of crystallisation of the LiMnBO glass reported elsewhere[3] we found that in the pristine glass, the manganese ions are predominantly present in valence states +2 and +3. With scanning electronic microscopy (SEM) we further observed that microscopic regions rich in Li and Mn atoms were spatially separated by B_2O_3. Below potentials of 4.5 V *vs.* Li/Li$^+$ the lithium ions cannot be extracted from the glass, since they are mainly bonded through O atoms to B atoms, which in turn have a hard electronic cloud and cannot change their valence state.

2 Inducing electrochemical activity in $0.5LiMnO_2$–$0.5B_2O_3$ glass

Will it be possible, despite the fact that as-prepared LiMnBO glass has poor electrochemical activity in the potential range of 2.5 to 4.5 V *vs.* Li/Li$^+$, to induce such an activity and use the glass as a cathode material? We had seen that in the glass, the manganese ions are in valence states +2 and +3. Therefore, we should first find out whether the Mn^{2+} ions can be oxidised to valence states +3 or +4, and secondly, whether an electrochemically active compound can be produced below the crystallisation temperature of the glass, since indications exist from our work that crystalline compounds derived from the glass are not suitable for lithium insertion and extraction.

2.1 An oxidation reaction of manganese was observed. The DTA traces for both a powder and a bulk sample are shown in Fig. 2. For the bulk sample, the glass transition temperature (T_g) is clearly recognised from the endothermal shift in the curve, but this is not the case for the powder sample. In our studies of the crystallisation mechanism of $0.5LiMnO_2$–$0.5B_2O_3$[3] we found that the major crystalline substance produced differs for the powder and bulk samples, *viz.*, the powder sample yields $MnBO_3$ while the bulk sample yields $Mn(BO_2)_2$. Thus, in the crystalline substance produced from the powder sample manganese has acquired a higher valence state during crystallisation. This effect can be attributed to air oxygen diffusing through the particle surfaces into the core of the glass powder particles. This conclusion was confirmed by the thermogravimetric (TG) experiment reported in Fig. 3. Above 350 °C a weight increase was noticed during heating of the powder sample, which indicates that at these temperatures an oxidation reaction occurred. The endothermic shift due to the glass transition overlaps with the exothermal Mn oxidation reaction in the DTA curve for the powder sample.

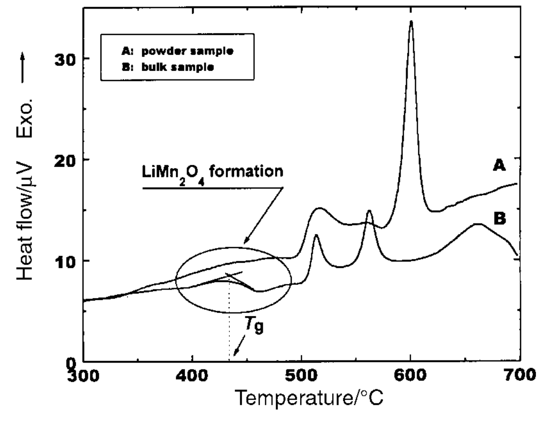

Fig. 2 Differential thermal analysis traces for powder (A) and bulk (B) samples of $0.5LiMnO_2$–$0.5B_2O_3$ glass; conditions: air flow, heating rate 10 °C min^{-1}.

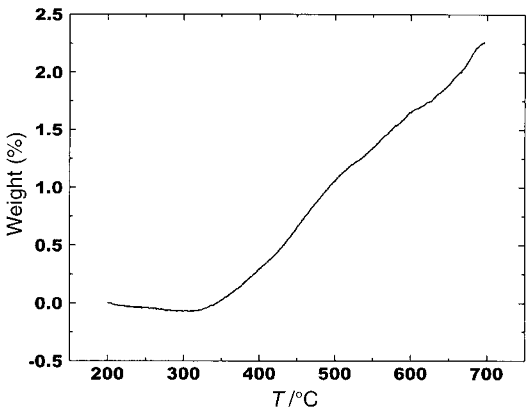

Fig. 3 Thermogravimetric trace for a powder sample of $0.5LiMnO_2$–$0.5B_2O_3$ glass; heating rate: 15 °C min^{-1}.

2.2 $LiMn_2O_4$ generated on the powder sample surface in air at 400 °C. Tests were performed for the reactions occurring during annealing of the bulk and powder samples in different atmospheres. Powders were annealed in air and in argon at 400 °C. The bulk samples were annealed in air at a slightly higher temperature (425 °C). The X-ray diffraction patterns for the three annealed samples are shown in Fig. 4. A crystalline compound was generated from the powder sample annealed in air, but no crystalline substance could be detected in the powder sample annealed in argon or for the bulk sample annealed in air. The latter two yield similar patterns. It can be concluded that a crystalline substance will only form at the surface of powder samples annealed in air. Both oxygen and a large specific surface area are needed. The crystalline substance was identified as $LiMn_2O_4$ (JCPDS NO. 18-736).

The mechanism by which the $LiMn_2O_4$ is formed on the glass powder particle surfaces in air differs remarkably from that by which the same substance crystallizes directly from the glass matrix. In fact, for the spinel to form in the glass matrix, oxygen must be available. Hence oxygen must diffuse from the surface to the core region of the material in order for $LiMn_2O_4$ to form from the LiMnBO glass, and oxygen diffusion in the matrix appears to be the condition controlling the process. The materials formed as a result of annealing in air can be described as a composite material, *viz.*, $LiMn_2O_4$+$LiBO_2$ glass.

3 Electrochemical properties of glass powder annealed at *ca.* 400 °C

Cyclic voltammetry was the test employed to study the electrochemical activity of annealed glass with reference to

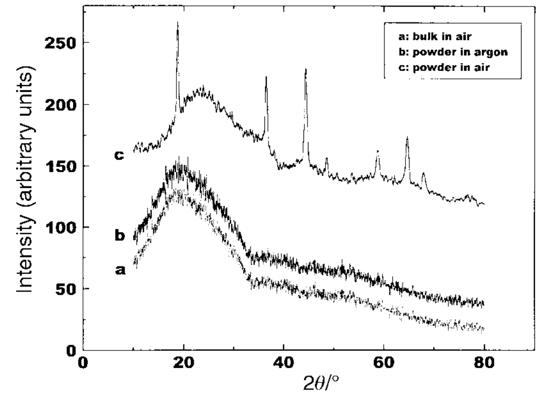

Fig. 4 X-Ray diffraction patterns for annealed samples (Cu K$_{\alpha1}$ radiation); annealing conditions: (a) bulk sample, 425 °C, air; (b) powder sample, 400 °C, argon; (c) powder sample, 400 °C, air. The intensity scale is valid only for curve a, curves b and c are displaced by intensity (arbitrary units) shifts of 20 and 100, respectively.

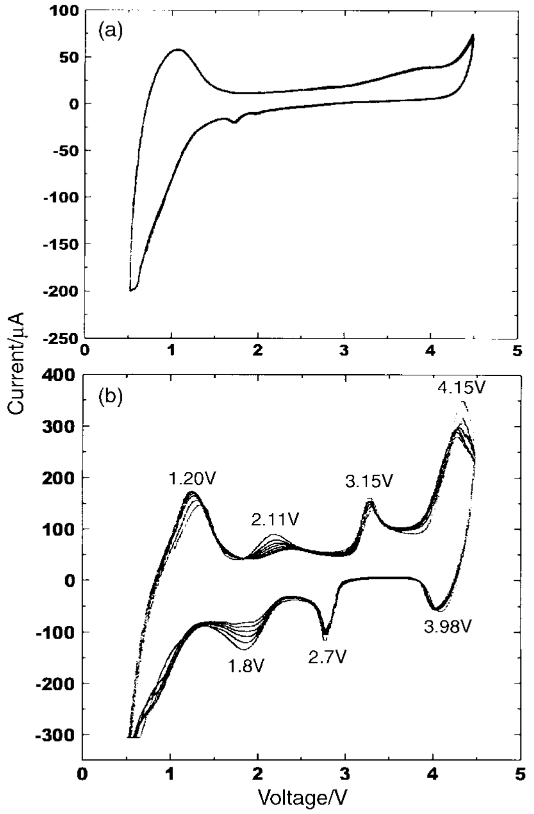

Fig. 5 Cyclic voltammograms for pristine (top) and annealed (bottom) $0.5LiMnO_2$–$0.5B_2O_3$ glass recorded in the cell: Li/EC+DME+1 M $LiPF_6$/glass; potential scanning rate: 1.2 mV min^{-1}.

that of the pristine glass. The results are shown in Fig. 5. The voltammogram recorded for pristine glass exhibits two small peaks between 1.8 and 2.0 V and a larger peak at about 1.0 V *vs.* Li/Li^+ during the cathodic scan. This observation is consistent with the galvanostatic tests described in section 1. The electrochemical activity of the air-annealed sample is much higher than that of the glass; all peaks increased remarkably, and two new pairs of peaks appeared at about 3.0 V and 4.0 V, in agreement with the electrochemical behaviour of $LiMn_2O_4$.

The composite material exhibits good cycling performance between potentials of 2.5 and 4.5 V. This is certainly related to the structure of this annealed material. A detailed discussion will be presented in another paper.

Conclusions

LiMnBO glass in its pristine state has almost no electrochemical activity when examined over the potential range of 2.5 to 4.5 V *vs.* Li+/Li^+; The reason for this is that microscopic regions rich in Li and Mn are separated by B_2O_3 and that manganese is present in lower valence states (+2, +3). At higher temperature in air, the manganese ions of LiMnBO glass can be oxidized to a higher valence state, and the spinel phase $LiMn_2O_4$ can form from the glass matrix when a powder sample is annealed in air at temperatures close to the glass transition temperature. The resultant, composite material consists in fact of an electrochemically active substance dispersed in a fast ion conductor. It exhibits much higher electrochemical activity than the pristine glass and a good cycling performance between potentials of 2.5 and 4.5 V *vs.* Li/Li^+, arising as we believe from the particular structure of this composite cathode material.

Acknowledgements

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