

Investigations of lithium manganese oxide materials for lithium-ion batteries

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Abstract

As candidates for cathode materials in lithium-ion batteries, lithium manganese oxides are attractive and competitive. In this work, the feasibility of using a novel manganese oxide with a large-tunnel structure (i.e. todorokite, tunnel size: 3x3) as cathode material in lithium-ion batteries has been explored. It is found that the initial capacity of todorokite material with Mg^{2+} in the tunnel is 151 mAh g^{-1} at a discharge current density of 0.1 mA cm^{-2} . It still has a capacity of 128 mAh g^{-1} after four charge–discharge cycles. The effects of different cations, such as Co^{2+} , Ni^{2+} , Li^+ etc., in the todorokite tunnel structure, on the electrochemical characteristics of the materials are also studied using slow-rate cyclic voltammetry and electrochemical impedance spectroscopy (EIS). Finally, the intercalation process of Li^+ in the spinel manganese oxide films has been investigated using the in situ electrochemical quartz crystal microbalance (EQCM) method. It is shown that the intercalation process of Li^+ in the films can be divided into at least two stages. The results also implied co-intercalation of solvent with Li^+ in the second stage.

Keywords: Lithium-ion secondary batteries; Manganese oxides

1. Introduction

In recent years, extensive work has been done on the research and development of lithium-ion batteries for portable electronic systems and electric vehicles [1]. As candidates for cathode materials, lithium manganese oxides are attractive and have the following advantages: low-cost, readily available and low pollution. It is well-known that MnO_2 exists in many polymorphic structural forms with different tunnel structures. For example, α - MnO_2 has a framework structure with one-dimensional (1x1) and (2x2) channels.

β - MnO_2 [2], α - MnO_2 [3], γ - MnO_2 [4], CDMO (composite dimensional manganese oxide) [5] and spinel MnO_2 [6] have been widely investigated as intercalation electrode materials for lithium-ion batteries, but manganese oxides with large tunnel structures such as todorokites have not been reported as electrode materials to our knowledge. In our view, evaluation and development of novel lithium manganese oxides as new electrode materials will not only help us to understand the structural effects (such as tunnel structure, cations in the tunnel) on the performance of the electrodes,

but also help to explore the use of some natural or modified manganese oxides in practical systems. In this paper, a novel todorokite-type manganese oxide composite is prepared using a modified method and its electrochemical behaviour is reported. It shows that todorokite-type material is promising, and worth exploring as a new class of electrode material for lithium-ion batteries. In addition, the intercalation process of Li^+ in the spinel manganese oxide films has been investigated using the in situ EQCM method. It is shown that the intercalation process of Li^+ in the films can be divided into at least two stages. The results also implied that co-intercalation of solvent with Li^+ occurs in the second stage.

2. Experimental

The todorokite manganese oxides were prepared according to the method in the literature [7], with some modification. At first, a layered birnessite MnO_2 was prepared by the oxidation of $Mn(OH)_2$, that is, by the slow addition of sodium hydroxide solution into 0.5 M $MnCl_2$ solution whilst bubbling oxygen. The choice of the reaction temperature is

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important for the control of the layered structure of the products.

It was found that iced water ($\sim 0^\circ\text{C}$) provides optimum reaction conditions. Then, the birnessite was ion-exchanged with MgCl_2 for 12–24 h to form Mg birnessite. The washed Mg^{2+} birnessite was autoclaved at 160°C for 24 h after ion-exchange. All autoclaved products were then filtered and washed three times with triple-distilled water and dried at 120°C for 7 h under vacuum. In addition, Co^{2+} -, Ni^{2+} - and Li^+ -containing todorokite were also prepared by similar procedures.

The structure of the prepared materials was examined by X-ray diffraction using the Rigaku Rotaflex d/Max C system and $\text{Cu K}\alpha$ radiation. It was demonstrated that the sample had characteristic peaks of todorokite material [8] (i.e. $2\theta = 9.32^\circ, 12.7^\circ, 18.7^\circ$). The working electrode was prepared according to the following procedure. 40 mg todorokite sample + 10 mg acetylene black + 10 mg PTFE were mixed and pressed onto a nickel mesh. This was dried at 150°C under vacuum for more than 8 h before being used as a working electrode. In addition, working electrodes of films of spinel LiMn_2O_4 were prepared according to the following procedure. A sol-gel solution with a ratio of $\text{Li}:\text{Mn} = 1:2$ was prepared, and then the solution was printed or spin-coated onto a quartz slice. After drying, the coated-slice was heated to 350°C for 2 h. This procedure was repeated two to three times to give a better and thicker film.

It has been demonstrated with XRD that the lithium manganese oxide film has similar diffraction peaks to spinel. The counter and reference electrodes were pure Li metal. The electrolyte in this study was 1 M $\text{LiClO}_4 + \text{PC} + \text{DME}$ ($\text{PC}:\text{DME} = 1:1$).

The cell assembly and treatment of Li metal were done in an inert-gas system (model Labmaster-100, M. Braun Co. Germany) using Ar as the inert gas. The cyclic experiments were done using a model 273 potentiostat/galvanostat (EG&G, PARC, USA). In addition electrochemical impedance spectra were measured using an impedance spectrum analyser (IM6, Zahner-electrik GmbH, Germany). The electrochemical quartz crystal microbalance (EQCM) experiments were performed using a model QCA 917 quartz-crystal analyser under electrochemical control, being coupled with the model 273 potentiostat. Shear-mode, 9 MHz, AT-cut quartz crystals with a deposit of platinum, 1000 \AA thick, on each side were used, and the electrode area was 0.2 cm^2 in all EQCM experiments.

3. Results and discussion

3.1. Novel todorokite electrode material and its electrochemical behaviour

The structure of the todorokite with its large-tunnel structure as described in this paper is shown in Fig. 1. It can be seen that the width of the tunnel is 6.9 \AA , and it has the

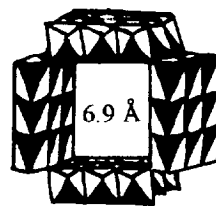


Fig. 1. A model of the crystal structure of todorokite.

characteristic (3×3) tunnel. Normally, it is thought that cations such as Mg^{2+} 'sit' in the centre of the tunnel and the role of the cations is to stabilise the large tunnel. However, whether these manganese oxides can be used as an electrode material or the stabilised structure of the material can be stable even without cations in the centre of the tunnel, has not been investigated to our knowledge. In our work, the synthesised todorokite material was first evaluated by using cyclic voltammetric experiments. The first and the second potential-scanning results are shown in Fig. 2. It is also observed that the cyclic voltammograms become quite stable after the second potential scan in the experiments. From the curves in Fig. 2, it is found that in the potential region between 2 and 4 V, there is only a couple of current peaks, which correspond to the intercalation and de-intercalation of Li^+ in the material. The positions and reversibilities of the anodic and cathodic peaks ($\varphi_{\text{anodic}} = 3.3 \text{ V}$, $\varphi_{\text{cathodic}} = 2.5 \text{ V}$) imply that Li^+ is intercalated into an octahedral site of the MnO_6 framework instead of replacing Mg^{2+} in the tunnel. As scanning times increased, the current peaks of the intercalation and de-intercalation of Li^+ decreased and moved slightly in a more positive direction. Fig. 3 shows a typical Nyquist plot of EIS for the electrodes before the experiment and after the first cyclic voltammogram. For the newly prepared electrode, it shows only a semi-circle in the high-frequency region. However, after potential-scanning, two semi-circles appeared in the high-frequency region for the electrodes, indicating some changes occurred in the electrode system. Some possible explanations may include the changes of charge-transfer resistance between todorokite and conducting material/binders such as carbon black, or a passive film being formed on

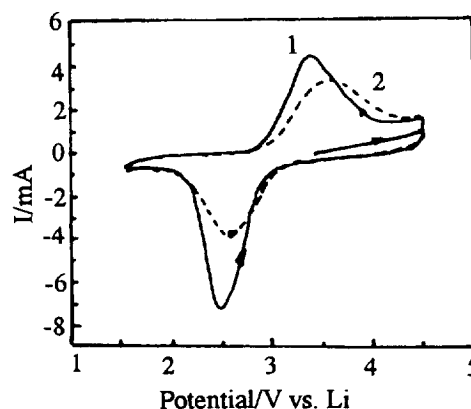


Fig. 2. Cyclic voltammograms of todorokite in 1 M $\text{LiClO}_4 + \text{PC} + \text{DME}$ at a scan rate of 0.2 mV s^{-1} . 1 and 2 are the cycle numbers.

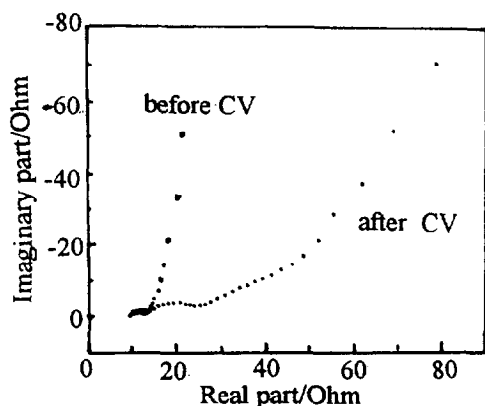


Fig. 3. Typical electrochemical impedance spectra (EIS) of todorokite electrodes with Mg^{2+} in the tunnels, before and after cyclic voltammetric experiments. The frequency range was 10^{-2} to 10^5 Hz.

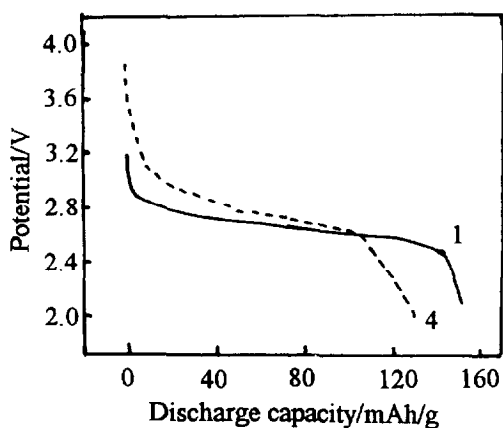


Fig. 4. Discharge curves of todorokite electrodes in 1 M $\text{LiClO}_4 + \text{PC} + \text{DME}$ at a current density of 0.1 mA cm^{-2} . 1 and 4 are the cycle numbers.

the electrodes. Detailed studies and simulation of impedance spectra are presently being carried out in our laboratory.

In order to evaluate the discharge behaviour of todorokite, this material was also mixed with conductor and binder and pressed into electrodes. It was assembled with Li metal as the cathode to produce a test battery. Two capacity versus time curves of the test battery are given in Fig. 4.

It is shown that the material only shows a plateau at $\sim 3 \text{ V}$ and if the end-potential of the discharge experiment is chosen as 2 V , the initial discharge capacity is as high as 151 mAh g^{-1} . After four charge–discharge cycles, the capacity of the electrode material slightly decreased. However, it was still kept at the quite high level of 128 mAh g^{-1} . In order to understand the possible structural changes of the todorokite material, it was also characterised using XRD and electrochemical impedance spectrum (EIS) techniques after four charge–discharge cycles. It was found that the characteristic peak of todorokite in the XRD spectra is still retained, although the intensity had decreased. It indicates the structural stability of the material is quite good during cyclic charge–discharge experiments.

In addition, todorokite-type material with different metals, such as Co^{2+} , Ni^{2+} and Li^+ , in the tunnel was also synthesised and primarily investigated. Table 1 shows the peak

Table 1

Cyclic voltammetric parameters of todorokite electrodes intercalated with different metal cations in the tunnels. The mass of active material is 40 mg ; electrolyte: $1 \text{ M LiClO}_4 + \text{PC} + \text{DME}$; scan rate: 0.2 mV s^{-1}

	Intercalating cations		
	Li^+	Co^{2+}	Ni^{2+}
i_{pa} (mA)	4.3	2.9	1.4
i_{pc} (mA)	4.1	6.1, 6.4	7.2
$i_{\text{pa}}/i_{\text{pc}}$	1.05	0.48, 0.51	0.19
E_{pa}	3.38	3.38	3.15
E_{pc}	2.50	2.30, 2.53	2.7
$(E_{\text{pa}} + E_{\text{pc}})/2$	2.94	2.84, 2.95	2.92

potential, peak current and quasi-equilibrium potential of the different electrodes. It can be seen that Co^{2+} -containing todorokite material has two cathodic peaks for intercalation of Li^+ , suggesting two different intercalating sites in the material. In addition, reversibility of intercalation of Li^+ in Ni^{2+} -containing todorokite material is not complete, based on the present results. Electrochemical impedance spectra (EIS) of these different todorokite materials show some characteristics which may correlate to their electrochemical behaviour.

3.2. Electrochemical quartz crystal microbalance (EQCM) studies on spinel lithium manganese oxide thin-film electrodes

Fig. 5 shows a cyclic voltammogram of spinel lithium manganese oxide thin film electrodes and corresponding $\Delta f-E$ curves of the electrodes. These show typical voltammetric characteristics of spinel electrodes in the lower potential region $2-4 \text{ V}$ (E versus Li), that is, a couple of current peaks corresponding to the intercalation and de-intercalation of Li^+ in the material. As Li^+ intercalation into the vacant sites progresses, the frequency of the thin film electrodes decreased. This indicates that lithium-ion intercalation results in an increase of the mass of the electrodes, assuming other

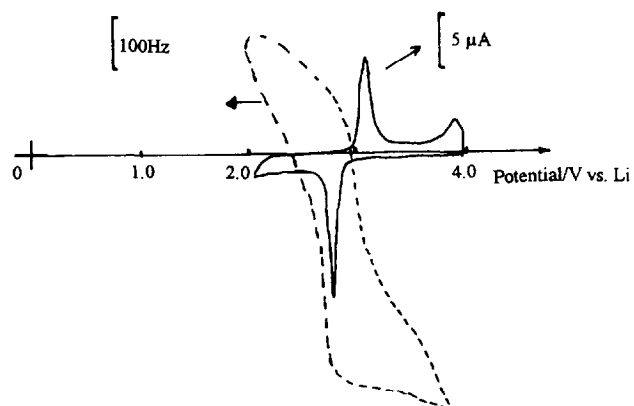


Fig. 5. Simultaneously recorded cyclic voltammogram and potential-dependent frequency change (Δf) curve of the spinel films in $1 \text{ M LiClO}_4 + \text{PC} + \text{DME}$. The potential scan rate was 0.2 mV s^{-1} .

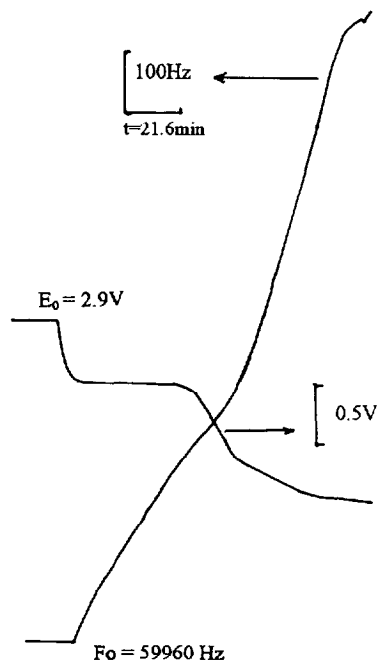


Fig. 6. Time-dependent potential and frequency changes of the spinel films under galvanostatic charging conditions. The constant current density was 0.01 mA cm^{-2} .

conditions were not changed according to the Sauerbrey equation.

In order to understand the detailed intercalation–de-intercalation process of Li^+ under potentiostatic and galvanostatic conditions, the frequency changes (i.e. Δf) of the electrodes and current or potential decay curves were recorded simultaneously. In fact, if we change the form of the Sauerbrey equation, we can calculate the change in mass associated with one-electron transfer (i.e. m.p.e.) [9]. Fig. 6 shows a set of $\Delta f-t$ and $E-t$ curves. From Fig. 6, the frequency changes can be divided into two stages. For example, in the charging process, when the potential of the electrodes reached a 3 V plateau, the m.p.e. (i.e. mass per electron) was 11 to 20. However, after the potential reached the 3.8 V plateau, the m.p.e. was as high as 33 to 43. These results may imply that at different intercalation stages, the mass of Li^+ or, more exactly, the Li^+ solvent complex or Li cluster, are co-intercalated into the Mn–O vacancies. This result is quite different from that of Park et al. who examined V_2O_5 xerogel films [10]. The reason for the difference is not clear at this moment,

but it must be related to the properties of the solvent and the characteristic structure of the electrode materials.

4. Conclusions

In conclusion, a novel todorokite-type manganese oxide composite has been prepared and its electrochemical behaviour investigated. It is shown that the material is a candidate for 3 V electrode material for lithium batteries, and its initial capacity is as high as 151 mAh g^{-1} , still giving 128 mAh g^{-1} after four charge–discharge cycles. It is suggested that todorokite-type lithium manganese oxides could be developed for use in future lithium-ion batteries.

In addition, our in situ EQCM results on spinel films of lithium manganese oxides show that the process of lithium intercalation can be divided into at least two stages. This result may imply that some Li^+ –solvent complexes are co-intercalated into the films.

Acknowledgements

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