Short Communication

Electrochemical behavior of Li–Mn spinel electrode material in aqueous solution

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Abstract

The electrochemical properties of $LiMn_2O_4$ are studied in aqueous solution with various pH values. The performance is similar to that in organic electrolyte. $Li_{1-x}Mn_2O_4 + xLi^+ + xe^- = LiMn_2O_4$ in aqueous solution involves two processes: (i) a two-phase reaction at 0.89 V versus saturated calomel electrode (SCE), and (ii) a one-phase reaction at 0.77 V versus SCE. $LiMn_2O_4$ in $LiNO_3/HNO_3$ from pH 2 to 5 is reversible for about 20 cycles. More cycles lead to a great loss in capacity, the reason for which is yet unknown.

Keywords: Lithium compounds; Manganese oxide; Electrochemical behavior; Voltage–pH relationship; Batteries; Charge/discharge performance

1. Introduction

Recently, 'lithium-ion' batteries have attracted considerable attention. The advantages of this type of battery are high specific capacity, high specific energy and good cycle-life performance. Commercial batteries of this type all use organic electrolyte and have the disadvantages of high cost, low safety, and low current density. Aqueous lithium-ion cells are not considered because cathode and anode materials that are stable in aqueous solution are hard to find. Dahn and co-workers [1–3] have proposed the concept of rocking-chair cells in aqueous solution: the cathode and anode are both complex metal oxides of lithium, e.g., $LiMn_2O_4$ is used as the anode and VO_2 or γ-$Li_{0.36}MnO_2$ is used for the cathode, the cell voltage (E) is 1.5 V, and the specific capacity is about 100 mAh per g $LiMn_2O_4$. The authors' laboratories operated on Li^+-ion batteries [4]. $LiCoO_2$ and $LiMn_2O_4$ are both high-potential materials and suitable as cathodes of rocking-chair cells. $LiMn_2O_4$ is preferable because of the high cost and toxicity of $LiCoO_2$. In aqueous solution, there are two important things to be considered: (i) are lithium intercalation and extraction the main reactions in aqueous solution? (ii) what is the influence of oxygen evolution when the cell is overcharged? In this work, we used $LiMn_2O_4$ as the test material and measured the cycle-life performance in $LiNO_3$ aqueous solution at various pH values. The E–pH pattern of $Li_xMn_2O_4$ is shown and the charge/discharge mechanism of

$LiMn_2O_4$ spinel in aqueous solution is proved. A new type of cell $Li_{1-x}Mn_2O_4/LiNO_3$, Zn^{2+}/Zn is also evaluated.

2. Experimental

$LiMn_2O_4$ was synthesized by the citrous acid method; it was heated at 250 °C for 1 h, and then at 600–800 °C for 2 h. The X-ray diffraction pattern of $LiMn_2O_4$ is given in Fig. 1. This shows that the product is a spinel phase with a 8.24 Å (cubic) unit cell. A tablet electrode of 2.3 cm × 2.3 cm was prepared by mixing 0.1 g $LiMn_2O_4$, 0.8 g ground graphite and 0.08 g polytetrafluoroethylene (PTFE) powder, and then applying a pressure of 20 MPa for 1 min.

5 M $LiNO_3$ solutions of different pH were prepared according to the conditions listed in Table 1. If zinc was used as an anode, a certain amount of $Zn(NO_3)_2$ was added to make $C_{Zn^{2+}} = 0.1$ M.
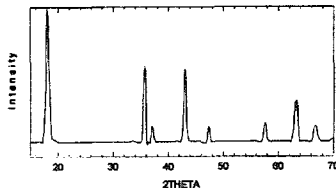
Fig. 1. X-ray diffraction pattern of $LiMn_2O_4$ (650 °C).

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Cyclic voltammetry was conducted at a scan rate of 1 mV s^{-1}. The potential range was -0.5 to 1.4 V (versus saturated calomel electrode (SCE)). The initial anodic scan was applied from the open-circuit potential of the electrode.

3. Results and discussion

When the cathode and the anode are both made from $LiMn_2O_4$, and pH of electrolyte is 7 to 8, the starting voltage is zero. During first charge, the anode becomes $Li_{1+x}Mn_2O_4$ ($0<x<1$), and there is a plateau at about -0.30 V (versus SCE). A plateau does not appear during discharge (Fig. 2), nor does it reappear during the following charge and discharging processes. Tests on a second electrode produced the same result. This phenomenon means that an irreversible process occurs during the initial charging of the anode. From the work of Ohzuku et al. [5], we conclude that the cubic
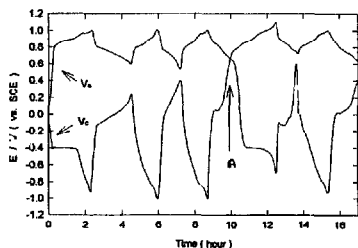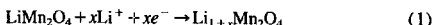

Fig. 2. Electrode potential curve of $LiMn_2O_4/LiNO_3/LiMn_2O_4$ during a charge/discharge cycle. V_a is the potential of the anode vs. SCE; V_c is the potential of the cathode vs. SCE. The anode and cathode were exchanged at point A.

structure changes to a tetragonal one during the following reaction

$$LiMn_2O_4 + xLi^+ + xe^- \rightarrow Li_{1+x}Mn_2O_4 \qquad (1)$$

Because of the Jahn–Teller effect of Mn^{3+} ions, the reaction is irreversible. This means that a rocking-chair battery using $LiMn_2O_4$ as both the anode and the cathode is not feasible.

Because $LiMn_2O_4$ is not suitable as an anode, attention was focused on the following reaction

$$LiMn_2O_4 \leftrightarrow Li_{1-x}Mn_2O_4 + xLi^+ + xe^- \qquad (2)$$

Cyclic voltammograms for $LiMn_2O_4$ in 5 M $LiNO_3$ solution of different pH's are given in Fig. 3. The oxidation peak cannot be distinguished from that of water, but the reduction peak at ~ 0.5 V is obvious. In solutions with pH values below 10.0, the reduction peaks of the first cycle and the following cycles coincide fairly well. This means there is only a slight loss in capacity. When the electrode is cycled in saturated LiOH (pH 12.3), the reduction peak does not appear. This is expected since the potential of $Li_{1-x}Mn_2O_4$ is much higher than the potential of oxygen evolution in a strong base.

A series of experiments was then performed to determine the open-circuit potential curve of $LiMn_2O_4$ in solutions of different pH's. First, an $LiMn_2O_4$ cathode was charged potentiostatically, then discharged intermittently (2 min on, 2 min off) at constant current (10 mA). This method is similar to that of Ohzuku et al. [4]. The results are given in Fig. 4. The potential of the cathode was kept at 1.000 V versus SCE. With increasing pH, I_{off}, the current at which the cell was open-circuited, becomes greater. This can be attributed to the greater extent of oxygen evolution at higher pH. Some type of side-reaction may account for the shape of the curve at pH 1.0, but an explanation for this has yet to be found.

The value of x in $Li_xMn_2O_4$ can calculated from the respective discharge capacity. The open-circuit potentials of

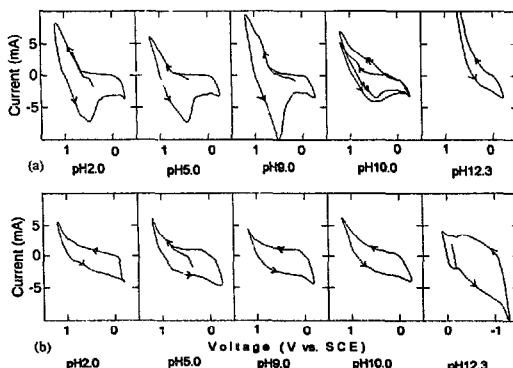Fig. 3. Cyclic voltammograms of: (a) $LiMn_2O_4$, and (b) pure graphite (used as reference) in solutions of various pH's.
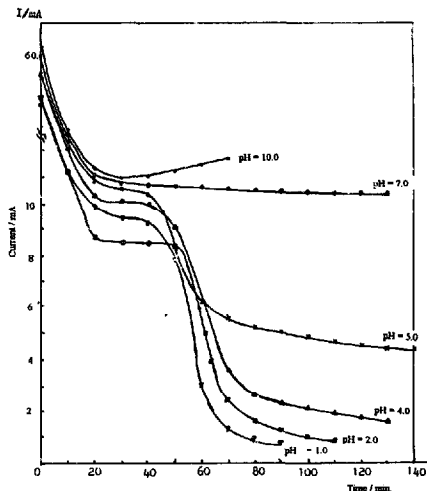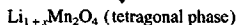
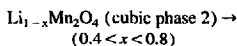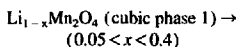Fig. 4. Current vs. time curve for LiMn$_2$O$_4$ when charged potentiostatically (1.0 V vs. SCE) at 25 °C.

Li$_x$Mn$_2$O$_4$ are given in Fig. 5. There is an obvious similarity between these results and the same E–x curve obtained in organic solutions [5,6]. Thus, it was concluded that the discharge mechanism of Li$_x$Mn$_2$O$_4$ in aqueous solution is similar to that in organic electrolyte

$$Li_{1-x}Mn_2O_4 \text{ (cubic phase 1)} \rightarrow$$
$$(0.05 < x < 0.4)$$

$$Li_{1-x}Mn_2O_4 \text{ (cubic phase 2)} \rightarrow$$
$$(0.4 < x < 0.8)$$

$$LiMn_2O_4 \text{ (cubic phase 2)}$$
$$\downarrow \qquad\qquad (3)$$
$$Li_{1+x}Mn_2O_4 \text{ (tetragonal phase)}$$

The reaction of Li$_{1-x}$Mn$_2$O$_4 \rightarrow$ LiMn$_2$O$_4$ in aqueous solution involves two processes: (i) a two-phase transition at 0.89 V versus SCE, and (ii) a one-phase transition at 0.77 V versus SCE. The first and second discharge plateau in Fig. 5 become shorter with increasing pH. This again proves that oxygen evolution plays a role in higher pH solution and that the capacity is affected adversely. The third 'plateau' at ~0.65 V in pH 1.0 electrolyte may be related to H$^+$ intercalation in strong acid, but this requires further proof.

The open-circuit potential as function of pH is shown in Fig. 6 [7]. It is found that the potential of LiMn$_2$O$_4$ is relatively high and the specific capacity reaches 120 mAh per g LiMn$_2$O$_4$ if 0.8 Li$^+$ per LiMn$_2$O$_4$ can be recycled each time. Thus, LiMn$_2$O$_4$ is a good electrode material in aqueous solution. Zinc foil was then used as a counter electrode in the following cell

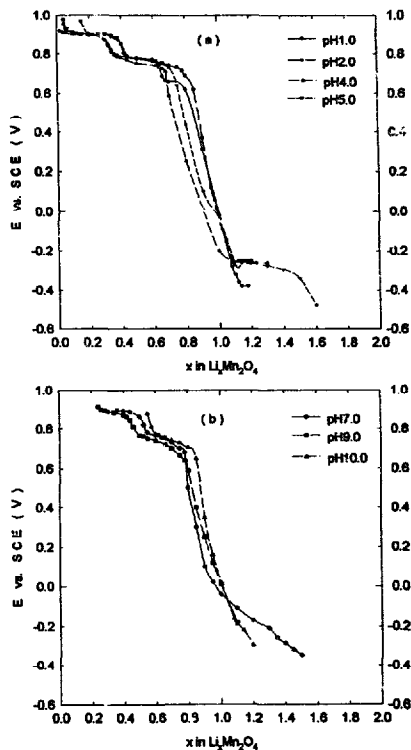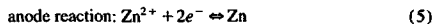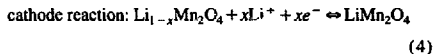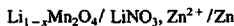Fig. 5. Electrode potential of Li$_x$Mn$_2$O$_4$ vs. SCE in aqueous solutions of various pH's.

$$Li_{1-x}Mn_2O_4 / LiNO_3, Zn^{2+} / Zn$$

cathode reaction: $Li_{1-x}Mn_2O_4 + xLi^+ + xe^- \Leftrightarrow LiMn_2O_4$
$$(4)$$

anode reaction: $Zn^{2+} + 2e^- \Leftrightarrow Zn$ $\qquad (5)$

Charge/discharge cycling of this cell was conducted in pH 2.0 and 5.0 solutions. The results are given in Fig. 7. The cells perform very well during the first 10 cycles, give a specific capacity of 70~80 mAh per g LiMn$_2$O$_4$, an average voltage of 1.4 V, and a specific energy of 100–110 Wh per kg LiMn$_2$O$_4$. The specific capacity is much smaller than the theoretical value (120 mAh per g LiMn$_2$O$_4$), and is due to the fact that the electrode reaction is a solid–solid phase one, and Li$^+$ intercalation requires time to reach equilibrium. Thus, if we enlarge the surface of the electrode, or use superfine LiMn$_2$O$_4$ powder, the specific capacity is expected to be enhanced.
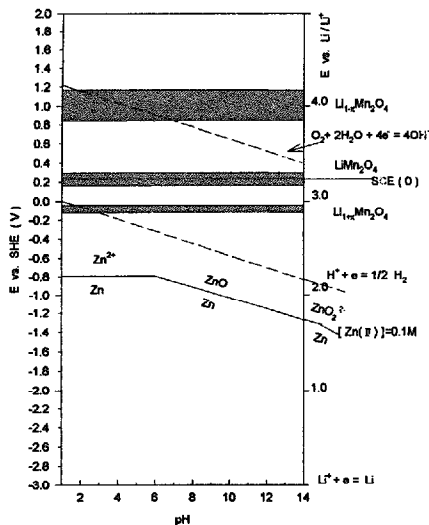
Fig. 6. E_n–pH diagram of cell materials. The H_2O stability window is also shown.

Fig. 7. Discharge performance of $Li_{1-x}Mn_2O_4/LiNO_3$, Zn^{2+}/Zn cell for: (a) pH = 5.0, and (b) pH = 2.0.

After the cell is recycled in pH 2.0 solution more than 30 times, the average potential and capacity of the cell drops dramatically, and the pH increases to ~4.0. Although this can be partly explained by the corrosion of the zinc foil, the possibility of H^+ intercalation cannot be ignored. Dahn and co-workers [1–3] also reported the loss of capacity of $LiMn_2O_4/LiNO_3$, pH 7–8/VO_2 or γ-$Li_{0.36}MnO_2$ batteries after 25 cycles. They concluded that this was due to decomposition of water, dissolution of materials, and other phase transitions, but they excluded the possibility of H^+ intercalation. In the studies here with pH 2.0 solution, Li^+ intercalation is the main reaction but, the effect of H^+ insertion must be further explored

4. Conclusions

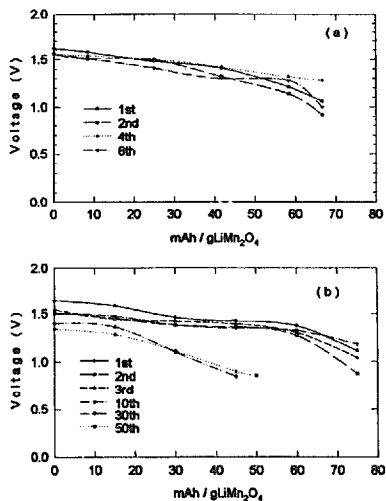The irreversible reaction of $LiMn_2O_4 \rightarrow Li_{1+x}Mn_2O_4$ makes $LiMn_2O_4$ not suitable as an anode for a rocking-chair battery. The reaction of $Li_{1-x}Mn_2O_4 \rightarrow LiMn_2O_4$ in aqueous solution involves two processes: (i) a two-phase transition at 0.89 V versus SCE, and (ii) a one-phase transition at 0.77 V versus SCE. Some features of a new type of battery, $Li_{1-x}Mn_2O_4/LiNO_3$, Zn^{2+}/Zn, are also discussed.

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