



Secondary aqueous lithium-ion batteries with spinel anodes and cathodes

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Abstract

Secondary aqueous lithium-ion batteries with spinel $\text{Li}_2\text{Mn}_4\text{O}_9$ or $\text{Li}_4\text{Mn}_5\text{O}_{12}$ as the anode and LiMn_2O_4 as the cathode are investigated. The aqueous electrolyte contains 6 M LiNO_3 and 0.0015 M OH^- . The $\text{Li}_2\text{Mn}_4\text{O}_9/\text{LiNO}_3/\text{LiMn}_2\text{O}_4$ and $\text{Li}_4\text{Mn}_5\text{O}_{12}/\text{LiNO}_3/\text{LiMn}_2\text{O}_4$ aqueous cells deliver approximately 100 m Ah g^{-1} capacity at an average voltage of 1–1.1 V. This aqueous lithium-ion system eliminates safety concerns and offers considerably cost-effective technology for manufacturing. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Aqueous lithium-ion batteries; Spinel $\text{Li}_2\text{Mn}_4\text{O}_9$, $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and LiMn_2O_4 ; Intercalation

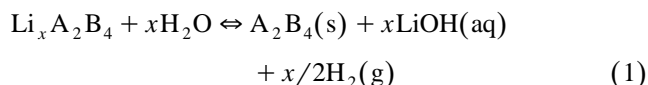
1. Introduction

Secondary lithium-ion batteries are under extensive development worldwide due to their high specific energy, high voltage, and long shelf life. Such batteries are promising power sources for consumer electronics and electric vehicles (EVs) [1–4]. All of the present lithium technologies use non-aqueous electrolyte in which a lithium salt is dissolved in an organic solvent. The conductivities of organic electrolytes are typically two orders of magnitude less than that of an aqueous system, which limits the rate capacity and specific power. Usually, non-aqueous cells must be assembled in an argon-filled chamber in which oxygen and moisture have to be strictly excluded. Thus, extra manufacturing costs are incurred.

The ‘rocking-chair’ concept takes advantage of the difference in chemical potential of the lithium-ions in the anode and cathode hosts. It is now understood that intercalation hosts in which the binding energy of lithium ions differs by several eV can be coupled to construct a lithium-ion cell. A variety of such systems has been developed with LiCoO_2 , LiNiO_2 , LiMn_2O_4 as the cathode and carbonaceous materials or other intercalation compounds as the anode [5–8].

Spinel lithiated oxide is an ideal host for lithium insertion/extraction due to its structural stability [9]. It is the

most promising electrode material for lithium-ion batteries. Recently, it has been demonstrated that lithium ions can intercalate into and de-intercalate from spinel LiMn_2O_4 in aqueous electrolyte [10,11]. With spinels, however, the following reaction can happen in aqueous solution.



Concentrated Li^+ can drive Eq. (1) to the left and thereby cause the lithium intercalation compound to become stable in aqueous solution. Consequently, it is theoretically possible for an aqueous secondary lithium battery to be made with appropriate intercalation compounds.

An aqueous lithium cell using $\text{VO}_2[\text{B}]$ as the anode and LiMn_2O_4 as the cathode with an average voltage 1.5 V has been reported [12,13], but the preparation of $\text{VO}_2[\text{B}]$ is tedious. In this paper, we have investigated aqueous lithium-ion systems with spinel $\text{Li}_2\text{Mn}_4\text{O}_9$, or $\text{Li}_4\text{Mn}_5\text{O}_{12}$ as the anode and LiMn_2O_4 as the cathode that are structurally stable compounds for the insertion and extraction of lithium-ions.

2. Experimental

The electrode materials were synthesized via a solid-state reaction at high temperature. The starting powders were mixed by ball-milling in ethanol for 12 h. The ethanol was evaporated. The samples were ground and

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Table 1
Conditions for the synthesis of spinel anode and cathode materials

Reactants		Firing temperature (°C)	Firing time (h)
<i>Cathode materials</i>			
LiMn ₂ O ₄	Li ₂ CO ₃ , Mn ₂ O ₃	750	20
<i>Anode materials</i>			
Li ₂ Mn ₄ O ₉	LiOH·H ₂ O, MnCO ₃	380	24
Li ₄ Mn ₅ O ₁₂	LiOH·H ₂ O, MnCO ₃	380	24

pressed into pellets, then fired at high temperature. The pellets were then pulverised and reground. The coarse powders thus obtained were ball-milled in ethanol for 24 h to produce fine powders. The synthesis conditions for anode and cathode materials are summarized in Table 1.

Powder X-ray diffraction was performed on the synthesized compounds to confirm the spinel structure; a Philips PW1010 diffractometer with Cu-K_α radiation was used. The lattice constants were refined against an internal silicon standard.

Electrochemical tests were carried out in a Teflon cell. LiNO₃ (Aldrich, 99.99%) and LiOH·H₂O (Aldrich, 99.99%) were used to prepare 6 M Li⁺, 0.0015 M OH⁻ electrolyte solution. The electrode was made by mixing 85 wt.% of the synthetic spinel compounds with 10 wt.% carbon black and 5 wt.% PTFE binder. The mixture were then pressed into nickel foil. The amount of active material used for the anode was 10% more than that for the cathode. The anode and cathode were separated by a microporous polypropylene separator (Celgard 2500, Hoechst). The cells were cycled at a constant current of 1 mA cm⁻² between 0.5–1.6 V. For comparison, non-aque-

ous cells containing Li₂Mn₄O₉ or Li₄Mn₅O₁₂ as the anode and LiMn₂O₄ as the cathode were also constructed in an argon-filled glove-box. The electrolyte was 1 M LiPF₆ (lithium hexafluorophosphate) dissolved in EC (ethylene carbonate)/DMC (dimethyl carbonate) (2:1 in volume). The non-aqueous cells were cycled at a constant current of 0.25 mA cm⁻² between 0.5–1.6 V.

3. Results and discussion

3.1. Structure of spinel compounds

The spinel Li₂Mn₄O₉ and Li₄Mn₅O₁₂ have a defect spinel-framework structure, which can be expressed as: [Li_{0.89}]_{8a}[Mn_{1.78}]_{16d}[O₄]_{32e} and [Li]_{8a}[Li_{0.33}Mn_{1.67}]_{16d}[O]₄, respectively [14]. Such a structure provides a three-dimensional tunnel for Li⁺ insertion and extraction with minimal change in the unit-cell volume [15]. The X-ray diffraction patterns for the synthesized spinels are shown in Fig. 1. Using a Rietveld refinement program, all peaks were indexed to the cubic spinel phase. The peaks of Li₂Mn₄O₉ and Li₄Mn₅O₁₂ spinels are much broader than that of LiMn₂O₄; this reflects a disordered characteristic and a low degree of crystallinity. The unit cell parameters, *a*₀, were calculated as 8.2495, 8.1092, and 8.1267 Å for LiMn₂O₄, Li₂Mn₄O₉, and Li₄Mn₅O₁₂, respectively.

Spinel Li₂Mn₄O₉, Li₄Mn₅O₁₂ were synthesized at low temperature (380°C). Oxygen evolves to form LiMn₂O₄ when the samples are heated above 400°C [11].

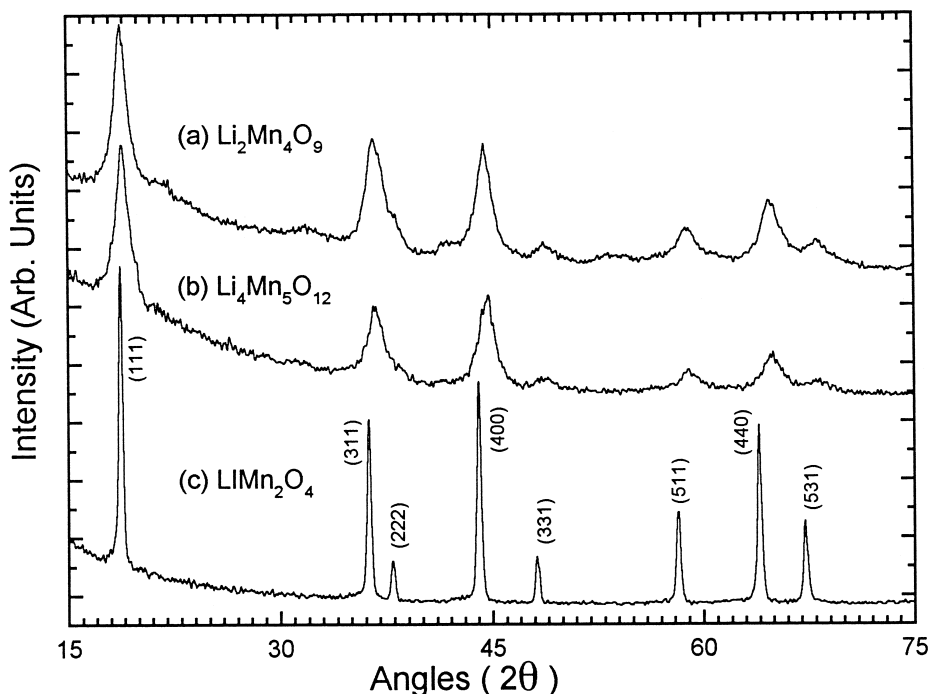
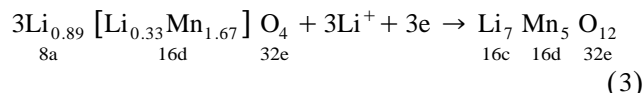
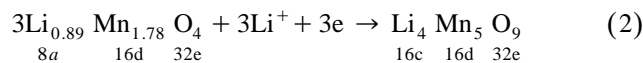


Fig. 1. X-ray diffraction patterns of synthesized spinels: (a) Li₂Mn₄O₉, (b) Li₄Mn₅O₁₂, (c) LiMn₂O₄.

$\text{Li}_2\text{Mn}_4\text{O}_9$ and LiMn_2O_4 can accommodate 3 Li ions per formula. The topotactic reactions for lithium intercalation are as follows:

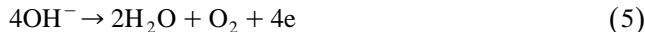


Thus, spinel $\text{Li}_2\text{Mn}_4\text{O}_9$ and LiMn_2O_4 have theoretical capacities of 156 and 202 mA h g^{-1} , respectively.

3.2. Electrochemical behaviour

The potential of $\text{Li}_2\text{Mn}_4\text{O}_9$ and LiMn_2O_4 vs. lithium is about 2.8 V, and the potential of LiMn_2O_4 vs. lithium is 3.8–4.1 V. Thus, on coupling $\text{Li}_2\text{Mn}_4\text{O}_9$ or $\text{Li}_4\text{Mn}_5\text{O}_{12}$ with LiMn_2O_4 , the resulting cell should deliver an average voltage of 1.0–1.3 V. The potentials (vs. SHE) of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$, $\text{Li}_{2+x}\text{Mn}_4\text{O}_9$ and $\text{Li}_{4+x}\text{Mn}_5\text{O}_{12}$ spinels, as well as of oxygen and hydrogen evolution, in basic electrolyte with 1 M OH^- and 1 M Li^+ are given in Fig. 2.

Hydrogen and oxygen evolution can be controlled by shifting the potential of reactions (4) and (5) via adjustment of the pH of the solution.



An aqueous electrolyte with 6 M Li^+ and 0.0015 M OH^- was used in study. Compared with the 1 M OH^- , the potential of H_2 and O_2 evolution are shifted by 0.16 V according to the Nernst equation. Thus, reactions (4) and

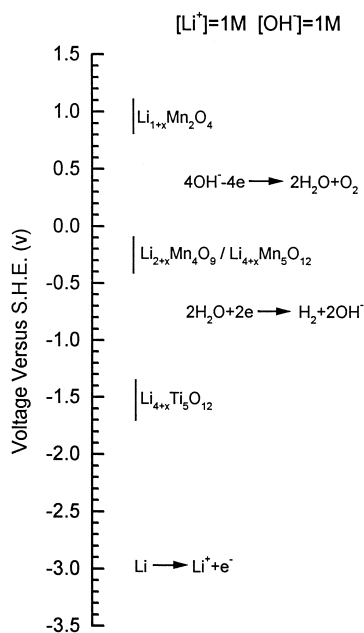


Fig. 2. Potentials of electrode materials, H_2 and O_2 evolution reactions vs. SHE, in 1 M OH^- and 1 M Li^+ aqueous electrolyte.

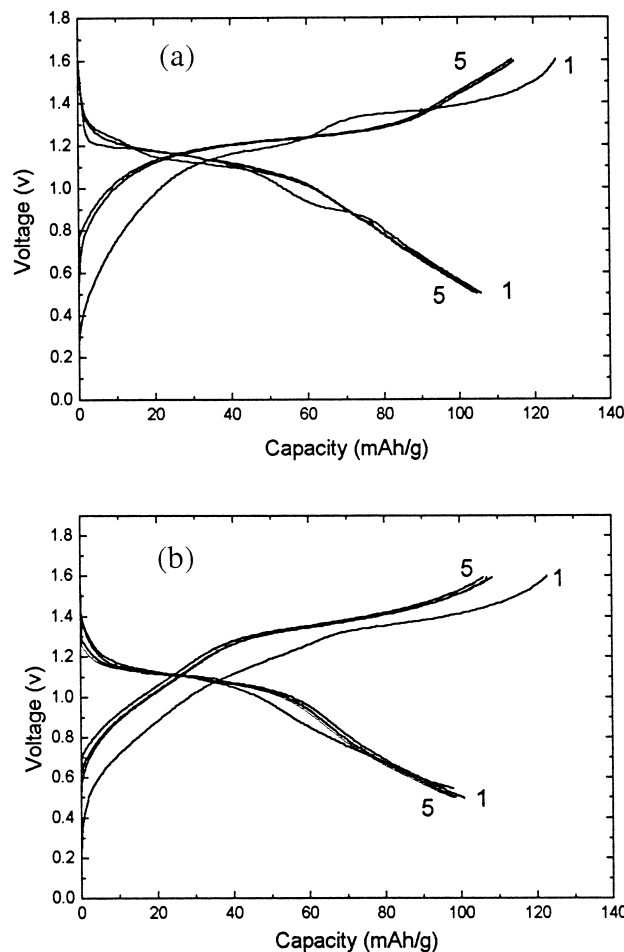
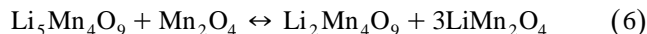


Fig. 3. Voltage profile of charge–discharge for aqueous lithium-ion cells; electrolyte 6 M LiNO_3 and 0.0015 M OH^- , Current density 1 mA cm^{-2} . (a) $\text{Li}_2\text{Mn}_4\text{O}_9/\text{LiMn}_2\text{O}_4$ cell; (b) $\text{Li}_4\text{Mn}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$ cell.

(5) are suppressed and Li-ion intercalation and de-intercalation become the predominant reactions.

The $\text{Li}_2\text{Mn}_4\text{O}_9/\text{LiMn}_2\text{O}_4$ and $\text{Li}_4\text{Mn}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$ cells used a 6 M LiNO_3 , 0.0015 M OH^- electrolyte. The cells were cycled at a current of 1 mA cm^{-2} between a lower voltage limit of 0.5 V and an upper voltage limit of 1.6 V. The ideal reactions in the $\text{Li}_2\text{Mn}_4\text{O}_9/\text{LiMn}_2\text{O}_4$ and $\text{Li}_4\text{Mn}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$ cells are:



During charging, the Li ions are extracted from the LiMn_2O_4 cathode host and inserted into the $\text{Li}_2\text{Mn}_4\text{O}_9$ or $\text{Li}_4\text{Mn}_5\text{O}_{12}$ anode. During discharge, Li ions deintercalate from the anode and intercalate into the cathode. The voltage profiles for charge/discharge are shown in Fig. 3. The cells deliver an average voltage of 1.1 V and a maximum capacity of 100 mA h g^{-1} (with respect to cathode active material). We note that the charge and discharge capacity is not in balance in Fig. 3. The charge capacity is almost 8–10% more than discharge capacity.

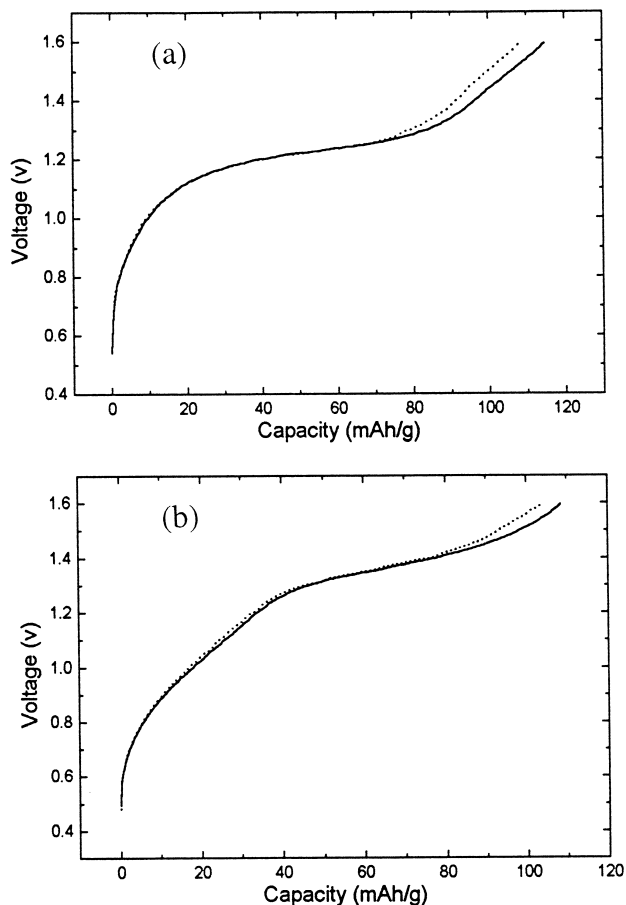


Fig. 4. Comparison of electrochemical behaviour of aqueous and non-aqueous lithium-ion cells. Current density 0.25 mA cm^{-2} . (a) $\text{Li}_2\text{Mn}_4\text{O}_9/\text{LiMn}_2\text{O}_4$ cell; (b) $\text{Li}_4\text{Mn}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$ cell.

This can be explained if a part of the current is used for the oxygen evolution reaction on the cathode during charging, which is similar to the behaviour in nickel–solidus cadmium batteries. About 10% of the first charging capacity is irreversible. This might be an intrinsic property of the low-temperature, synthesized, defect spinel $\text{Li}_2\text{Mn}_4\text{O}_9$ and $\text{Li}_4\text{Mn}_5\text{O}_{12}$, rather than of the aqueous electrolyte [9]. From the second cycle, the reversibility is good. Both cells deliver approximate 50% capacity under 1 V. The H_2 evolution reaction (Eq. (4)) is easy at low voltage, which induces instability of the discharge performance (see Fig. 3). Thus, electrochemical reaction of the lithium-ion system in aqueous electrolyte is more complicated than in non-aqueous electrolyte.

In order to determine whether the Li ion intercalation reaction is a predominant reaction in aqueous electrolyte cells, $\text{Li}_2\text{Mn}_4\text{O}_9/\text{LiMn}_2\text{O}_4$ and $\text{Li}_4\text{Mn}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$ cells with an organic electrolyte (1 M LiPF_6 in EC/DMC) were constructed and cycled between 0.5 and ~ 1.6 V at a constant current of 0.25 mA cm^{-2} . A comparison of the second charge voltage profile of aqueous and non-aqueous cells is given in Fig. 4. The dotted line is for the non-aqueous cell. The electrochemical behaviour of the cells is very

similar, except that the aqueous cells consume more charge capacity due to O_2 evolution. This demonstrates that Li ions shuttle in aqueous electrolyte in a manner equivalent to that in non-aqueous cells.

We also constructed a $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$ aqueous cell. This cell should deliver 2.4–2.5 V according to the data of Fig. 2. But, unfortunately, it could be charged to only 2.0 V in the first charging before failure. The H_2 evolution on the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode could be responsible for the cell failure due to the potential gap between the H_2 evolution reaction and the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode.

At present, $\text{Li}_2\text{Mn}_4\text{O}_9/\text{LiMn}_2\text{O}_4$ and $\text{Li}_4\text{Mn}_5\text{O}_{12}/\text{LiMn}_2\text{O}_4$ aqueous cells cannot compete with nickel/cadmium cells in terms of specific energy and electrochemical behaviour. Nevertheless, optimization of the synthesis of Li–Mn–O oxides might be expected to improve their electrochemical performance in aqueous electrolytes. Addition of organic and inorganic additives to the aqueous electrolyte can inhibit the hydrogen evolution reaction. Also, low-potential anode materials such as TiS_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are possible anodes for aqueous lithium-ion cells.

4. Conclusions

Aqueous lithium-ion systems would provide a very cost-effective technology for manufacturing. Accordingly, lithium-ion cells have been fabricated with spinel $\text{Li}_2\text{Mn}_4\text{O}_9$ or $\text{Li}_4\text{Mn}_5\text{O}_{12}$ as the anode and LiMn_2O_4 as the cathode in an aqueous electrolyte. In preliminary testing, the cells delivered $\sim 100 \text{ mA h g}^{-1}$ capacity at an average voltage of 1–1.1 V. Further work is required to determine the most appropriate electrode materials and electrolyte systems.

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