

Preparation and characterization of LiMn_2O_4 powders by the emulsion drying method

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Abstract

Spinel-type lithium manganese oxide is evaluated as a positive electrode material for lithium-ion batteries. Powders of lithium manganese oxide are prepared by the emulsion drying method which is simplified by omitting the toluene washing stage. We investigated the powder and electrochemical characteristics of LiMn_2O_4 with lithium salts such as LiNO_3 and $\text{LiOH} \cdot \text{H}_2\text{O}$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium ion battery; Lithium manganese oxide; Emulsion drying method; Lithium salt

1. Introduction

Portable electronic devices such as cellular telephones, camcorders and notebook computers which are called 3C are becoming smaller and lighter through the development of LSI and VLSI. Therefore, the demand for lighter and higher specific energy secondary batteries to power these devices has increased. The lithium-ion battery is considered to be the most suitable system.

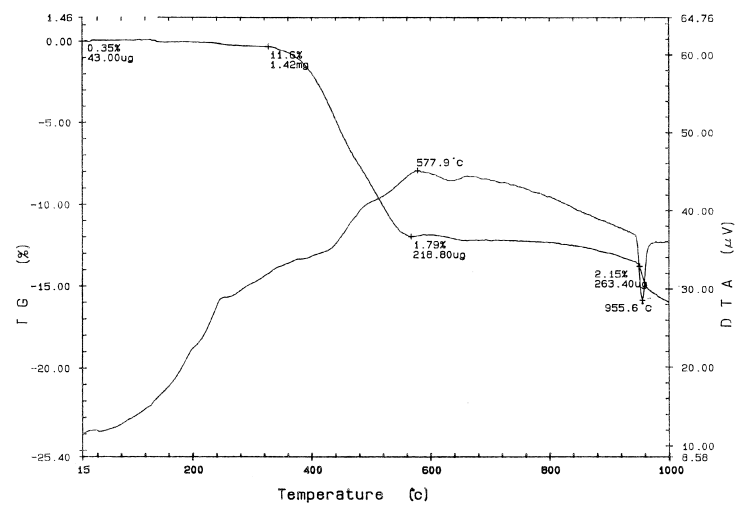
The voltage and cycleability of the lithium-ion battery depends on the choice of cathode materials, viz., LiCoO_2 , LiNiO_2 or LiMn_2O_4 . Among these materials, LiCoO_2 is now commercially used, but is very expensive. Thus, LiNiO_2 and LiMn_2O_4 are now being studied extensively as substitutes for LiCoO_2 . Nickel is cheaper than cobalt, and the theoretical capacity of LiNiO_2 is very high, but the material is difficult to prepare. LiMn_2O_4 is cheap and easy to prepare, but suffers capacity fading with use [1–6]. Therefore, the urgent research target for the latter material is to decrease the capacity fading.

LiMn_2O_4 prepared by solid-state reaction is not mixed homogeneously and thus may contain intermediate compounds such as Li_2MnO_3 , LiMnO_2 and MnO_2 result that in degradation of battery performance. Xia et al. [7–9] prepared very homogeneous, fine particle LiMn_2O_4 using

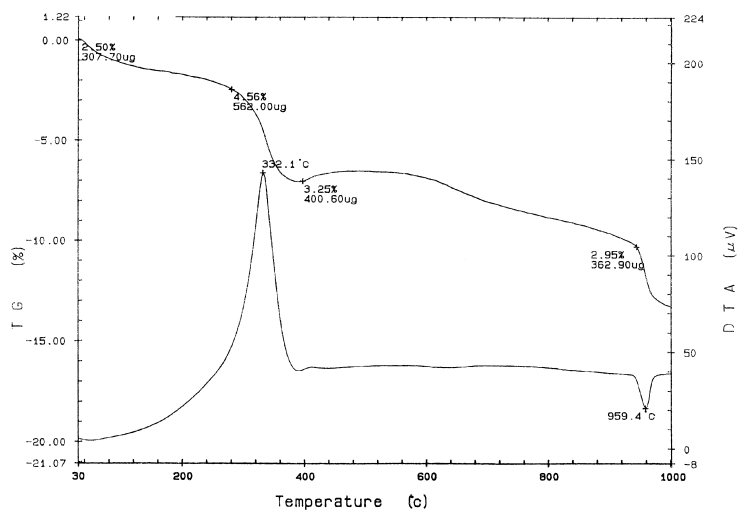
a melt-impregnation method and reported that the stoichiometric spinel LiMn_2O_4 delivered a large capacity with low capacity fading on cycling. Jiang and Abraham [10] synthesized micron-sized LiMn_2O_4 by dispersing Li_2CO_3 and MnCO_3 in hexane, and reported a good interface contact of LiMn_2O_4 /electrolyte/carbon and cycleability due to its small particle size and high crystallinity. Chen et al. [11] prepared powder of about 1 μm size by means of a wet chemical method. They reported that the diffusion rate was approximately 10 times faster than that for LiMn_2O_4 prepared by solid-state reaction. This suggested that the diffusion rate increases with decreasing particle size. Using the Pechini process, Liu et al. [12,13] prepared LiMnO_2 with small particle size at low temperature and obtained approximately 94% theoretical capacity. Therefore, in most cases, homogeneous and small particle size cathode materials made by the wet process exhibit good cycleability and high initial capacity.

Recently, Hwang et al. [14] reported that LiMn_2O_4 powders could be prepared by the emulsion drying method. They used LiCO_3 and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as starting materials, and dissolved them in diluted nitric acid to prepare an emulsion. The aim of the research reported here is to study the electrochemical characteristics of LiMn_2O_4 prepared by the emulsion drying method, but changing the starting materials and solvent. In this study, $\text{LiOH} \cdot \text{H}_2\text{O}$, LiNO_3 and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are used as starting materials, and are dissolved in distilled water. In general, a toluene washing stage has been adopted to remove the oil

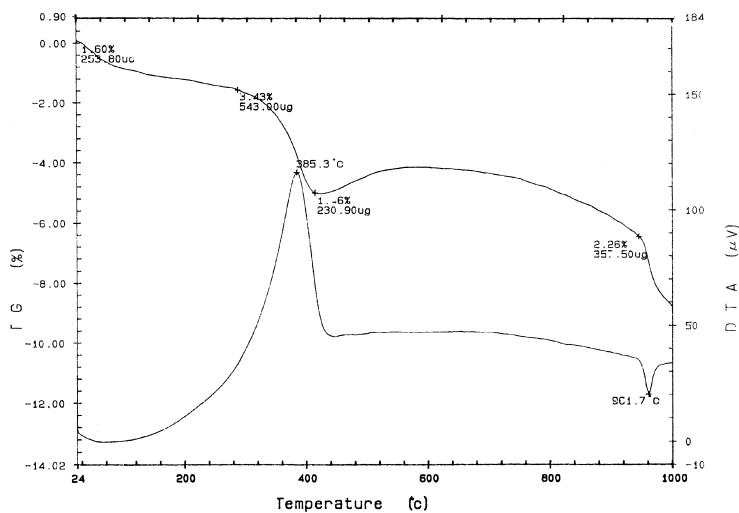
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(a)



(b)



(c)

Fig. 1. TG-DTA results of: (a) ball-milled mixture of Li_2CO_3 and MnO_2 , (b) LiMn_2O_4 as-received powder using $\text{LiOH} \cdot \text{H}_2\text{O}$; (c) LiMn_2O_4 as-received powder using LiNO_3 .

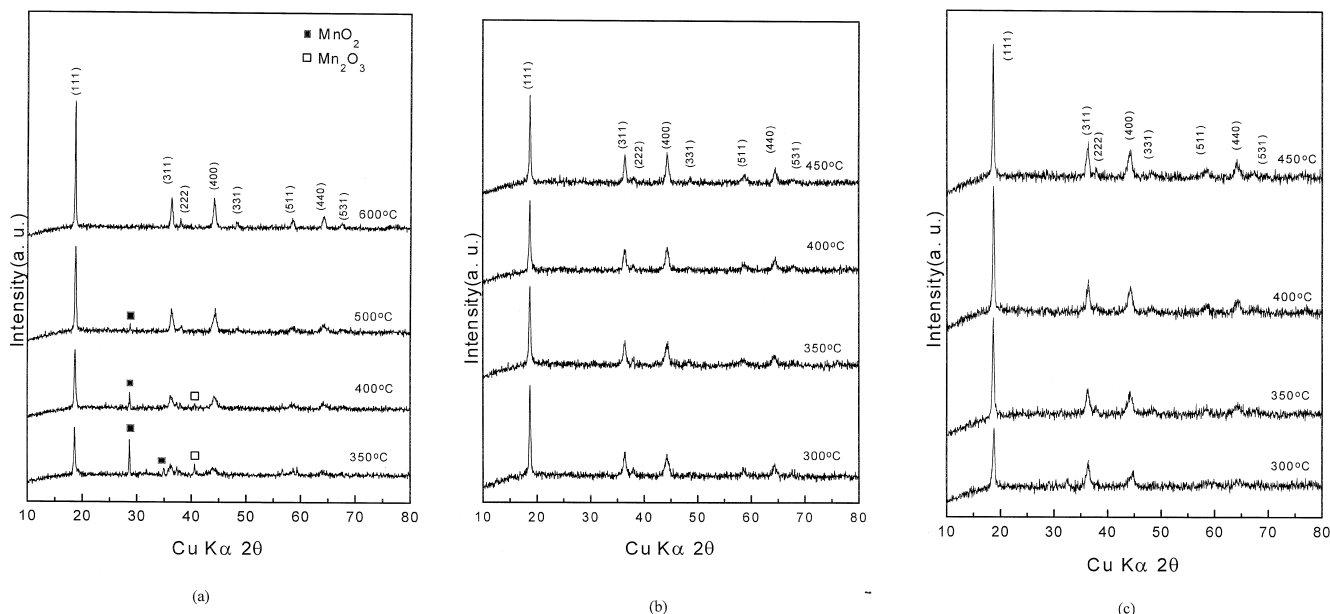


Fig. 2. X-ray diffraction patterns of samples calcined in weight loss region: (a) solid-state reaction method; (b) emulsion drying method using $\text{LiOH} \cdot \text{H}_2\text{O}$; (c) emulsion drying method using LiNO_3 .

phase from the powder precursor, but is omitted here to decrease the process time and reduce costs.

2. Experimental

An aqueous solution was prepared by dissolving $\text{LiOH} \cdot \text{H}_2\text{O}$ (Junsei, 95%), LiNO_3 (Kanto, 99%) and $\text{Mn}(\text{NO}_2)_3 \cdot 6\text{H}_2\text{O}$ (Junsei, 98%) in distilled water at a mole ratio of $\text{Li}:\text{Mn} = 1:2$ with mixing for 12 h. LiNO_3 is hygroscopic at room temperature. Weighing was conducted as soon as possible after preliminary heating in oven at 100°C for 3 h. An emulsifying agent named Tween #85 (Polyoxyethylene Sorbitan Trioleate) was mixed with kerosene, and stirred vigorously for 12 h. The aqueous solution was introduced to the oil mixture at a rate of 4 or 5 droplets per second, and was stirred at 1000 rpm by an impeller to produce an emulsion. The precursor powders were obtained by dropping the emulsion into hot kerosene (170 to 180°C). Water and kerosene contained in emulsion were distilled through a spiral-type condenser and the resultant, dark brown, powder sank to the bottom of the reaction vessel. The latter powder contained kerosene and Tween85 and was heated at 300°C for 15 min on a steel tray to remove the residual oil.

The LiMn_2O_4 was also prepared by a solid-state reaction using Li_2CO_3 (Aldrich, 99.997%) and MnO_2 (Aldrich, 99%) as starting materials, in order to compare the characteristics with LiMn_2O_4 prepared by the emulsion drying method. These reagents were mixed in an agate mortar. A stoichiometric mixture of powders was calcined at 850°C for 24 h.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA; MAC, Japan) were performed, to determine the thermal treatment temperature of the obtained precursor powders, with a heating rate of 20°C per minute in air. The powders were analyzed by means of an automated X-ray diffractometer (XRD; Rigaku, Japan) using $\text{K}\alpha$ radiation to identify the crystalline phases. The shape and size of the synthesized powders were measured with a scanning electron microscope (SEM; JEOL, Japan). The chemical compositions of the powders were determined by the atomic absorption spectroscopy (AAS).

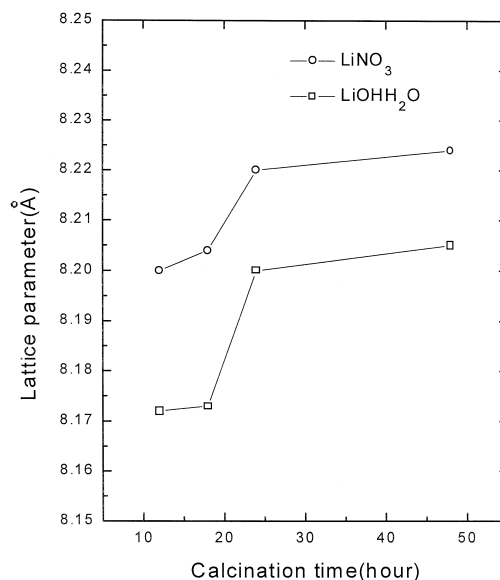


Fig. 3. Variation of lattice parameter with calcination time; powders calcined at 650°C .

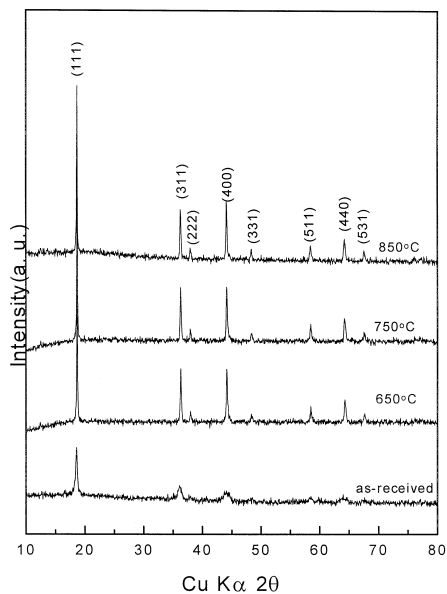


Fig. 4. X-ray diffraction patterns of powders: (a) as-received; (b) calcined at 650°C; (c) 750°C; (d) 850°C, for 24 h prepared by emulsion drying method using $\text{LiOH} \cdot \text{H}_2\text{O}$.

The electrochemical properties of the LiMn_2O_4 powders were investigated in an electrochemical cell which comprised a cathode, an anode and an electrolyte of 1 M LiPF_6 in EC (ethylene carbonate)–DEC (diethylene carbonate) solution. The cathode was prepared by mixing LiMn_2O_4 -based powders with 5 wt.% carbon black and 2 wt.% polyvinylidene fluoride (PVDF) in *n*-methyl-2 pyrrolidone (NMP) solution. The mixture was pasted on nickel exmet and dried at 120°C for 5 h in a vacuum oven.

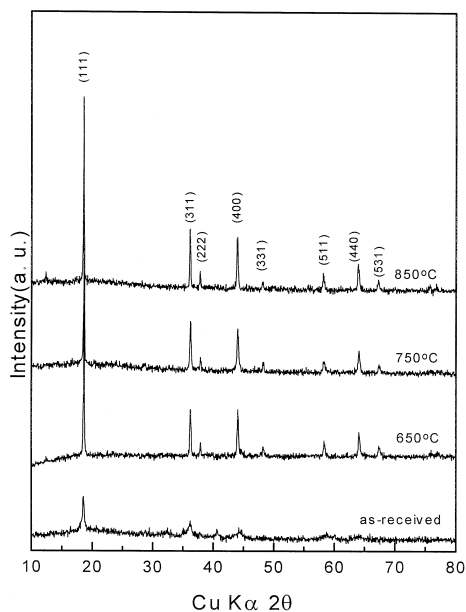


Fig. 5. X-ray diffraction patterns of powders: (a) as-received; (b) calcined at 650°C; (c) 750°C; (d) 850°C for 24 h prepared by emulsion drying method using LiNO_3 .

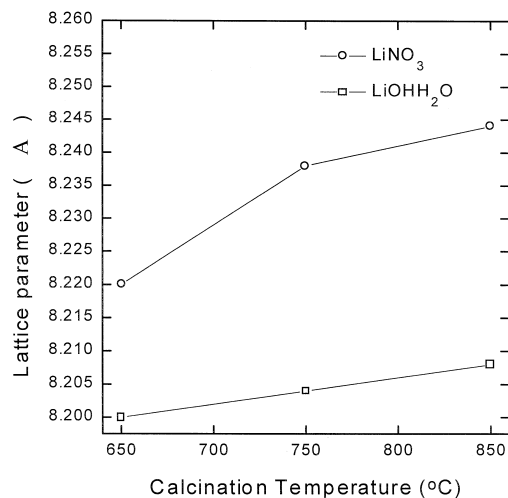


Fig. 6. Variation of lattice parameter with calcination temperature.

A typical cathode had dimensions of $1 \times 1 \text{ cm}^2$ and contained 15 mg of LiMn_2O_4 -based powder. The charge and discharge characteristics of the cathode were evaluated at a current of 0.1 mA cm^{-2} in the range 2.9 to 4.4 V Li/Li^+ . All electrochemical experiments were conducted at room temperature in a glove-box filled with high purity argon gas (99.999%).

3. Results and discussion

The results of TG-DTA analysis of the samples are presented in Fig. 1. The DTA data of the solid-state reaction are complicated, while these of the modified emulsion drying method are simple. The XRD results in the range 300 to 600°C for each preparation methods are given in Fig. 2. In case of the solid-state reaction, intermediate compounds are observed, but no intermediate compounds are found with the emulsion drying method. Therefore, with the emulsion drying method, the LiMn_2O_4 phase is directly synthesized without any intermediate compound. By contrast, Hwang et al. [14] reported the presence of intermediate compounds when using this method [14]. This difference may be caused by the use of different lithium salts and solvent.

The variation in the lattice parameter of LiMn_2O_4 as a function of calcination time at 650°C is shown in Fig. 3. The lattice parameter increased drastically after 18 h when using LiNO_3 or $\text{LiOH} \cdot \text{H}_2\text{O}$. This may be due to an

Table 1

Results of atomic absorption spectroscopic analysis of LiMn_2O_4 powders prepared from different lithium salts such as $\text{LiOH} \cdot \text{H}_2\text{O}$ and LiNO_3

| Used salt | Li (%) | Mn (%) | Chemical formula |
|----------------------------------------|--------|--------|------------------------------------------|
| $\text{LiOH} \cdot \text{H}_2\text{O}$ | 4.42 | 56.3 | $\text{Li}_{1.124}\text{Mn}_2\text{O}_4$ |
| LiNO_3 | 3.81 | 58.8 | $\text{Li}_{1.028}\text{Mn}_2\text{O}_4$ |

increase in the amount of Mn^{3+} (0.66 Å) for which the ionic radius is larger than that of Mn^{4+} (0.60 Å). Only a slight variation in the lattice parameter was observed after 24 h. Thus, in this research, the thermal treatment time was set at 24 h.

The X-ray diffraction patterns of each sample as a function of temperature are shown in Figs. 4 and 5. All diffraction peaks can be indexed by the cubic spinel structure. In all cases, no second phase peaks were detected. The variation of the lattice parameter is shown in

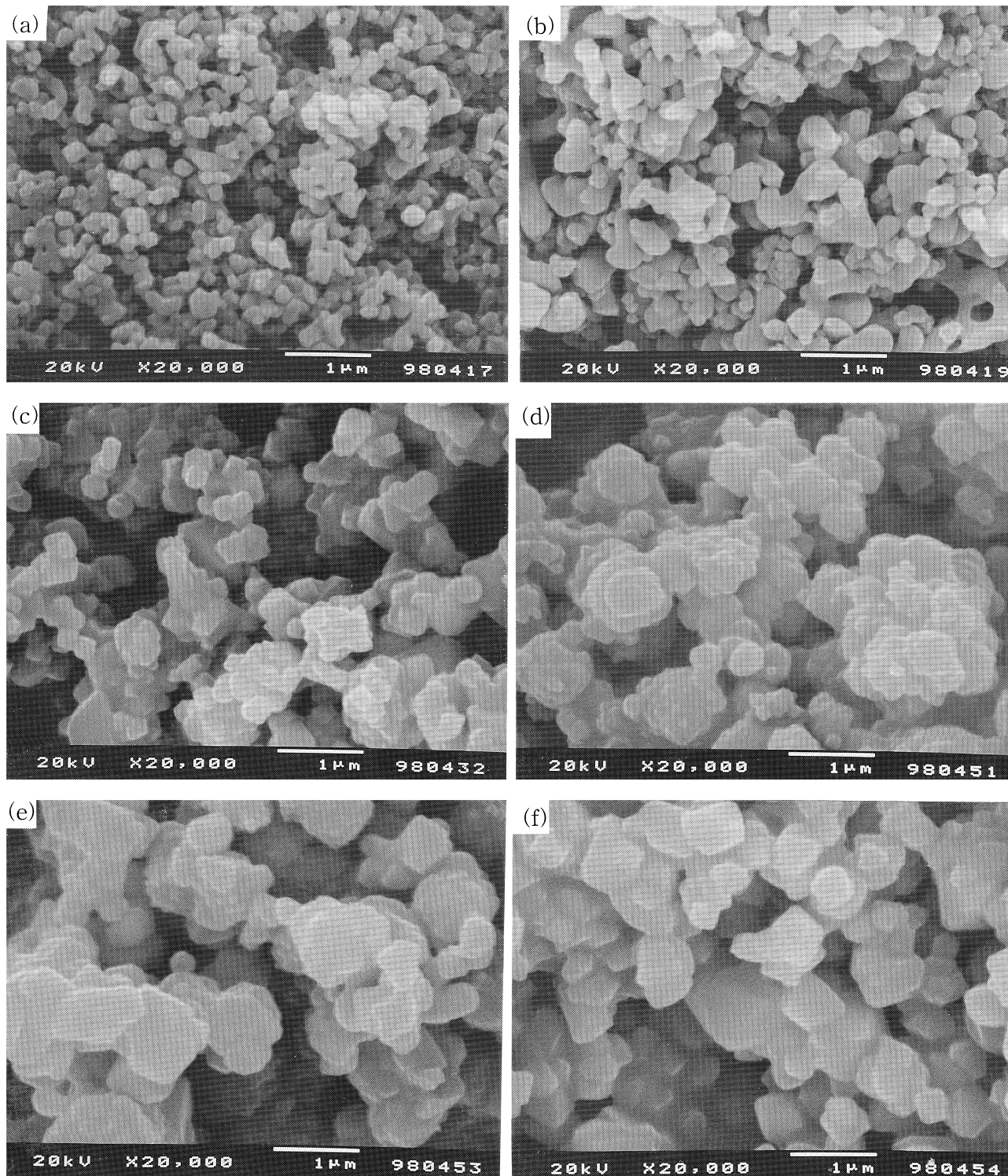


Fig. 7. Electron micrographs of sample prepared by emulsion drying method using $\text{LiOH} \cdot \text{H}_2\text{O}$ calcined at (a) 650°C, (b) 750°C and 850°C for 24 h; and using LiNO_3 calcined at (a) 650°C, (b) 750°C and 850°C for 24 h.

Fig. 6. The lattice parameter increases with temperature, irrespective of the lithium salt. Therefore, it can be deduced that the amount of Mn^{3+} may increase with temperature and cause an increase in the lattice parameter of $LiMn_2O_4$. One interesting point is that the lattice parameter of $LiMn_2O_4$ made from $LiNO_3$ is larger than that of $LiMn_2O_4$ which uses $LiOH \cdot H_2O$, irrespective of the calcination time and the temperature. The AAS results are

listed in Table 1. The chemical composition of the sample which used $LiOH \cdot H_2O$ was $Li_{1.124}Mn_2O_4$, and that which used $LiNO_3$ was $Li_{1.028}Mn_2O_4$. Cras et al. [15] reported that the lattice parameter decreases in a lithium excess composition due to an increase in the amount of Mn^{4+} . Thus, the results of chemical analysis are coincident with those of the lattice parameter, which show that the chemical composition of the powder deviates from stoichiometry

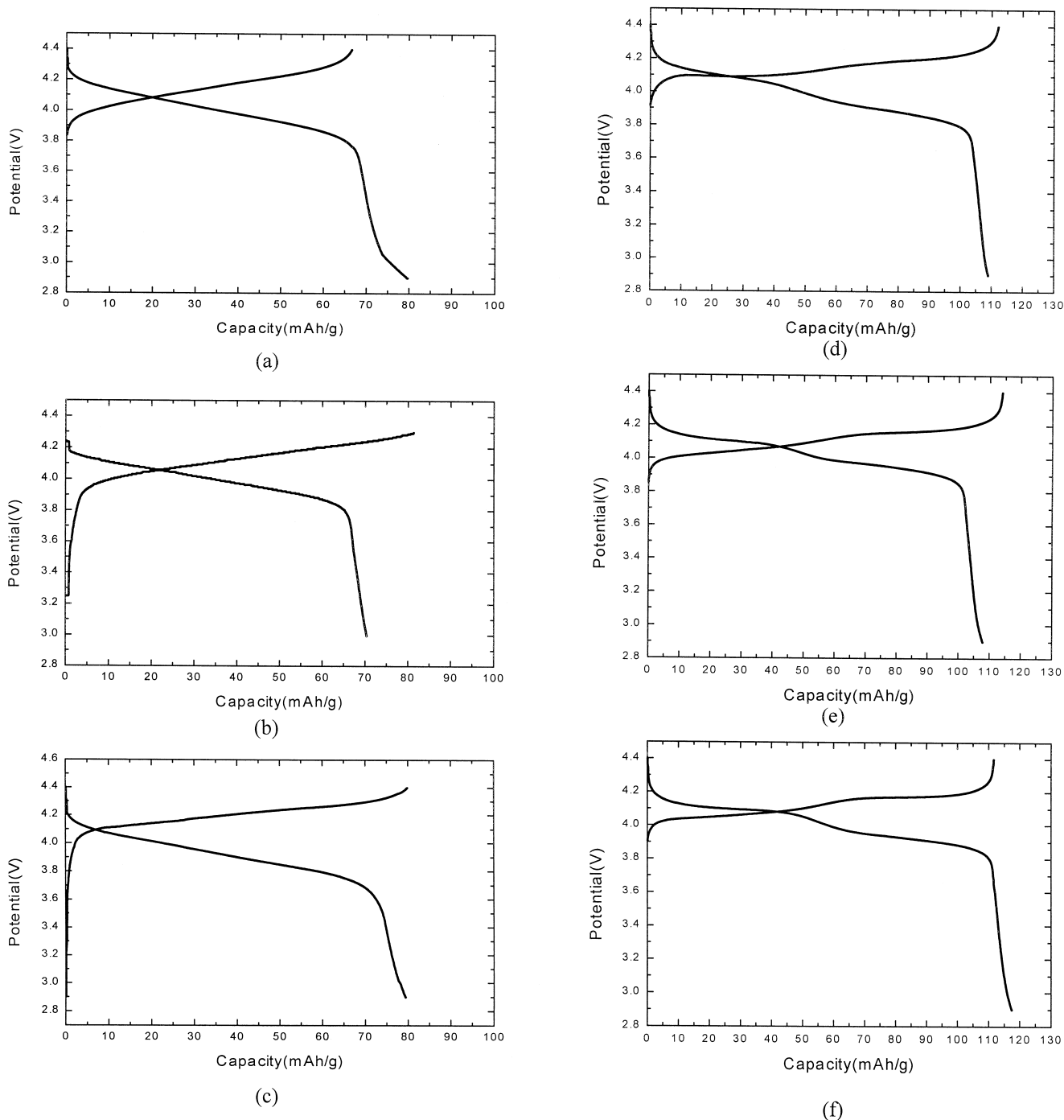


Fig. 8. Charge and discharge curves of cells of $Li/1M LiPF_6$ EC-DEC solution/ $LiMn_2O_4$ electrode calcined at (a) $650^\circ C$, (b) $750^\circ C$ and (c) $850^\circ C$ for 24 h using $LiOH \cdot H_2O$. (d) $650^\circ C$, (e) $750^\circ C$ and (f) $850^\circ C$ for 24 h synthesized by the emulsion drying method using $LiNO_3$.

when $\text{LiOH} \cdot \text{H}_2\text{O}$ is used as the lithium salt. This means that no complete reaction occurs between $\text{LiOH} \cdot \text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Scanning electron micrographs for the LiMn_2O_4 powders are presented in Fig. 7. Although grain growth occurs with calcination temperature, the size is less than $1 \mu\text{m}$ at all temperatures. When using LiCO_3 and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as starting materials, it has been reported [14] that the powder is needle like at low temperatures but becomes spherical with increase in temperature. In this study, however, the powders are spherical at low temperatures and become polygonal with increasing temperature.

The initial charge and discharge profiles of cells for all six samples are shown in Fig. 8. The cells were activated by charging first to 4.4 V and then were cycled between 2.9 and 4.4 V. The six samples can be clearly divided into two groups in terms of their charge and discharge performance. Samples using $\text{LiOH} \cdot \text{H}_2\text{O}$ provide a relatively low capacity of about 80 mA h g^{-1} , and do not display a plateau in the charge and discharge curves. By contrast, samples using LiNO_3 deliver an initial charge capacity of about 110 mA h g^{-1} , and give a two-step voltage profile. This difference is most likely due to the difference in chemical composition. Another characteristic found in samples using LiNO_3 is that the slope of the potential plateau in the 4-V region becomes flatter and its length increases with calcination temperature. This shape change in the potential plateau is considered [16] to be caused by an increase in the amount of active Mn^{3+} : the more the amount of active Mn^{3+} , the flatter and longer the plateau. This result is in agreement with the change in lattice parameter described in Fig. 6, in which the lattice parameter increases with temperature, which also implies an increase in the amount of active Mn^{3+} .

Therefore, it is found that LiMn_2O_4 can be successfully synthesized by the emulsion drying method by dissolving LiNO_3 in distilled water. More precise control is needed, however, in preparing LiMn_2O_4 by dissolving $\text{LiOH} \cdot \text{H}_2\text{O}$ in distilled water.

4. Conclusions

LiMn_2O_4 powders of less than $1 \mu\text{m}$ in size have been synthesized by the emulsion drying method by dissolving

LiNO_3 and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water. The powders have good electrochemical characteristics and deliver about 110 mA h g^{-1} at temperatures as low as 650°C . Powders using $\text{LiOH} \cdot \text{H}_2\text{O}$ produce a lithium-excess composition due to incomplete reaction between $\text{LiOH} \cdot \text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and result in a low initial capacity of about 80 mA h g^{-1} .

Acknowledgements

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