Emulsion-derived lithium manganese oxide powder for positive electrodes in lithium-ion batteries

Chung-Hsin Lu[*], Shang-Wei Lin

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, ROC

Abstract

Lithium manganese oxide ($LiMn_2O_4$) used as a positive-electrode material in lithium-ion batteries is prepared by a new water-in-oil emulsion process. An aqueous solution containing lithium and manganese cations is emulsified in kerosene by adding sorbitan monooleate as the surfactant. When the precursor solution is agitated by a magnetic mixer, impure products are obtained. $LiMn_2O_4$ is formed along with residual Mn_2O_3 at elevated temperatures because of insufficient dispersion and mixing of the reactive cations. When a homogenizer with a greater agitation speed is used, however, a well-mixed precursor solution is prepared, and pure $LiMn_2O_4$ with a Fd 3 m structure is synthesized after calcination at 800°C for 1 h. $LiMn_2O_4$ powder prepared by the homogenizer has higher crystallinity, smaller particle size, and narrower size distribution than that prepared by the magnetic stirrer. Compared with powder prepared by the solid-state method, the $LiMn_2O_4$ powder exhibits smaller particle size and less agglomeration. Moreover, the emulsion process significantly shortens the heating time required. The prepared $LiMn_2O_4$ powder has a high discharge capacity (120.4 mA h g^{-1}) on the first cycle and good cycleability. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Battery; Emulsion; Lithium manganese oxide; Synthesis; Discharge capacity

1. Introduction

Recently, lithium-on batteries have been widely adopted as the most promising portable energy source in electronic products because of their high working voltage, high specific energy, and long shelf-life [1–4]. In these batteries, oxides such as $LiCoO_2$, $LiNiO_2$ or $LiMn_2O_4$ are used as the as the positive electrodes and carbon as the negative electrode. Among these cathode materials, $LiMn_2O_4$ has been intensively developed on account of its inexpensive material cost, acceptable environmental characteristics, and better safety compared with $LiCoO_2$ [5,6]. To date, much effort has been devoted to synthesize $LiMn_2O_4$ powders for enhancing their cycleability and specific capacity [7–9].

$LiMn_2O_4$ powders are usually prepared by a solid-state reaction [8–11]. In this process, oxides or carbonates containing manganese and lithium cations are physically mixed by mechanical methods, and the mixtures are calcined at elevated temperatures, which range from 600 to 1100°C. Usually, a long calcination time (about 24–48 h) is required for synthesizing $LiMn_2O_4$ powders because of the insuffi-

cient reactivity and inhomogeneous dispersion of the mixtures. The long calcination process causes coarsening of the powders as well as deviation in composition due to evaporation of lithium species. In addition, a long calcination time is very energy-consuming.

Various solution methods, such as sol–gel [12,13], precipitation [14], and freeze–drying [15] processes, have also been used to prepare $LiMn_2O_4$ powder. Recently, a new kind of emulsion process has been developed [16,17]. In this process, an aqueous phase containing manganese and lithium cations is dispersed in an oil-phase to form micelles. With calcining precursors derived from the micelles, $LiMn_2O_4$ powders can be obtained. Unfortunately, a long calcination time (24–48 h) is still required. Probably, due to the long calcination time and insufficient dispersion of the aqueous phase in the oil-phase, the obtained powders exhibit serious agglomeration and large grain size (>1 μm). This kind of morphology is unfavorabIe as regards the electrochemical characteristics of batteries.

In order to reduce the required reaction time for synthesizing pure $LiMn_2O_4$ powder, and also to decrease the particle size, a new water-in-oil emulsion process has been developed in our laboratories. Lithium and manganese acetates instead of the nitrates are used as the raw materials for preparing the aqueous phase in order to avoid the

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* Corresponding author. Tel.: +886-2-2365-1428;
fax: +886-2-2362-3040.
E-mail address: chlu@ccms.ntu.edu (C.-H. Lu).

production of NO or NO_2 gases during the heating processes. A homogenizer is used to disperse efficiently the aqueous phase into the oil-phase in order to form tiny micelles. The water/oil volume ratio is reduced for enhancing the stability of micelles. The effects of the agitation method on the phase purity, and the morphology of the obtained powders are investigated. The phase development and microstructural evolution of the heated specimens are analyzed. The capacity and cycleability of the obtained powders are also examined.

2. Experimental

In the emulsion process, stoichiometric amounts of lithium and manganese acetates were mixed in de-ionized water to prepare the aqueous phase. The concentration of total cations was 2 M. After the reactants were completely dissolved, kerosene (the oil-phase) was added to the aqueous solution, followed by adding sorbitan monooleate (5 wt.%) to stabilize the water-in-oil emulsion solution. The water:oil volume ratio was fixed at 1:5. Either, a magnetic stirrer or a homogenizer was used to agitate the mixed solution for 1 h to obtain a stable emulsion solution. The rotation rates of the magnetic stirrer and the homogenizer were 600 and 7200 rpm, respectively. The prepared emulsion solution was dropped into hot kerosene to evaporate the aqueous phase. This produced a brown gel. After drying the gel at 300°C for 1 h, the precursors of $LiMn_2O_4$ were obtained. The precursors were calcined at elevated temperatures for 1 h for synthesizing $LiMn_2O_4$. The heated specimens were examined by X-ray powder diffraction to identify the formed phases. Microstructures and particle sizes of the resulting powder were observed by scanning electron microscopy (SEM). The electrochemical behavior of the obtained $LiMn_2O_4$ powder was examined in a two-electrode cell. The electrochemical cell consisted of a $LiMn_2O_4$-based composite as the positive electrode, lithium foil as the negative electrode, and an electrolyte of 1 M $LiPF_6$ in a 1:1 (volume ratio) mixture of EC:DMC. The cell was charged and discharged at 0.2 mA cm^{-2} within the potential range 3–4.3 V.

3. Results and discussion

3.1. Effect of agitation process on synthesizing $LiMn_2O_4$

The emulsion-derived precursors prepared with a magnetic stirrer at 600 rpm were calcined at different temperatures for 1 h to synthesize $LiMn_2O_4$. The XRD patterns of the as-dried powders and heated samples are illustrated in Fig. 1. After drying at 300°C, broad peaks of $LiMn_2O_4$ are observed. These indicate the initial formation of the spinel structure. As the heating temperature rises, the crystallinity of $LiMn_2O_4$ increases. At a temperature above 500°C,
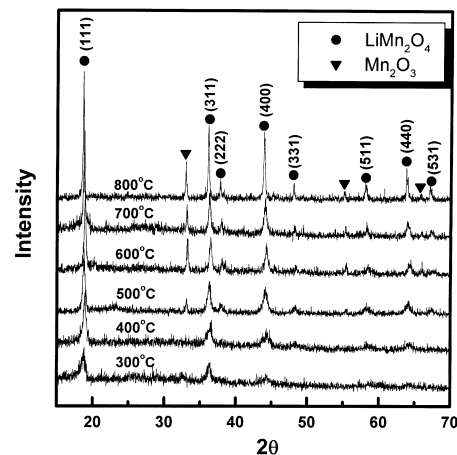

Fig. 1. X-ray diffraction patterns of calcined $LiMn_2O_4$ powders derived from the emulsion process, emulsion solution prepared with a magnetic stirrer.

however, a secondary phase-Mn_2O_3 begins to form. With a rise in heating temperature, the content of Mn_2O_3 significantly increases. Even after heating up to 800°C, a large amount of Mn_2O_3 still coexists with $LiMn_2O_4$. Therefore, the single phase of $LiMn_2O_4$ cannot be obtained, when a magnetic stirrer is used to prepare the emulsion solution.

The morphology of the powders prepared by the above emulsion process after calcining at 400 and 700°C is shown in Fig. 2(a and b), respectively. In Fig. 2(a), an uniform microstructure is observed, and it is found that spherical powders with a size distribution, which ranges from 0.1 to 0.15 μm are formed. On the other hand, when the calcination temperature is raised to 700°C (Fig. 2(b)), the microstructure becomes non-uniform, and a large amount of rod-like particles is found to coexist with the spherical particles. According to the XRD patterns in Fig. 1, these rod-like particles result from the formation of Mn_2O_3.

In order to obtain the pure $LiMn_2O_4$ phase, a homogenizer with 7200 rpm was used to prepare the emulsion solution. After calcining the emulsion-derived precursors at elevated temperatures for 1 h, the calcined powders were examined by XRD. The XRD patterns show (Fig. 3) that monophasic $LiMn_2O_4$ powder without the existence of impure Mn_2O_3 is successfully synthesized at all calcination temperatures After heating at 800°C, well-crystallized $LiMn_2O_4$ is produced. The diffraction peaks of the resulting powders are identical to those recorded in JCPDS no. 35–782 [18]. This shows that $LiMn_2O_4$ with a Fd $\bar{3}$ m structure is obtained. Compared with the previous emulsion process [16], the reaction time for synthesizing $LiMn_2O_4$ powders is markedly shortened from 48 to 1 h. The decrease in the reaction time, in this study, is attributed to the enhanced reactivity and improved homogeneity of the constituent cations in the precursors prepared by the emulsion process using a homogenizer with high dispersion power. The effect of using the emulsion process on curtailing the reaction time is similar to that reported in our previous study of the synthesis of $LiNiO_2$ [19].
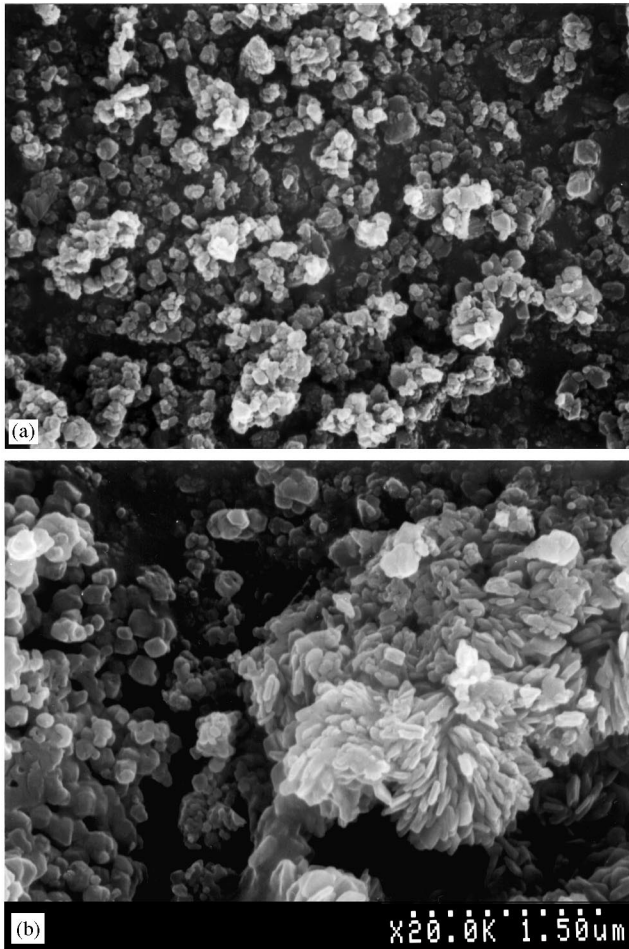
Fig. 2. Electron micrographs of emulsion-derived $LiMn_2O_4$ powders calcined at (a) 400 and (b) 700°C, emulsion solution prepared with a magnetic stirrer.
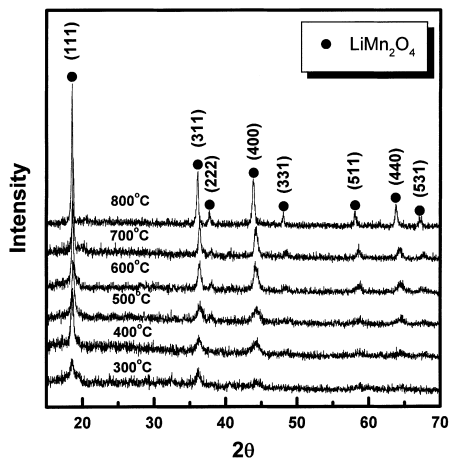
From the above results, the agitation process is found to affect significantly the formation of $LiMn_2O_4$ powder. During agitating the emulsion solution, the magnetic stirrer with low agitation rate and low dispersion power cannot disperse efficiently the aqueous phase into the oil-phase. Therefore, the formed micelles are not stable in the oil-phase. When the unstable emulsion drops are dried, the composition of the formed powders tends to become inhomogeneous, and some regions only consist of manganese cations. Therefore, in the calcination process, these manganese cations directly react with oxygen rather than lithium ions to form manganese oxide at elevated temperatures. By contrast, the homogenizer can well disperse the aqueous phase into the oil-phase to form stable emulsion drops with homogeneous chemical distribution. Thus, pure $LiMn_2O_4$ is synthesized from the precursors prepared by the homogenizer.

3.2. Effect of agitation process on crystallite size and morphology of $LiMn_2O_4$ powder

The effect of calcination temperature on the crystallite size of $LiMn_2O_4$ powder prepared by the two different agitation processes is shown in Fig. 4. The crystallite size of the specimens was calculated from the width at the half maximum of the (1 1 1) peak by the Scherrer formula [20]. The rise in the calcination temperature markedly increases the crystallite size in both processes. As the calcination temperature increases from 300 to 800°C, the crystallite size of the power prepared by the homogenizer increases from 15 to 47 nm, and that prepared by the magnetic stirrer increases from 18 to 54 nm. At the same calcination temperature, the powder prepared with the homogenizer exhibits smaller crystallite size than that produced with the magnetic stirrer.

The diffraction intensities of powders obtained by the two agitation processes at different calcination temperatures are compared in Fig. 5. The diffraction intensity of plane (1 1 1)
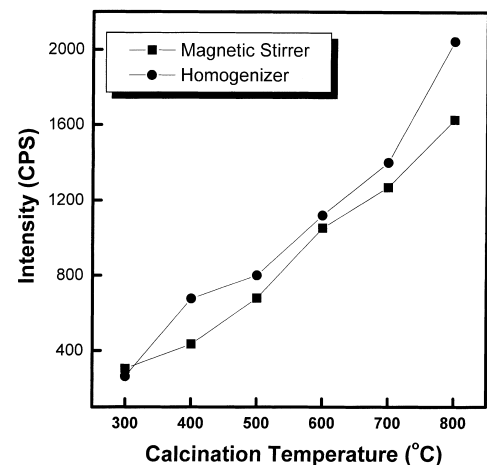

Fig. 3. X-ray diffraction patterns of calcined $LiMn_2O_4$ powders derived from emulsion process, emulsion solution prepared with a homogenizer.

Fig. 4. Intensity of diffraction peak (1 1 1) for $LiMn_2O_4$ powders prepared by two agitation processes at various calcination temperatures.
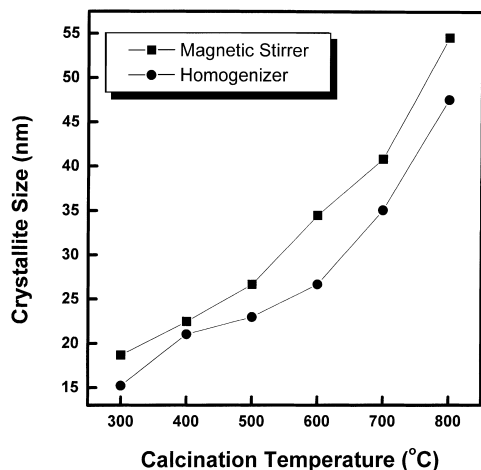
Fig. 5. Crystallite size of $LiMn_2O_4$ powders prepared by two agitation processes at various calcination temperatures.
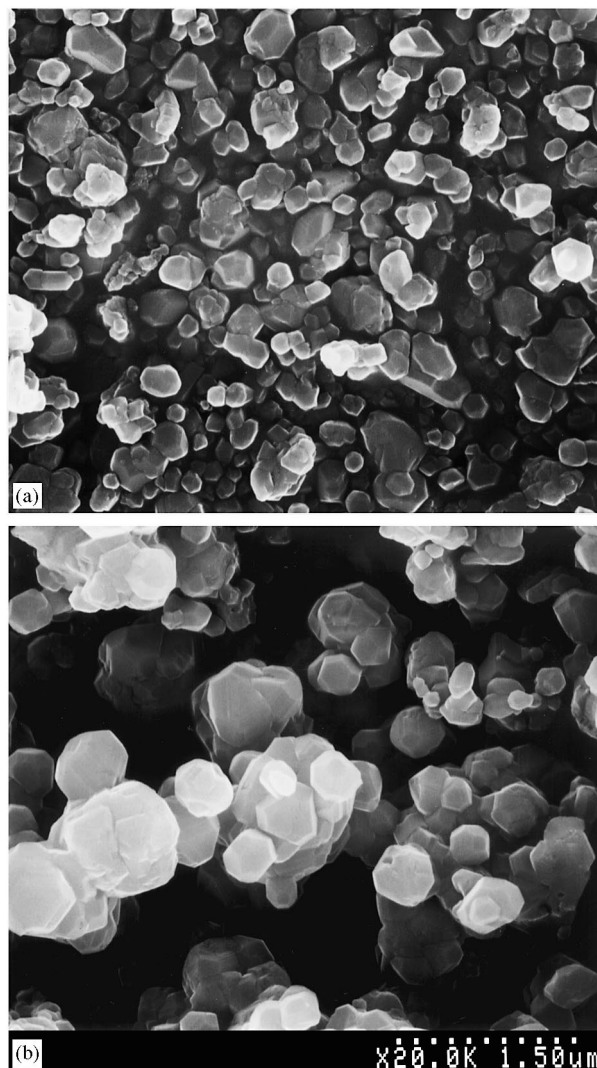

Fig. 6. Electron micrographs of emulsion-derived $LiMn_2O_4$ powders calcined at 800°C, emulsion solution prepared by (a) homogenizer and (b) magnetic stirrer.

was measured for each sample. The intensities of the powders derived from both processes increase with increase of the calcination temperature. This indicates that the crystallinity of the powders in both processes increase with calcination temperature. Furthermore, it is found that at the same calcination temperature, $LiMn_2O_4$ powder prepared with the homogenizer has a higher diffraction intensity than that prepared with the magnetic stirrer. This implies that the former powder exhibits higher crystallinity than the latter one.

Electron micrographs of $LiMn_2O_4$ powder calcined at 800°C using two different agitation processes are shown in Fig. 6. As seen in Fig. 6(a), the powder obtained using the homogenizer exhibits a homogeneous morphology with a dispersed state. The particle size of this powder ranges from 0.1 to 0.2 μm. On the other hand, the particle size of the powder prepared with the magnetic stirrer ranges from 0.1 to 0.4 μm (Fig. 6(b)). Comparing these two powders, the former has a smaller particle size with a narrower size distribution, and is less agglomerated. In addition, the particle size of $LiMn_2O_4$ powders obtained, in this study, is much smaller than those obtained from other emulsion processes [16,17].

According to the above results, it is evident that the agitation process for preparing emulsion solution influences not only the formation of pure phase, but also the crystallite size and morphology of the resulting powders. Since the magnetic stirrer cannot sufficiently and evenly disperse the aqueous phase, the formed micelles are unstable. These unstable micelles tend to coalesce together to produce large emulsion drops. Therefore, the formed powders exhibit large particle size and non-uniform size distribution. When a homogenizer is used to agitate the solution, the high level of agitation generates a strong turbulent flow to form tiny stable micelles in the emulsion system. The decrease in the size of micelles improves the reactivity of the reactants as well as the nucleation rate of $LiMn_2O_4$. Thus, $LiMn_2O_4$

powder with high crystallinity and small crystalline size is obtained.

3.3. Electrochemical properties

Charge–discharge curves for $LiMn_2O_4$ powder prepared with the homogenizer are presented in Fig. 7. (Note, the powder prepared with the magnetic stirrer was not measured in the cell test on account of the coexistence of Mn_2O_3.) Both the charge and discharge curves contain two distinct plateau at around 4 V and about l00 mV apart. These are typical electrochemical characteristics of $LiMn_2O_4$. It signifies that $LiMn_2O_4$ with a spinel structure has been successfully synthesized by the emulsion process. From a previous study [10], the upper plateau region of discharge curve represents a two-phase equilibrium between λ-MnO_2 and $Li_{0.5}Mn_2O_4$, while the second plateau represents a phase equilibrium between $Li_{0.5}Mn_2O_4$ and $LiMn_2O_4$.
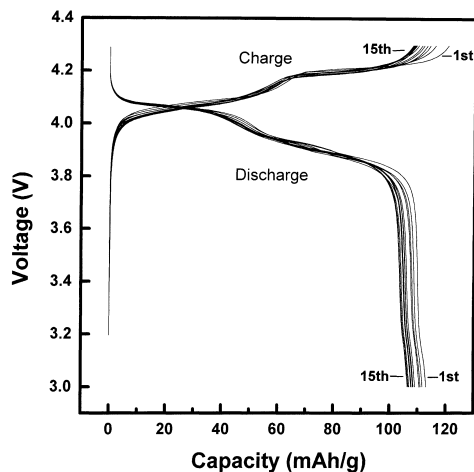
Fig. 7. Charge and discharge curves of emulsion-derived $LiMn_2O_4$ powder at current density of $0.2 \, \text{mA cm}^{-2}$.

The relationship between the specific capacity and the cycle number are plotted in Fig. 8(a). In the first cycle, the charge and discharge capacities are 120.4 and 113.1 mA h g^{-1}, respectively. After 15 cycles, the discharge capacity, slowly reduces with cycling, but still retains 94% of the initial value. Thus, the prepared powder exhibits good cycleability. The coulomb efficiency of $LiMn_2O_4$ is presented in Fig. 8(b). This efficiency is defined as the discharge capacity divided by the charge capacity. The efficiency on the first cycle is 94%, which suggests that lithium ions extracted from the spinel structure do not completely intercalate into the positive electrode. The efficiency increases with the cycle number, however, and becomes 99.4% after 15 cycles. Thus, the amount of intercalated lithium ions becomes gradually equal to that of de-intercalated lithium ions in $LiMn_2O_4$. From the above results, it is found that the $LiMn_2O_4$ powder prepared by the emulsion process exhibits

satisfactory capacity and good cycleability for use in lithium-ion secondary batteries.

4. Conclusions

A new emulsion process has been developed for synthesizing monophasic $LiMn_2O_4$ powder. In this process, an aqueous solution containing lithium and manganese cations is emulsified in kerosene by adding sorbitan monooleate as the surfactant. Using the magnetic stirrer to mix the precursor solution, results in the production of impure materials which consist of Mn_2O_3 and $LiMn_2O_4$ at temperatures above 500°C. When the mixing and the homogeneity of the precursor solution are improved using a homogenizer, monophasic $LiMn_2O_4$ powder is successfully synthesized after calcination at 800°C for 1 h. The heating time is much shorter than that required in the solid state reaction. In addition to the phase purity, the mixing process for preparing emulsion solution also influences the crystallinity, crystallite size, and morphology of the prepared powder. In comparison with powder prepared with the magnetic mixer, the powder synthesized using the homogenizer exhibits higher crystallinity, smaller crystallite sizes, less agglomeration, and finer particle size. The prepared $LiMn_2O_4$ powder has a high initial discharge capacity (120.4 mA h g^{-1}) and exhibits good cycleability.
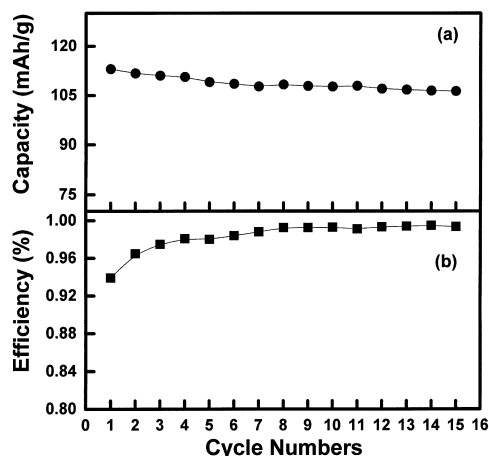
Fig. 8. (a) Discharge capacity and (b) coulomb efficiency vs. cycle number for emulsion-derived $LiMn_2O_4$ powder at current density of $0.2 \, \text{mA cm}^{-2}$.

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