



Powder synthesis and electrochemical properties of LiMn_2O_4 prepared by an emulsion-drying method

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Abstract

Spinel LiMn_2O_4 powder, used as a cathode material for lithium-ion batteries, is prepared from a water-in-oil emulsion by loading the lithium and manganese ions into the aqueous phase. For optimum electrochemical properties, both the heating temperature and the time are controlled. As the heating temperature is increased, the particles grew linearly and the specific surface-area is reduced. The LiMn_2O_4 phase starts to form at 450°C and is produced up to 750°C for 48 h without the development of other phases. Optimum heating conditions, based on the resulting electrochemical properties, were 750°C and 850°C for 48 h. The capacities of the powders are 112 and 115 mA h g^{-1} , respectively. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Cathode materials, such as LiCoO_2 , LiNiO_2 and LiMn_2O_4 , for lithium secondary batteries, have been studied intensively [1–6]. LiCoO_2 is a favoured material because of its electrochemical properties, but it is relatively expensive [7]. Although LiNiO_2 is comparatively cheap, this material is difficult to fabricate. By comparison, LiMn_2O_4 has economic and environmental advantages. There are various stoichiometric spinels in Li–Mn–O system, such as LiMn_2O_4 , $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and LiMn_5O_8 [8]. The chemical composition of the synthesized powders is changed by processing conditions, i.e., heating temperature and atmosphere [9], and the change affects the electrochemical properties of powders. Solid-state reaction [10,11], melt-impregnation [12,13], the Pechini process

[14] and sol–gel methods [15,16] have been used to prepare LiMn_2O_4 powder with optimized electrochemical properties.

In the present investigations, the emulsion-drying method, which is a simple and easily controlled powder preparation process, has been used to synthesize LiMn_2O_4 materials. The powder characteristics and electrochemical properties of LiMn_2O_4 materials thus synthesized, have been examined in detail.

2. Experimental

An aqueous solution was prepared by dissolving lithium carbonate, Li_2CO_3 , and manganese nitrate hexahydrate, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in a dilute nitric acid of the mole ratio 1 Li per 2 Mn. The aqueous solution was dropped into a mixture of an emulsifying agent and oil, with stirring at room temperature, to make an emulsion. Kerosene and Tween 85 were used as the oil phase and the emulsifying agent, respectively. The volume ratio of the kerosene, the

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aqueous solution and the emulsifying agent, was 55:30:15. The resulting emulsion was a water-in-oil type, which means that droplets of the aqueous solution were dispersed in the oil phase. After storing for 6 h, the emulsion was treated with an ultrasonic agitator for 10 min to reduce the size of the aqueous droplets. Precursor powders were obtained by the dropwise addition of the emulsion to hot kerosene. During this process, the temperature was maintained at 200°C. The precursor powders were washed with toluene to remove any residual oil phase, and dried at 100°C for 5 h in air. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed in air at a heating rate of 10°C/min in order to determine the thermal properties of the powder. The precursor powders were heated from 450°C to 950°C and 750°C for 5–48 h to elucidate the optimum heating condition for the formation of a pure, spinel, LiMn_2O_4 phase.

X-ray diffraction (XRD) analysis using $\text{CuK}\alpha$ radiation was performed on synthesized powders in order to identify the crystalline phase. The particle-size distribution was measured by a laser scattering, particle-size analyzer, and the particle shape of some powders was observed with a scanning electron microscope (SEM). The specific surface-area was determined by the Brunauer–Emmett–Teller (BET) method and the total pore volume was measured using N_2 adsorption.

The effect of heating temperature on the electrochemical properties of LiMn_2O_4 powder was investigated. The electrochemical cell consisted of a cathode, counter electrode, an anode of Li foil (CFM), and an electrolyte of 1 M LiClO_4 in propylene carbonate (PC) solution. The cathode was prepared by mixing LiMn_2O_4 -based powders with 5 wt.% carbon black and 2 wt.% polyvinylidene fluoride (PVDF, Aldrich) in 1-Methyl-2-pyrrolidone (Aldrich) solution. The mixture was pasted on 316 stainless steel ex-met and dried at 120°C for 1 h in vacuum oven. A typical cathode had an area of 1 cm^2 and contained 15 mg of LiMn_2O_4 -based powder. The charge and discharge characteristics of the cathode were evaluated at the C/5 rate over the voltage range 2.9 to 4.3 V vs. Li/Li^+ .

3. Results and discussion

The TG-DTA curves for raw powders obtained by emulsion-drying and heat-treatment powder at 200°C for 10 h are shown in Figs. 1 and 2, respectively. The weight loss of the raw powder is due to the evaporation of residual water and organics, and continued up to 500°C. After heat-treatment at 200°C, a rapid change in weight occurs between 240 and 360°C, and slowly decreased over this range. It is assumed that the formation of the LiMn_2O_4 phase starts at a lower temperature than 400°C, as will be confirmed later from XRD data.

The XRD patterns of powders heated at 750°C for different times are presented in Fig. 3. Peaks of the

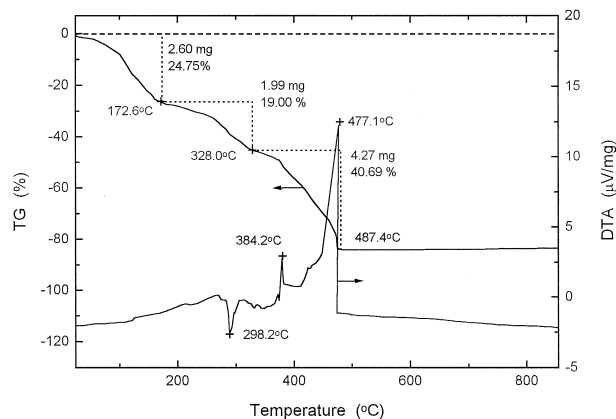


Fig. 1. TG-DTA curve for raw powder prepared by the emulsion-drying method.

LiMn_2O_4 phase are present in powder heated for 5 h at 750°C, and the Mn_2O_3 phase is also detected. The peak intensity of the latter phase gradually decreases with prolonged heating times, and is not detected in the powder heat-treated at 750°C for 48 h. From this result, the heating time is fixed to 48 h in our work.

The XRD patterns of powders dried and heat-treated at various temperatures in air are given in Fig. 4. Raw powder after emulsion-drying consists of imperfect LiMn_2O_4 , MnO , and Li_2CO_3 . After heat-treatment at 450°C for 48 h, the broad peak of LiMn_2O_4 phase is mainly observed. Thus, the formation of the spinel LiMn_2O_4 structure is not complete. As the heating temperature increased, the broad peak of the LiMn_2O_4 splits and intermediate phases are observed in the powder heated at 650°C. Only LiMn_2O_4 peaks are found at 750°C, but some minor peaks of a secondary phase are detected at a temperature above 850°C.

Electron micrographs of the powders are shown in Fig. 5. The powder heated at 450°C is acicular (Fig. 5a). As the heating temperature increased, the morphology of powder changes from needle-like to spherical, and the particle size is increased. The particle in powders heated at 850°C

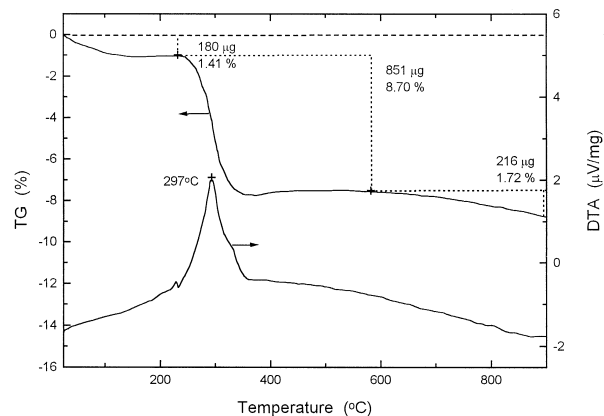


Fig. 2. TG-DTA curve for emulsion dried powder heated at 200°C for 10 h.

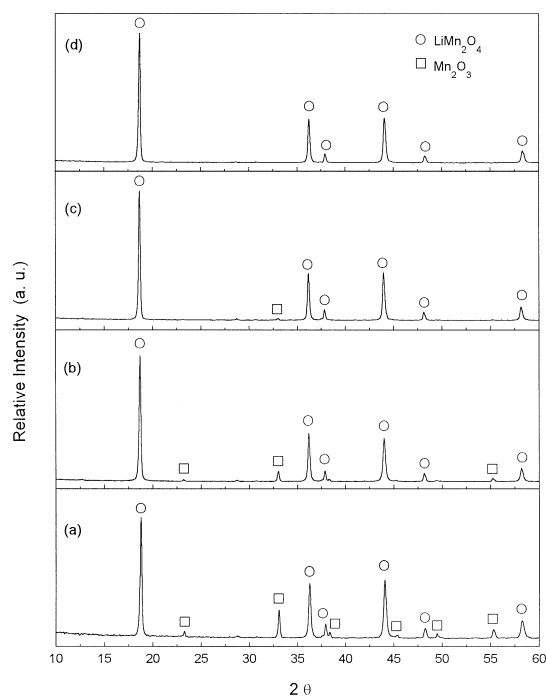


Fig. 3. X-ray diffraction patterns for LiMn_2O_4 powder heated at 750°C for: (a) 5 h; (b) 10 h; (c) 20 h; (d) 48 h.

(Fig. 5e) are highly uniform in size, and become square-shaped in powder heated at 950°C (Fig. 5f).

The variation of mean particle-size with heating temperature is shown in Fig. 6. The LiMn_2O_4 particles grow linearly. The specific surface-area and the pore volume of powders as a function of the heat-treatment temperature are given in Fig. 7a and b. The specific surface-area is rapidly reduced with increasing heating temperature up to 850°C and then, gradually decreases at higher temperatures. The pore volume variation exhibits the opposite behaviour. The decrease in surface-area is attributed mainly to the growth in the particles up to 850°C and the reduced porosity above 850°C . Manev et al. [6] reported that LiMn_2O_4 powder prepared by the solid-reaction method displays a virtually constant specific surface-area between 600 and 750°C , with a value of a $1.5 \text{ m}^2 \text{ g}^{-1}$. A region of constant specific surface-area is not observed in powders prepared by the emulsion-drying method. Moreover, the surface-area of such powders is higher than that of powder prepared by the solid-reaction method, on account of the smaller size of the particles at a given temperature.

The charge–discharge curves ($C/5$ rate) of LiMn_2O_4 samples heated at 650 , 750 , 850 and 950°C for 48 h are presented in Fig. 8. The specific capacity increases with heating temperature up to 750°C , while similar values (112

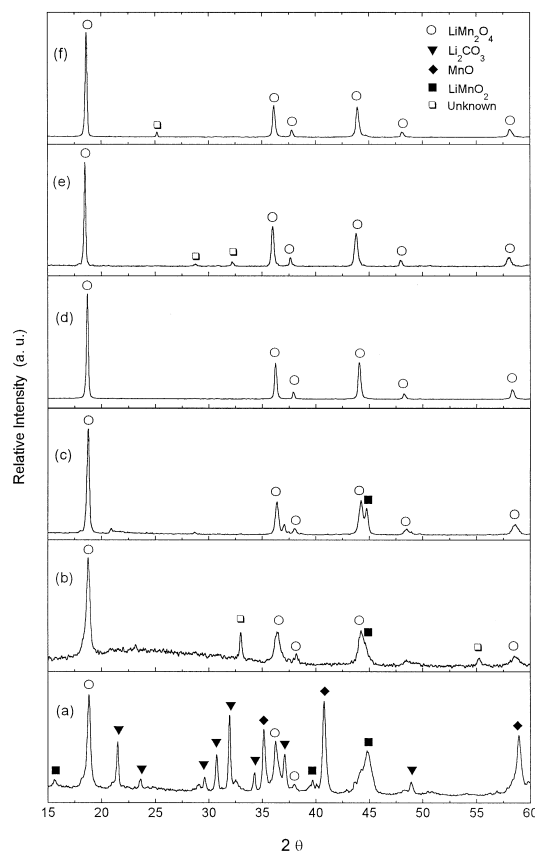


Fig. 4. X-ray diffraction patterns for LiMn_2O_4 powders. (a) Raw powder, powder heated for 48 h at: (b) 450°C ; (c) 650°C ; (d) 750°C ; (e) 850°C ; (f) 950°C .

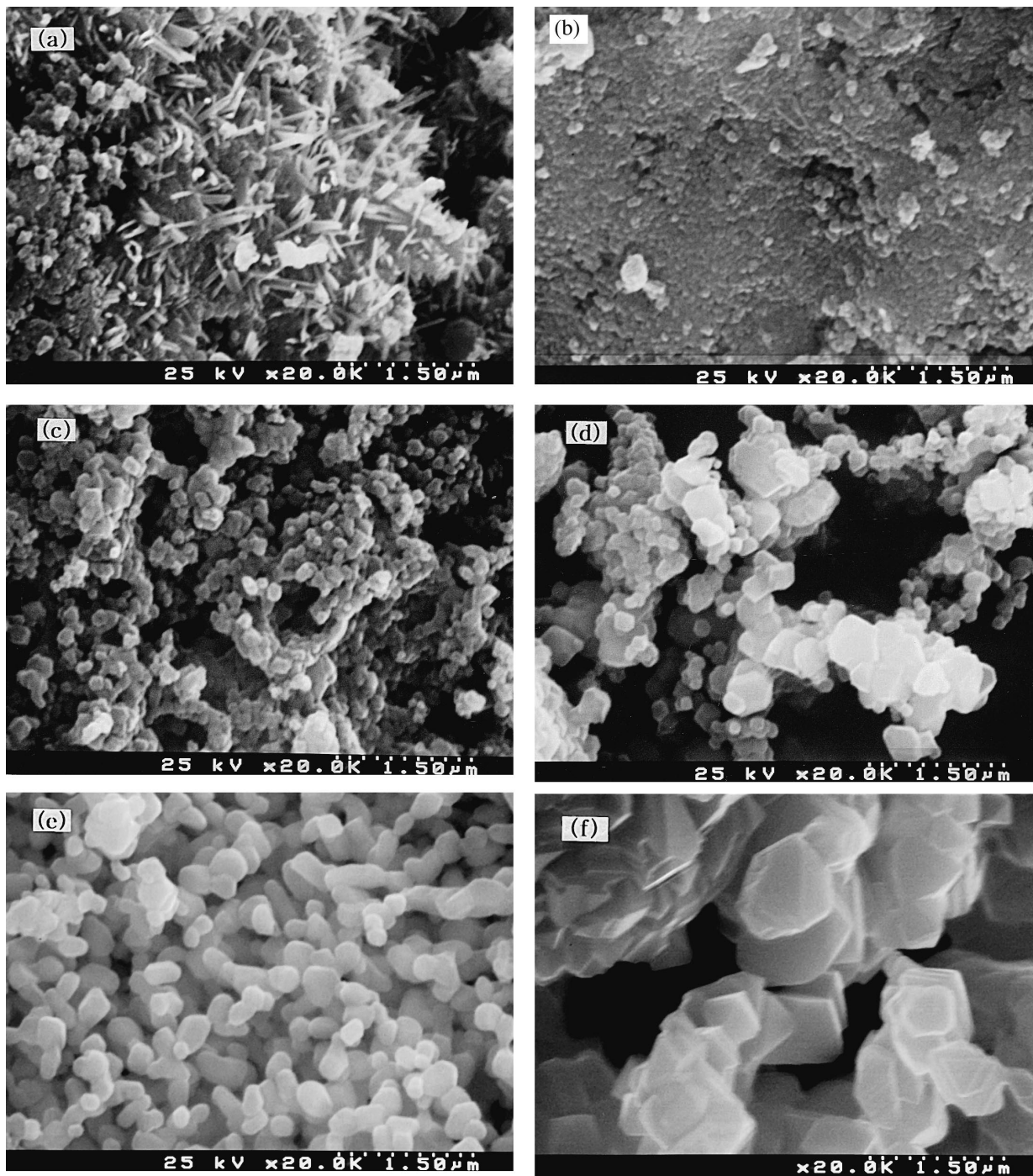


Fig. 5. Electron micrographs of LiMn_2O_4 powders heated for 48 h at: (a) 450°C; (b) 550°C; (c) 650°C; (d) 750°C; (e) 850°C; (f) 950°C.

and 115 mA h g^{-1}) are obtained from samples heated at 750 and 850°C. Above 850°C, the initial charge capacity of samples decreases. This may be attributed to the altered structure of the powders that results from the loss of oxygen [17,18].

It has been reported [13] that specific capacity is consistent with BET surface-area and that the secondary phase detected in the XRD patterns causes a detrimental effect

on capacity [14], such as observed for the 850°C heated powder (Fig. 4e). Although the capacity of an 850°C heated sample is expected to be lower than that of 750°C heated sample (based on XRD and BET results in Figs. 4 and 7), the capacity of the two samples is in fact similar. It is assumed that heat-treatment from 750 to 850°C optimizes factors such as oxygen content, crystalline structure and BET surface-area to moderate the specific capacity of

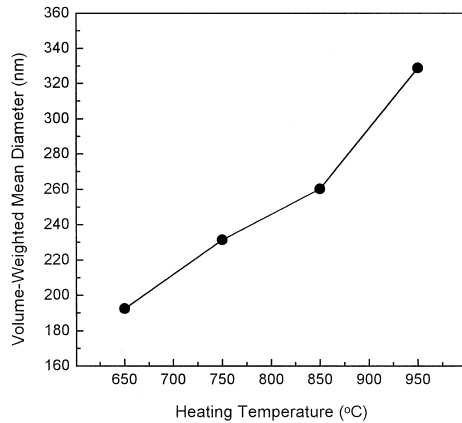


Fig. 6. Variation of mean diameter of LiMn_2O_4 powder with heating temperature.

LiMn_2O_4 powder prepared by the emulsion-drying method [17,18]. Since the oxygen content of the raw organic material used in the powder preparation is high, the heat-treatment temperature required for the optimum oxygen content of the structure may be higher than reported values of near 750°C [17]. This would explain the similarity in capacity without degradation, shown in Fig. 8b and c.

The maximum specific capacity of LiMn_2O_4 powder prepared by the emulsion-drying method is a little lower than that reported [6,14,18]. This is because the mole ratio of Li/Mn was set to 1:2 and it is reported [19,20] that the excess of lithium salt has a positive effect on both the specific capacity and the reversibility. The effect of oxy-

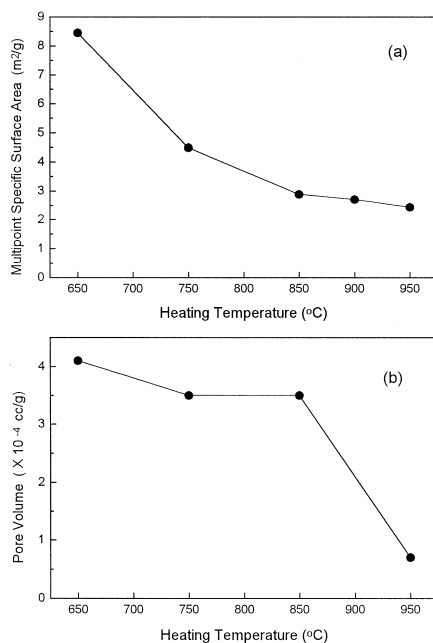


Fig. 7. (a) Multi-point specific surface-area and (b) total pore volume of LiMn_2O_4 powder with heating temperature.

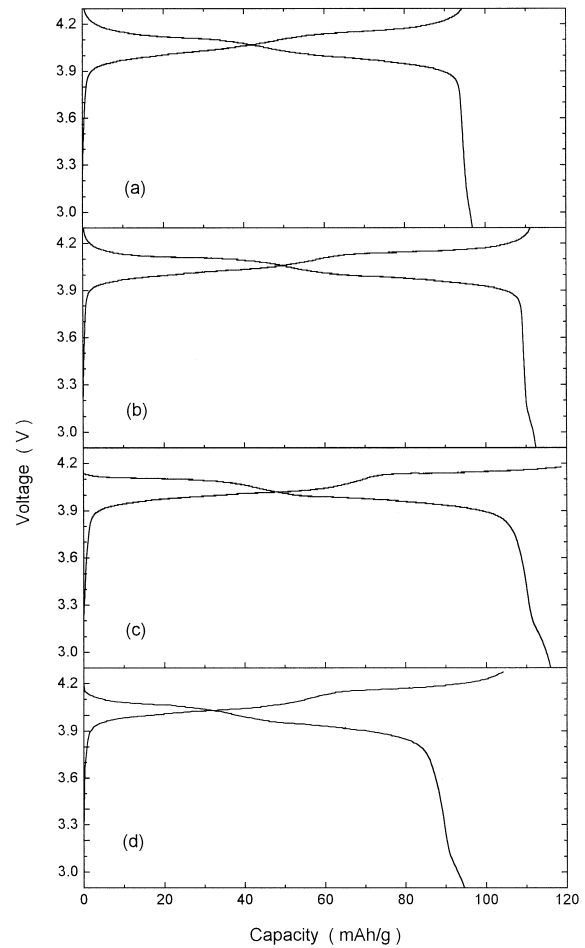


Fig. 8. Charge-discharge curves for a Li/1 M LiClO_4 -PC solution/ LiMn_2O_4 cell heated for 48 h at: (a) 650°C ; (b) 750°C ; (c) 850°C ; (d) 950°C . Current rate: $C/5$.

gen content and excess lithium salt on LiMn_2O_4 powder prepared by the emulsion-drying method has been studied and will be published in the near future.

4. Conclusions

LiMn_2O_4 powder as a cathode material for lithium-ion batteries is synthesized by the emulsion-drying method using Li_2CO_3 , $\text{Mn}(\text{NO})_2 \cdot 6\text{H}_2\text{O}$, an oil phase, and an emulsifying agent. Weight loss of the precursor powder rapidly occurs below 400°C and the formation of spinel LiMn_2O_4 phase starts. The heating condition for obtaining pure LiMn_2O_4 phase is above 750°C for 48 h. The mean particle-size increases with the heating temperature and is accompanied by a reduction in both the specific surface-area and the pore volume. The content of oxygen in the structure, mean particle-size, surface-area and crystalline phase influences the capacity of the powder. The specific capacity of powders heated at 750 and 850°C for 48 h are 112 and 115 mA h g^{-1} , respectively, which are the highest

values obtained. These heating conditions are optimum for powders prepared by the emulsion-drying method. It is expected that the specific capacity of the powder prepared by the emulsion-drying method can be increased by controlling the excess of lithium salt.

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