Capacity fading of $LiMn_2O_4$ electrode synthesized by the emulsion drying method

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Abstract

We adapted the emulsion drying method to obtain highly crystalline spinel $LiMn_2O_4$ phase using $LiNO_3$ and $Mn(NO_3)_2 \cdot 6H_2O$ as starting materials. The emulsion-dried powders were calcined at various temperatures for 24 h in air, and their crystalline phases were identified as a cubic spinel structure with the space group Fd3m by X-ray diffraction study. The initial discharge capacity of the samples calcined at 650°C, 750°C and 850°C were approximately 120 mA h/g, irrespective of calcination temperature. However, their capacity fadings were significantly dependent on the calcination temperature. To investigate the structural changes in the oxide cathode, XRD experiment was carried out as functions of lithium content and charge–discharge cycling number. Through the SEM observation, it was found that particles were disrupted, and the degree of disruption increased with lithium content and cycling. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Emulsion drying method; $LiMn_2O_4$; Capacity fading; Particle disruption

1. Introduction

Recently, as portable communication is developing, demands for the lithium ion battery as portable energy sources, which have light and long cycle life, increased drastically. $LiMn_2O_4$ is one of the most promising cathode materials for use as lithium ion battery cathode material because of its low cost and environmental characteristic. Unfortunately, it exhibits significant capacity fading with cycling [1].

Capacity loss is generally attributed to several possible factors [2]: an instability of an organic-based electrolyte at a high charge potential, a slow dissolution of manganese into electrolyte, the onset of the Jahn–Teller effect in deeply discharged $Li_xMn_2O_4$, and so on. On the other hand, other researchers insisted that the Jahn–Teller effect is not an important factor for the capacity losses of spinel oxide in 4 V, and the capacity loss is caused by the simple dissolution of Mn^{3+} [3,4].

In actual, as the particle size, homogeneity and crystallinity may affect the electrochemical property of $LiMn_2O_4$ electrode, it is important to control these factors. In case of using solution method for the synthesis, as lithium and manganese were mixed in nano-scale, leading to lower temperature nucleation reaction, the resultant $LiMn_2O_4$ powder exhibited more homogeneous particle distribution, larger specific area and smaller particle size than using solid state reaction method [5–7].

In our previous reports, we reported mainly the syntheses and characterization of $LiMn_2O_4$ [8], $LiNiO_2$ [9], and $LiCoO_2$ [10] by the emulsion drying method, that is a kind of soft chemistry-solution technique. In the present work, we have adapted the emulsion drying method to obtain highly crystalline spinel $LiMn_2O_4$ phase. Electrochemical study was performed to show that the material prepared by the emulsion drying method appears to offer high quality performance, and also to understand the relationship between the capacity fading in charge–discharge capacity

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and the structural stability during lithium intercalation and charge–discharge cycling.

2. Experimental

An aqueous solution was prepared by dissolving $LiNO_3$ (Kanto, 95%) and $Mn(NO_2)_3 \cdot 6H_2O$ (Kanto, 98%) in distilled water with the molar ratio of Li:Mn = 1:2, and mixed for 12 h. An emulsifying agent named Tween #85 (Polyoxyethylene Sorbitan Trioleate) was also mixed with kerosene, and stirred vigorously for 12 h. The detailed experimental process of the emulsion drying method was previously reported [8]. The aqueous solution fell into the oil mixture at a rate of 4 or 5 droplets per s with stirring in a speed of 1000 rpm by an impeller to synthesize the emulsion. The colour of the emulsion was white because light could not pass through emulsion, resulting to scattering of light. As soon as the emulsion was dropped into the hot kerosene around 180°C, at the same time water and kerosene contained in the emulsion was distilled through a spiral type condenser, the resultant powder precursor precipitated on the bottom of a glass bottle. The obtained powder precursor was heated in a steel tray to burn out the residual oil phase at approximately 300°C for 15 min, and then, that was calcined at various temperatures for 24 h in air. The calcined powders were examined by the automated X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation. The shape and size of the synthesized powders were measured with a scanning electron microscope (JEOL, Japan).

The electrochemical cell consisted of the $LiMn_2O_4$-based composite as a cathode, Li ribbon (FMC) as an anode, and an electrolyte of 1 M $LiPF_6$ in ethylene carbonate (EC)-diethylene carbonate (DEC) solution. For the preparation of the cathode composite, a slurry mixed with 93 wt.% of active material, 5 wt.% of carbon black (Vulcan XC-72) and 2 wt.% of PVDF (Polyvinylidene fluoride, Aldrich) in NMP was pasted on a nickel ex-met followed by vacuum drying at 120°C for 5 h in a vacuum oven. The typical cathode (1×1 cm^2) was prepared by cutting the ex-met. The charge and discharge characteristics of the cathode were investigated at a current of 0.1 mA cm^{-2}. X-ray diffraction and scanning electron microscopy experiments were also performed to know the structural changes at various cut-off voltages as functions of lithium content and cycling. Preparation and tests of cells were carried out in argon-filled glove box. All electrochemical tests were carried out at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples obtained by heat treating at various temperatures in air and the
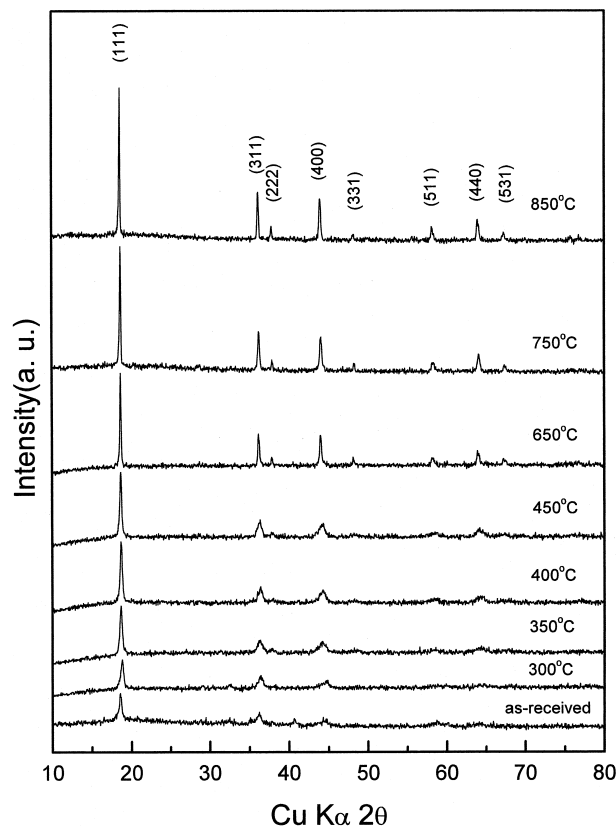

Fig. 1. X-ray diffraction patterns of the as-received powder precursor and powders calcined at various temperatures for 24 h in air.

as-received precursor. The Mn_2O_3 phase appeared about 40° in 2θ in the as-received. However, the spinel oxide phase was already formed at low temperature of 300°C due to the homogeneous mixing of cations in the emulsion state, as we previously reported [8]. All the diffraction peaks could be indexed by assuming the cubic spinel structure with the space group Fd3m. As the calcination temperature was getting higher, the main diffraction peaks of cubic spinel $LiMn_2O_4$ phase, such as (111), (311), and (400), were well developed. This means that lithium ions occupied tetrahedral 8a sites and manganese also occupied octahedral 16d sites. The diffraction peaks were a little shifted to lower 2θ position with increasing calcination temperature due to the increase in the amount of Mn^{3+} [8]. Furthermore, the diffraction peak intensity ratio between (111) and (311) or (400) is highly in accord with that of $LiMn_2O_4$ in the JCPDS card [11]. The sample calcined at 850°C for 24 h in air exhibited the highest diffraction intensity, indicating the highest crystallinity. The lattice parameter of that sample ($a = 8.244$ Å) agreed well with those of other research groups [12–14]. In our previous report [8], the change in mass in the TG-DTA analysis from 650°C to 850°C was small enough to think that the constant molar ratio between Li and Mn would be maintained. Therefore, the atomic absorption spectroscopy analysis was done by using only one sample calcined at 850°C. The chemical composition of the powder calcined at 850°C
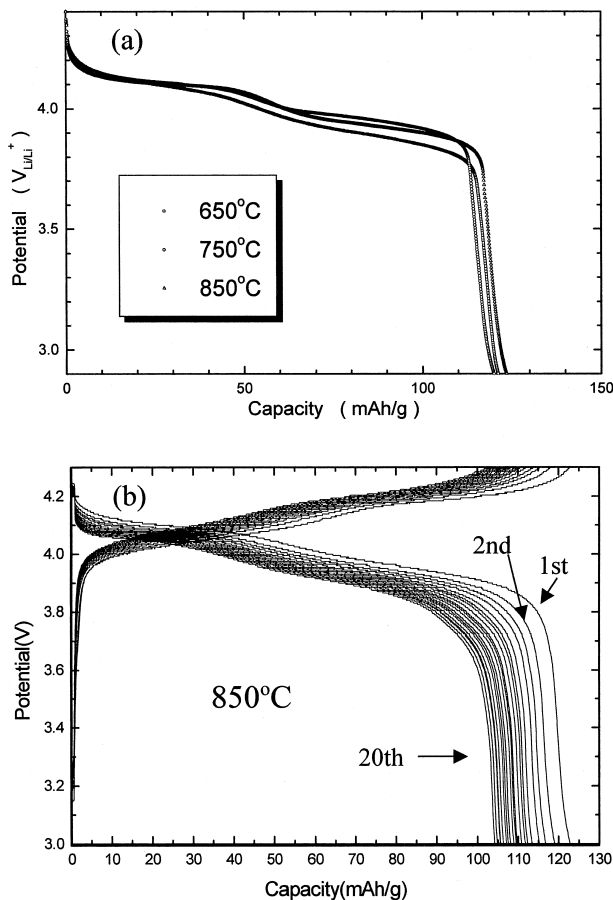
Fig. 2. (a) Initial discharge profiles of the samples calcined at 650°C, 750°C and 850°C for 24 h in air, (b) continuous charge and discharge curves of the sample fired at 850°C for 24 h in air.

was determined to be a slight lithium excess composition, $Li_{1.028}Mn_2O_4$.

Fig. 2 shows the comparison of discharge behaviors for the powder calcined at 650°C, 750°C and 850°C for 24 h in air. In lithium intercalation reaction into oxide electrode, the radius of lithium ion and the tetrahedral site size are 0.67Å and 0.38Å, respectively. Therefore, lithium ions should move through a narrow diffusion path so that much stress could be formed in the surrounding [15]. From that fact, it was expected that sample, which has relatively poorer crystallinity, is able to relax strain during intercalation or deintercalation, resulting to improvement of charge and discharge efficiency as well as capacity fading. The initial cycling behaviors of the powder calcined at 650°C, 750°C, and 850°C were very similar as shown in Fig. 2a. Those electrode materials exhibited the two potential plateaus, that is, one is over the 4 V, and the other is around the 4 V. With increasing the calcination temperature, the potential plateau over the 4 V was getting clearer, proving increasing the amount of Mn^{3+} in the final product, as we previously described [8]. From the continuous cycling performance in Fig. 2b, the capacity loss was the largest in the 2nd cycling. As the cycling progressed, the

potential dropping was getting larger, leading to the reduced charge and discharge capacities. The two potential plateaus were also maintained after the 20th cycling as shown in Fig. 2b. The capacity fading was significantly dependent on the calcination temperature as seen in Fig. 3. After 20 times cyclings, the material prepared at 850°C has a capacity about 40 mA h/g greater than that of the material fired at 650°C.

To discuss the relation between the capacity fading and the structural changes in oxide cathode, XRD experiment was carried out as functions of lithium content, δ, in $Li_\delta Mn_2O_4$ and cycling, as depicted in Fig. 4. The lithium content, δ, was calculated from the weight of used active material and the total charge transferred. The used samples were prepared by the electrochemical reduction. When Li^+ ions are removed from the spinel by electrochemical oxidation, the structure shrinks as the removal from the structure is accompanied by a progressive oxidation of Mn^{3+} (0.66 Å) to Mn^{4+} (0.60 Å), thus bringing about a marked decrease in the ionic radius [12]. Broad peaks appearing in the 2θ range from 15° to 25° are due mainly to the PVDF and carbon black. When δ in $Li_\delta Mn_2O_4$ was 0.25, the (400) peak was obviously split into two peaks owing mainly to the existence of two cubic phases [4,16]. These phases consisted of thermodynamically stable λ-MnO_2 and $Li_\delta Mn_2O_4$ phases over the 4-V range. As the intercalation content of lithium increased, the (400) peaks moved to lower 2θ position, indicating that the lattice parameter increased with increasing lithium content due to the reduction of Mn^{4+} to Mn^{3+}. Also, the diffracted (111) peak intensity increased with increasing lithium content. Notably, in the case of the $LiMn_2O_4$ powders prepared by the emulsion drying method, the spinel structure was continuously maintained during 20 cyclings in all the samples, compared with Fig. 1. This is indicative that the reversible lithium intercalation–deintercalation into the oxide electrode occurred. Thus, it may be concluded that the capacity fading is not related to the structural change during cyclings.
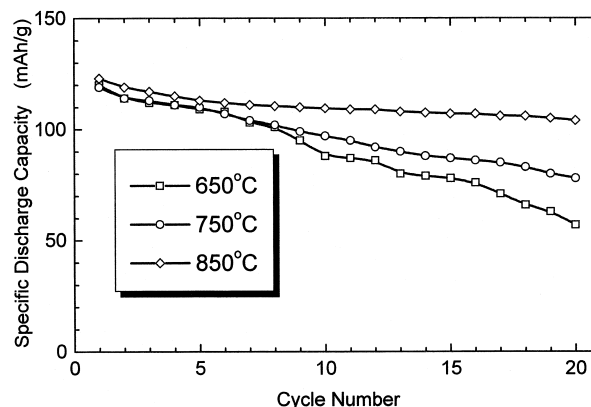

Fig. 3. Continuous discharge capacity plots of 650°C, 750°C and 850°C samples.
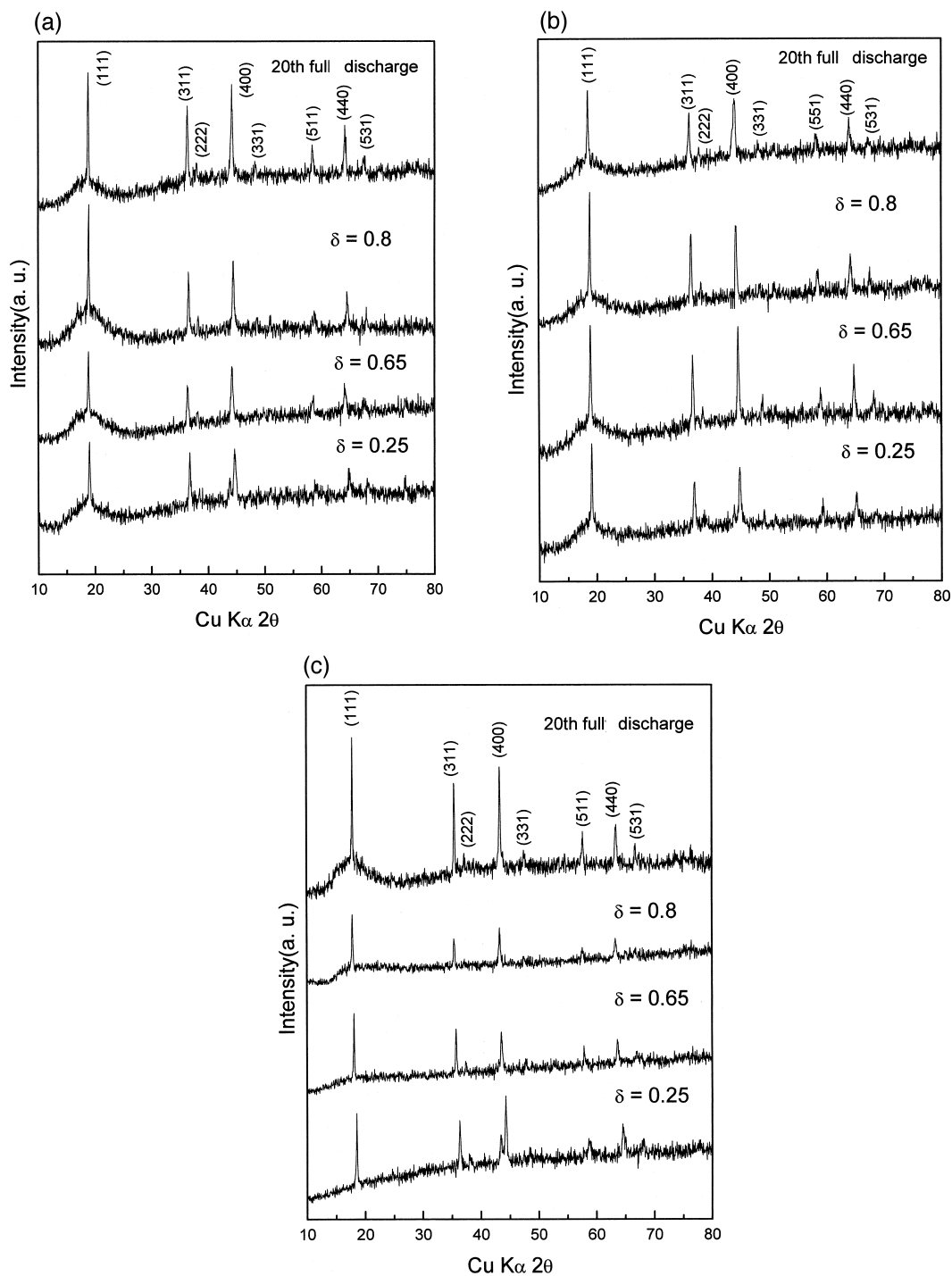
Fig. 4. X-ray diffraction patterns of $Li_\delta Mn_2O_4$ electrode with the amount of intercalated lithium, δ. Used samples were prepared by the electrochemical reduction and after 20 times discharge. The base material was calcined at (a) 650°C, (b) 750°C, and (c) 850°C for 24 h in air.

SEM micrographs of the sample calcined at 850°C on different δ in $Li_\delta Mn_2O_4$ and after the 20th discharge are illustrated in Figs. 5 and 6. Used samples were prepared by the electrochemical reduction. It is notable that it is possible to directly observe the steps of particle disruption, since a product with considerably homogeneous particle shape and size can be formed by the emulsion drying method. As Li^+ ions were inserted into the particles, the

surfaces of the particles started to disrupt partly, as can be seen in Fig. 5. The surfaces of particles were cracked by the progressing intercalation of Li^+. When lithium ions were fully inserted into the structure ($\delta = 0.81$), the surfaces of the parent particles were significantly disrupted while maintaining their particle shapes. Comparing with the samples after 20 times discharge (Fig. 6), it could be deduced that much severe disruption occurred in the two
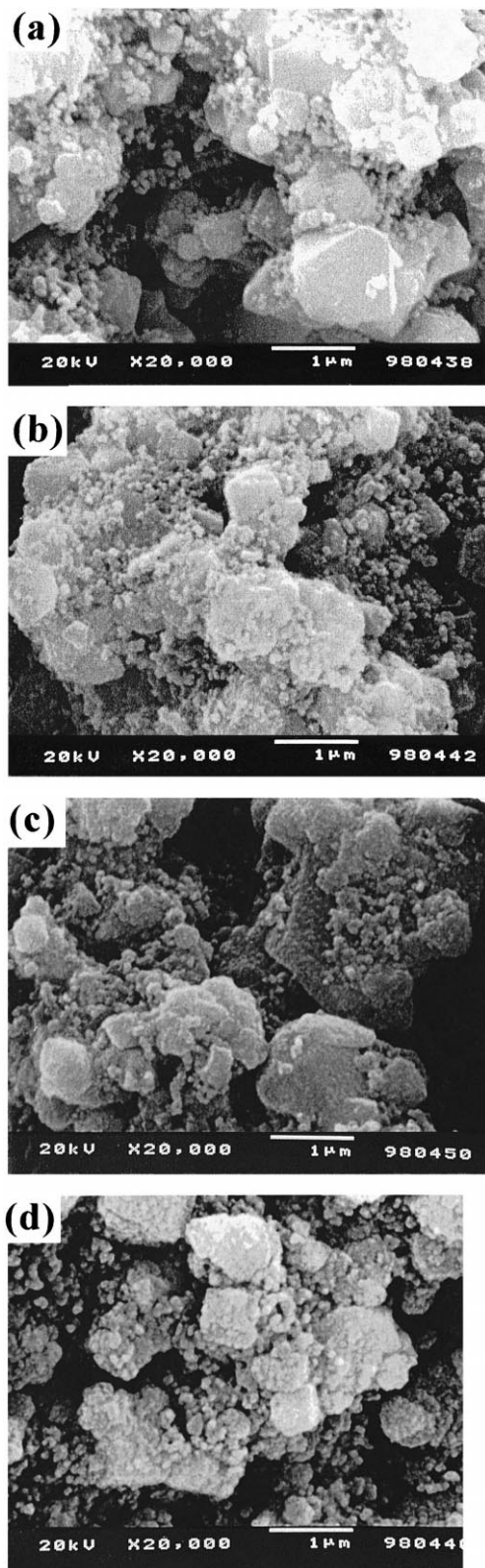
Fig. 6. SEM micrographs of the $LiMn_2O_4$ electrodes after 20 times discharge. Used base materials were calcined at (a) 650°C, (b) 750°C, and (c) 850°C for 24 h in air.

Fig. 5. SEM micrographs of the $Li_\delta Mn_2O_4$ electrode with the amount of intercalated lithium amount, δ. Used samples were prepared by the electrochemical reduction; (a) before charge, (b) $\delta = 0.25$, (c) $\delta = 0.65$, and (d) $\delta = 0.8$. The base material was calcined at 850°C for 24 h in air.
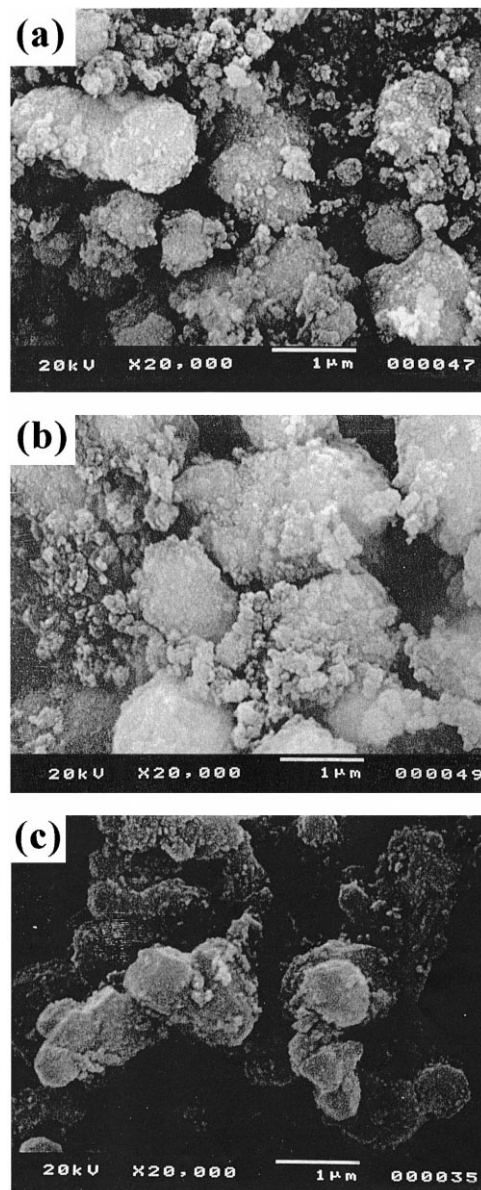
electrodes, 650°C and 750°C than 850°C. It was thought that some fragments aparted from their parent particles by disruption might be disjoined by Li^+ intercalation and/or deintercalation. At the same time, the amount of the active material would decrease by the disruption of particles, and the internal resistance of the cathode would increase as seen in Fig. 2b. Therefore, we believe that the capacity loss was caused by this surface disruption on Li^+ intercalation and/or deintercalation. Although the particle disruption occurred in the all samples, the sample calcined at 850°C exhibited the best crystallinity, as shown in Fig. 1, so that the severe disruption might be suppressed, resulting in better capacity retention.

4. Conclusion

Spinel $LiMn_2O_4$ powders prepared by the emulsion drying method using $LiNO_3$ and $Mn(NO_3)_2 \cdot 6H_2O$ as starting materials were calcined at 650°C, 750°C and 850°C for 24 h in air, and the origin of capacity loss in spinel $LiMn_2O_4$ was investigated. By the XRD experiment, spinel structure was continuously maintained after 20th cycling in the all samples, irrespective of calcination temperature, and capacity fading is not related with the structural change in our study. Through the SEM observation with lithium content, it was found that particles were disrupted with maintaining their particle shape. Moreover, as cycling performance was continuously done, the degree of disruption was severe, resulting to capacity loss; spinel oxide material loss.

Acknowledgements

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