Electrochemical Characteristics of LiMn_2O_4 (Li/Ni) Cathode Materials

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The present study used the Pechini process with a continuous furnace to synthesize LiMn_2O_4 powders. After heat treatment, the particle size and lattice constant of the LiMn_2O_4 powder increased. For heat treatment cathode powders (LMO800), due to both the average valence of Mn cations approaching the theoretical value and the higher crystallinity, the discharge capacities are raised significantly. The charge and discharge cycling capacity of LMO800 powder was best at 25°C. Under the charge-discharge cycling test at 55°C, some Mn ions dissolved easily into the electrolyte resulting in a significant decrease in the charge and discharge capacity with increasing the cycling number. The surface modification powder (LMO-Ni) contains a surface oxidative film of lithium-nickel-manganese that not only restrains Mn ions dissolved into the electrolyte, but also improves the charge and discharge capacity at 55°C. [doi:10.2320/matertrans.47.2759]

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1. Introduction

Comparing LiCoO_2 and LiNiO_2 with LiMn_2O_4 , the latter possesses the characteristics of a spinel cubic structure and stable oxidation potential.^{1,2)} In addition, the toxicity and cost of LiMn_2O_4 is lower than other transition metal oxide systems, however its capacity is lower.³⁾ Considering environmental concerns, its low cost and the safety coefficient of overwork in electrical charges, LiMn_2O_4 cathode material is worthy of further investigation. Much research has been focusing on the application of several lithium manganese oxides in lithium ion batteries,^{4,5)} however, LiMn_2O_4 synthesized using the Pechini process with heat treatment and the surface modification has not yet been examined. This study uses the Pechini process^{6,7)} and heat treatment to produce LiMn_2O_4 powder. In addition to investigating effects of carbon black content, heat treatment and the surface modification of lithium-nickel ions on the discharge capacities, the charge-discharge cycling characteristics at 25 and 55°C were also examined.

2. Experimental Procedure

2.1 LiMn_2O_4 powder synthesis

We used the Pechini process to synthesize LiMn_2O_4 powder.^{6,7)} Manganese nitrate, lithium carbonate, citric acid and glycol were mixed to form an organic acid lithium-manganese glycol solution. Meanwhile, the pH value of the solution was controlled at 7–8 using ammonia water addition. After that, the LiMn_2O_4 powder (hereafter referred to as LMO600) was synthesized from the syntactic solution using a continuous furnace (with temperature held at 200–600°C for 4 hours).

Next, some of this LMO600 powder was put into an oxidizing furnace to perform heat treatment. The temperature was raised by at 5°C per minute until it reached 800°C, then held at this temperature for 12 hours, followed by furnace cooling to room temperature. This heat treatment LiMn_2O_4 powder is designated as LMO800. Additionally, to under-

stand the influence of carbon black content on the capacity, LMO800 powders with various content of carbon black were also given charge-discharge testing.

For doping the lithium ions and nickel ions on the surface of LiMn_2O_4 powders, the LMO800 powders were mixed with an organic acid lithium-nickel glycol solution to produce the surface modification powders. After that, the surface modification powders were held at 800°C for 6 hours, followed by furnace cooling to room temperature (hereafter referred to as LMO-Ni, that contain a surface oxidative film of lithium-nickel-manganese).

2.2 Characteristic analysis and charge-discharge testing

X-ray diffraction was used for structural analysis. The scanning angle was varied from 10 to 70° and the scanning velocity was 2° min⁻¹. Furthermore, the appearance of the powders was examined by SEM observation. The exact composition of the powders was identified using ICP (inductively coupled plasma). The electrovalence of Mn was measured by titration. Meanwhile, XPS (X-ray Photoelectron Spectroscopy) was used to obtain Mn binding energy data.

In addition, the active powders, carbon black and binder (PVDF) were first mixed and then an appropriate amount of N-methyl-2-pyrrolidone (NMP) was added to form a paste. After scraping-form and vacuum heat treatment at 130°C, a round electrode of 13 mm in diameter was obtained. The electrical current of charge-discharge testing was fixed at 74 mAh/g (the theoretical capacity of LiMn_2O_4 is 148 mAh/g). The voltage was limited to the range of 3.0 and 4.3 V. The electrolyte was a mixture of LiPF_6 , EC and DEC (EC : DEC = 1 : 1 vol.). Each analysis datum was the average of 3–4 test results.

3. Results and Discussion

3.1 Properties of LiMn_2O_4 powders

Figure 1 shows the appearances of the LiMn_2O_4 cathode powders. LiMn_2O_4 powder (LMO600) is shown in Fig. 1(a) and its particle size is in the range of 10–100 nm. After 800°C oxidizing for 12 hours, the heat treatment powders (LMO800) grew in size significantly (Fig. 1(b)). The particle

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Fig. 1 SEM photographs of LiMn_2O_4 : (a) LMO600 and (b) LMO800.

size of LMO800 was about 0.1–1 μm and was a polyhedron. X-ray diffraction patterns of LMO600 powder and LMO800 powders are shown in Fig. 2, revealing both had spinel cubic structures. Notably, comparing the LMO800 powder with the LMO600 powder, the diffraction degree of the LMO800 powder had shifted to a lower degree (Fig. 3). The lattice constant of the LMO800 powder was calculated to be 0.8236 nm, while that of the LMO600 powder calculating to be 0.8226 nm.

According to ICP results, the molar ratio of $\text{Li} : \text{Mn}$ was 1.021 : 2 for the LMO600 powder, while that of the LMO800 powder was 1.015 : 2. This result also indicates no obvious change in the ratio of cations after the powder was oxidized at 800°C for 12 hours. Due to the electrovalence of Mn having a major influence on the electrochemical properties of cathode powder, the average electrovalence of Mn was measured using titration. The average electrovalence of Mn in the LMO800 powder and the LMO600 powder were found to be 3.57 and 3.52. The concentration of Mn^{4+} for the LMO600 powder was higher, and the average electrovalence of Mn for the LMO800 powder was close to the theoretical value (3.5). In addition, the radius of Mn^{4+} was 0.067 nm and the radius of Mn^{3+} was 0.072 nm.⁸⁾ It can be seen that the lattice constant of the LMO800 powder was larger than the LMO600 powder. Table 1 shows the lattice constant, the average electrovalence of Mn and the molar ratio of positive ions for both the LMO600 powder and the LMO800 powder.

Fig. 2 X-ray diffraction patterns of LMO600 powder and LMO800 powder.

Fig. 3 XRD analysis of the cathode powders at the peak of (311).

Table 1 Properties of the LiMn_2O_4 powders.			
	Lattice constant (nm)	Average electrovalence of Mn	Li : Mn : (Ni) (molar ratio)
LMO600	0.8226	3.57	1.021 : 2
LMO800	0.8236	3.52	1.015 : 2
LMO-Ni	0.8232	3.55	1.056 : 2 : 0.039

Fig. 4 XPS spectra analysis of the LMO800 powder for Mn ($2p_{3/2}$).

Table 2 Cathode materials with various carbon black contents (mass%).

Cathodes	LMO800	Carbon Black	PVDF
CB4	91	4	5
CB7	88	7	5
CB10	85	10	5
CB13	82	13	5
CB16	79	16	5

To understand the relationship between the electrovalence of Mn and the binding energy, the surface binding energy of Mn $2p_{3/2}$ of the LMO800 powder was measured using XPS (Fig. 4). According to the result of curve fitting,⁹⁾ the peak was mostly composed of Mn^{3+} (641.79 eV) and Mn^{4+} (642.86 eV). After integration, the concentration of Mn^{4+} was found to be about 51% (the concentration of LMO600 was more than 51%).

3.2 The influence of carbon black content on the discharge capacity

Carbon black was used as a conductive additive. Five carbon black contents of 4%, 7%, 10%, 13% and 16 mass% were chosen for capacity testing (see Table 2, here designated as CBx, x being the carbon black content). Only the LMO800 powder was investigated. The carbon black was added into the cathode material (LMO800 powder and PVDF) to form a cathode specimen. The SEM image of the CB10 specimen is shown in Fig. 5, revealing that the carbon black was well dispersed.

The initial discharge capacity of the specimens with various carbon black contents was tested at 25°C (Fig. 6). Results show that the CB10 specimen possessed the highest discharge capacity (124 mAh/g). When the carbon black content was lower (the CB4 specimen), the conductivity was insufficient to cause the discharge capacity to be reduced significantly. On the other hand, when the carbon black

Fig. 5 SEM photograph of the cathode materials (adding 10 mass% carbon black).

Fig. 6 Initial discharge curves of the LiMn_2O_4 with various carbon black contents.

content was more than 7 mass%, the conductivity increased and improved the discharge capacity. Notably, the discharge capacities of the CB13 specimen and the CB16 specimen were lower than the CB10 specimen. The most likely explanation for this is that in the present voltage range of 3.0–4.3 V, the carbon black could not store Lithium ions. So, even adding a large amount of carbon black does not promote the discharge capacity. According to the above findings, the carbon black content of the LMO800 powder and the LMO600 powder was fixed at 10 mass% to understand the effect of heat treatment as well as charge-discharge capacity.

3.3 Charge-discharge characteristics of the electrode

From the curves of initial discharge capacities at 25°C (Fig. 7) show that both the LMO800 powder and the LMO600 powder had two obvious horizontal discharge zones. The First horizontal zone was in the voltage range of 4.09–4.13 V and the other was at 3.89–4.05 V. This shows

Fig. 7 Initial discharge curves of LMO600 powder and LMO800 powder.

that the Lithium ions embedded and disembedded had in LiMn_2O_4 powders in two stages. This result is also very similar to those reported in the literature.^{10,11} According to our previous data, the horizontal zone of 4.13–4.09 V was induced by $\lambda\text{-MnO}_2$ inlaid into Li^+ to form $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$. The other zone was induced by $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ inlaid into Li^+ to form $\lambda\text{-MnO}_2$. Notably, both the LMO800 powder and the LMO600 powder had spinel cubic structures (Fig. 2). However, the discharge capacity could be raised from 84 to 124 mAh/g through heat treatment.

In Fig. 3, the half-peak width of (311) of the LMO800 powder was narrower than that of the LMO600 powder. There are two probable explanations for the above findings. First: according to the Scherrer equation, the grain size of the LMO800 powder was larger (Fig. 1) resulting in the half-peak width of the diffraction pattern being narrower. Second: the atomic arrangement of the LMO800 powder was better and possessed higher crystallinity. In addition, the average electrovalence of Mn for the LMO800 powder was 3.52 close to the theoretical value of 3.5, while that of the LMO600 powder was 3.57. When the average electrovalence of Mn exceeded 3.5, the concentration of Mn^{3+} was lower, and Li^+ could not be discharged resulting in the capacity of the LMO600 powder being lower than the LMO800 powder.

3.4 Charge-discharge cycling capacity

The LMO800 powder possessed a higher initial discharge capacity and was thus chosen for charge-discharge cycling capacity testing at 25 and 55°C (Fig. 8). The discharge capacity reduced slowly when tested at 25°C. Even after testing for 50 cycles, the discharge capacity was 109 mAh/g, which is about 88% of the initial discharge capacity. However, the discharge capacity reduced rapidly when tested at 55°C. According to a relevant report,¹² when testing at 55°C, some Mn^{3+} in LiMn_2O_4 can be reduced to Mn^{2+} and dissolved easily into the electrolyte resulting in the capacity decrease.

Fig. 8 Charge and discharge capacities as a function of cycle number for LMO800 in 25 and 55°C.

Table 3 ICP analyses of the electrolytes on Li, Mn and Ni.

	Li (ppm)	Mn (ppm)	Ni (ppm)
LMO800 (25°C)	10.90	3.76	—
LMO800 (55°C)	15.12	6.38	—
LMO-Ni (25°C)	12.03	0.56	0.07
LMO-Ni (55°C)	18.12	0.81	0.24

In order to clarify the above behavior, the LMO800 powders were immersed in two electrolytes (25 and 55°C) for 48 hours. There upon ICP analysis was performed on the two electrolytes (Table 3). The results show that the 55°C electrolyte contained a large number of Mn ions compared with the 25°C electrolyte. So, it can be inferred that Mn ions diffused easily from the powder into the electrolyte at high temperature. So, this must be one reason why Mn ions dissolved from the lattice into the electrolyte during 55°C discharge testing, resulting in the active materials decreasing and the charge-discharge cycling number reducing significantly.

3.5 Characteristics of surface modification powders

Figure 9(a) shows the appearances of the surface modification cathode powders (LMO-Ni) and many very small particles are observed on the surface. The LMO-Ni powder contains a surface oxidative film of lithium-nickel-manganese (Fig. 9(b)). Comparing X-ray diffraction patterns of LMO-Ni powders with LMO800 powders (Fig. 10), revealing both had spinel cubic structures. So, the surface modification process had no change on the structures. In addition, the lattice constant, the average electrovalence of Mn and the molar ratio of positive ions for LMO-Ni powder are shown in Table 1.

Figure 11 shows the curves of initial discharge capacities of the LMO-Ni powder and the LMO800 powder at 25°C. Notably, the average electrovalence of Mn of the LMO-Ni

Fig. 9 LMO-Ni powder: (a) SEM photograph and (b) EDS analysis.

Fig. 10 X-ray diffraction patterns of LMO800 and LMO-Ni.

exceeded 3.5 (Table 1) resulting in the initial capacity of the LMO-Ni powder being lower than the LMO800 powder. However, the LMO-Ni powder possessed a higher charge-discharge cycling capacity at 25 and 55°C than that of the

Fig. 11 Initial discharge curves of LMO800 and LMO-Ni.

LMO800 powder (Fig. 12). This revealed that the surface modification was able to improve the charge-discharge cycling capacity, especially, at 55°C.

In order to understand why the LMO-Ni powder enhanced the charge-discharge cycling capacity, the LMO-Ni powders also were immersed in two electrolytes (25 and 55°C) for 48 hours, and ICP analysis of the two electrolytes are shown in Table 3. The results, Figs. 10 and 13 show that the Li-Mn-Ni surface oxidative film was a spinel cubic structure and the mechanism was closer together through two steps treatments (due to Li and Ni elements coating). In addition, the thickness of film is detected to be about 20 nm using EDS (an electron beam with 1 nm in diameter) that provided a protective film between the LiMn_2O_4 powders and electrolyte, and restrained Mn ions dissolved into the electrolyte during cycling tests.

4. Summary

Both the LMO600 powder and the LMO800 powder had spinel cubic structures. Notably, the particle size and lattice constant of the heat treatment powder (LMO800) was larger than the LMO600 powder. The heat treatment assisted the average electrovalence of Mn to approach the theoretical value and to have higher crystallinity. In addition, the cathode specimen with 10 mass% carbon blacks possessed the highest discharge capacity.

At 55°C charge-discharge cycle testing, some of the Mn ions dissolved into the electrolyte and contributed to the decrease in the capacity. However, the surface modification (LMO-Ni) can avoid the LiMn_2O_4 cathode powders and the electrolyte in direct contact to enhance the charge-discharge cycling capacity.

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(a)

(b)

Fig. 12 Charge and discharge capacities as a function of cycle number for LMO800 and LMO-Ni: (a) 25°C and (b) 55°C.

Fig. 13 TEM observation of the Li-Mn-Ni oxidative film.

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