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# Synthesis of cathode material $LiMn_2O_4$ for lithium-ion batteries by high-energy ball milling①

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**[Abstract]** Using electrolytic manganese dioxide and $Li_2CO_3$ as starting materials, the precursor of $LiMn_2O_4$ as cathode materials for lithium-ion batteries was obtained by high-energy ball milling. The $LiMn_2O_4$ powder was synthesized by calcinating the as-milling powder at 750 ℃ for 24 h. X-ray diffraction, SEM, cyclic voltammograms and charge-discharge were carried out to investigate the property of $LiMn_2O_4$ cathode materials. Results show that the synthesized material, which is of standard spinel structure, possesses high reversibility of electrochemistry. The capacity in EC-DMC(1∶1) +1 mol/L $LiPF_6$ electrolyte during first discharge is determined to be 125 mA·h/g.

**[Key words]** lithium-ion batteries; cathode materials; high-energy ball milling
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## 1 INTRODUCTION

Li-ion batteries have recently received considerable interest as rechargeable power sources for portable/commercial electronics since the commercialization of Sony lithium-ion cell in 1990. The composite oxides of transition metals and lithium, possessing high potential of Li-ion intercalation/extraction, are used commonly as cathode materials for Li-ion batteries. The cathodes materials investigated most extensively at present are layer-structured $LiCoO_2$[1] and $LiNiO_2$[2] as well as spinel-structured $LiMn_2O_4$[3]. Among these cathode materials, $LiCoO_2$ is expensive and $LiNiO_2$ is difficult to synthesize, so their applications are limited greatly. The spinel-structured $LiMn_2O_4$ is a promising candidate for cathode materials of Li-ion batteries because of its high voltage, long life-span of cycle, low cost, abundance of resource and free-pollution.

The conventional method to synthesize $LiMn_2O_4$ is the solid reaction of lithium and manganese compounds at high temperature[4]. The performance of the materials could not be improved effectively because of heterogencity in the solid reaction. The key to prepare $LiMn_2O_4$ is full mixing of lithium and manganese compounds. Researchers developed a variety of synthesis processes, such as sol-gel[5], melt-impregnation method[6], Pechini[7] and co-precipitation[8]. The $LiMn_2O_4$ which possesses excellent performance of electrochemistry can be synthesized in shorter time of calcination using homogeneous precursors obtained through the above means. However, the above processes do not suit to commercial production because of complicated technology and high cost.

In recent years, high-energy ball milling has received wide application in materials preparation[9,10]. In this work, the precursor of $LiMn_2O_4$ was prepared by high-energy ball milling. The spinel structure $LiMn_2O_4$ was synthesized by calcination of the precursor at a relative low temperature and short duration. The $LiMn_2O_4$ powder was characterized by X-ray diffraction, scanning electronic microscopy (SEM) and cyclic voltammograms. A prototype cell, in which the synthesized $LiMn_2O_4$ was used as cathode, was assembled and electrochemical measurement was carried out. The results exhibited that the synthesized $LiMn_2O_4$ possessed good reversibility of electrochemistry and high capacity of charge/discharge.

## 2 EXPERIMENTAL

### 2.1 Synthesis techniques

Electrolytic manganese dioxide ($MnO_2$) and $Li_2CO_3$ were mixed in a molar ratio of 1 and milled for 6 h in air. The milling was performed using a planetary ball mill(QM-ISP) equipped with a 500 mL zirconia grinding jar. The rotation speeds of the sun disc and the jar were 150, 350 r/min, respectively. The precursor powder obtained by ball milling was heated to 750 ℃ at a rate of 10 ℃/min in air, and kept at the temperature for 24 h, and then cooled slowly to room temperature. The $LiMn_2O_4$ powder was obtained by grinding the heat treated precursor.

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### 2.2 Composite electrode preparation and electrochemical cell

The electrochemical properties of $LiMn_2O_4$ as cathode materials were evaluated using prototype coin cells. The cathode, which was consisted of the mixture of $LiMn_2O_4$, acetylene black (AB) and polytetrafluornethylene (PTFE), was pressed into a film with thickness of 100 ~ 200 μm thickness on a roller. The specific composition of the mixture was $w(LiMn_2O_4)$: $w(AB)$: $w(PTFE)$ = 80: 10: 10. The anode was a lithium metal foil. The electrolyte was the solution of 1 mol/L $LiPF_6$ in a solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC). The separator was made from a Celgard 2 400 film. The test cells were fabricated in a dry glove-box full of argon. The charge/discharge measurement was carried out outside the glove-box.

In addition, a three-electrode cell was employed for the cyclic voltammetric measurement. In that cell, $LiMn_2O_4$ powder was made as powder microcathode, lithium metal foils were used as the counter and reference electrodes.

## 3 RESULTS AND DISCUSSION

### 3.1 X-ray diffraction analysis

Fig.1 is the pattern of X-ray diffraction for the $LiMn_2O_4$ synthesized by high-energy ball milling. All of the diffraction peaks are attributed to the spinel structure of $LiMn_2O_4$.

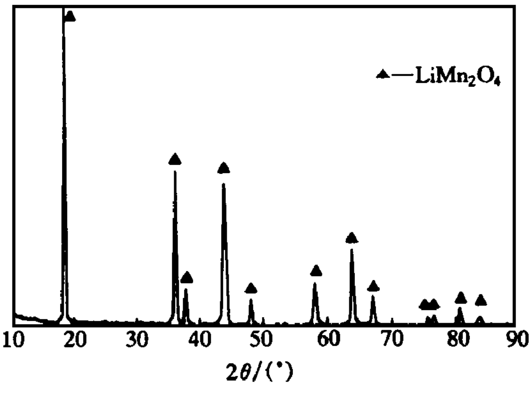


**Fig.1** XRD pattern of $LiMn_2O_4$ synthesized by high-energy ball milling

### 3.2 Morphology of $LiMn_2O_4$ powder

SEM micrographs (see Fig.2) reveal that the $LiMn_2O_4$ powder synthesized by high-energy ball milling possesses homogeneous small particle size of about 1 μm.

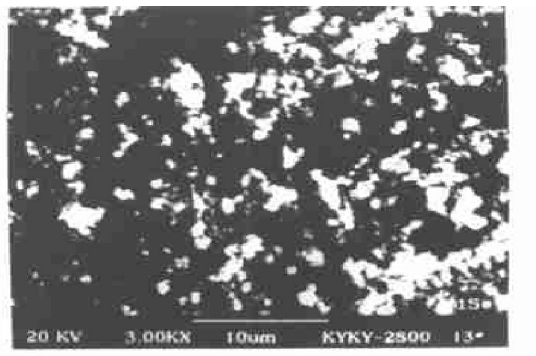


**Fig.2** SEM micrographs of $LiMn_2O_4$ powder synthesized by high-energy ball milling

### 3.3 Cyclic voltammetric measurement

Fig.3 shows the cyclic voltammogram (CV) of Li/EC-DMC-$LiPF_6$/$LiMn_2O_4$ cell with voltage ranging from 3.0 ~ 4.5 V and scanning rate of 1 mV/s. It

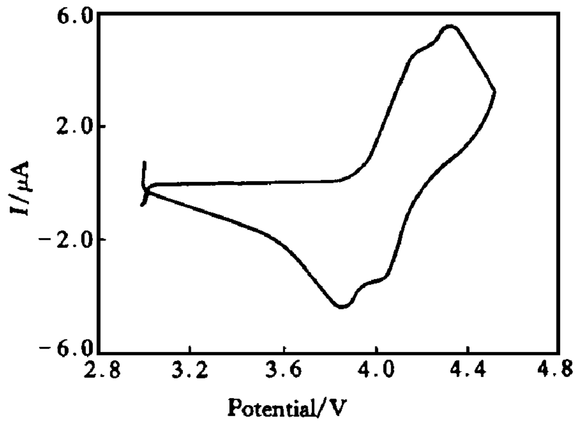


**Fig.3** Cyclic voltammogram for Li/EC-DMC-$LiPF_6$/$LiMn_2O_4$ cell at scanning rate of 1 mV/s

is seen from Fig.3 that there are two redox couples, which is different from the one-electron transfer mechanism in rechargeable lithium batteries. It is often considered that lithium ions are intercalated from the electrolyte into the tetrahedral sites of the $LiMn_2O_4$ spinel structure. When a small number of $Li^+$ ion move into the tetrahedral sites of the spinel structure, the interaction between the adjacent lithium ion is weak. With the increase of $Li^+$ ion into the tetrahedral sites, the activity of each $Li^+$ ion would be influenced by the $Li^+$ ions that surround it. As a result, the peak splits into two on the CV curves. The peak split was also accompanied by the two stages on the typical charge/discharge curve of the Li/$LiMn_2O_4$ cell (see Fig.4). It is also observed from Fig.4 that the spinel structure $LiMn_2O_4$ displays reversible lithium intercalation/de-intercalation.

### 3.4 Charge and discharge profile

The charge/discharge test was carried out in a prototype coin cell. A typical charge/discharge curve for the Li/EC-DMC-$LiPF_6$/$LiMn_2O_4$ cell at a current of 0.5 $mA/cm^2$ with voltage range of 3.4 ~ 4.3 V is given in Fig.4.

It is shown that there are two obvious plateaus in

**Fig. 4** Charge-discharge curves for Li/ EC-DMC-$LiPF_6$/ $LiMn_2O_4$ cell

the charge-discharge curves for the Li/ EC-DMC-$LiPF_6$/ $LiMn_2O_4$ cell. The voltage of the two plateaus are about 4.10 V and 4.20 V for charging, and 4.20 V and 3.90 V for discharging respectively. The capacity of the first discharge for $LiMn_2O_4$ cathode is 125 mAh/ g.

## 4 CONCLUSIONS

The $LiMn_2O_4$ cathode materials for lithium ion batteries have been synthesized by calcinating the precursor obtained by high-energy ball milling of electrolytic manganese dioxide( $MnO_2$) and $Li_2CO_3$ powder mixture. In the synthesis technology of the $LiMn_2O_4$ presented in the present work, the process is simple, the temperature and time for calcinating are low and short, and the powder particles are small and homogeneous. The X-ray diffraction analysis indicate that the materials are of standard spinel structure. The cyclic voltammetric measurement reveales that the $LiMn_2O_4$ possesses good electrochemical reversibility. The results of charge/ discharge test for laboratory cell show that the $LiMn_2O_4$ cathode materials possess favorable cyclic properties and high electrochemical capacity.

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