Modification of LiMn$_2$O$_4$ Surface using Surfactant Micelles

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A simple technique has been developed to surface modification from liquid solution by the solvent evaporation method. Using this technique, the preparation of lithium manganese oxide, LiMn$_2$O$_4$, which are the most promising cathode materials for lithium secondary battery, has been carried out for various operating conditions. The as-prepared samples exhibited a monophonic cubic spinel structure (fd3m) without any impurities in the XRD patterns, and the chemical composition of as-prepared powders showed in a good agreement with the one of precursor solution.

The as-prepared sample was used as cathode active materials for lithium secondary battery and their charge/discharge properties have been investigated. Test experiments in the electro chemical cell Li|1M LiPF$_6$ in EC with DEC|LiMn$_2$O$_4$ demonstrated that the sample, prepared by the solvent evaporation method, was a promising cathode material for 4V lithium secondary batteries.

Key words: Lithium secondary battery, Cathode material, Specific surface area, nano-rod structure

1. INTRODUCTION

The high-power performance of the lithium secondary batteries is increasingly required in electric vehicles, hybrid electric vehicles, and other automotive fields and their applications, much attention has been focused on the study of the cathode materials with very fast Li$^+$ diffusivity to satisfy the high power demands. In this battery, the most candidates as cathode materials are a family of lithium transition metal oxides such as LiCoO$_2$, LiNiO$_2$, LiMn$_2$O$_4$ and more [1-5]. Among these cathode materials, LiCoO$_2$ is now commercially used, but is very expensive (also Ni). Spinel type LiMn$_2$O$_4$ is at present a very prospective candidate for the cathode material of lithium secondary batteries because of its low cost, acceptable environmental impact, and high voltage profile characteristics [6-7]. Therefore the battery system based on LiMn$_2$O$_4$ / carbon couple has been used in many types of electronic equipments. Although LiMn$_2$O$_4$ are attractive power-storage devices with high-energy density, their power density is generally low because of the large polarization at high charge-discharge rates due to the low kinetics limited by the slow solid-state lithium-ion diffusion compared with other cathode materials. It is generally considered that the mesoporous materials can be used in batteries because the meso-pores in the active material can reduce the Li$^+$ diffusion path and increase the specific surface area of the materials greatly, thus enhancing the electrochemical performance of the active materials at high current densities.

Soft chemistry template routes have been used to synthesize mesoporous transition-metal compounds, for example, SiO$_2$, TiO$_2$, MnO$_2$ and more; however, the materials often have poorly crystallized walls and are thermally unstable, which limits their applications [8]. However, Jiao et al. have recently reported that the mesoporous LiCoO$_2$ is successfully prepared using a post-templating reaction [9]. It has also been reported that the Li$^+$ diffusion is affected by the porous properties such as morphology and specific surface area.

In this work, we synthesized LiMn$_2$O$_4$ samples using a solvent evaporation method from various precursor solutions with cationic surfactant, examined their particle, surface and electrochemical properties.

2. EXPERIMENTAL

2.1 Experimental apparatus and procedure

In the present study, Spinel LiMn$_2$O$_4$ materials were synthesized by vacuum-assisted solvent evaporation method. A schematic diagram of the experimental apparatus is presented in Fig. 1. Precursor solutions were prepared by dissolving a stoichiometric ratio of Li-salt (LiNO$_3$ or CH$_3$COOLi), M-salt (Mn(NO$_3$)$_2$·6H$_2$O or Mn(CH$_3$COO)$_2$·4H$_2$O) and/or n-cetyltrimethylammonium chloride (C$_{16}$TAC) as templates in a ultra pure water. After EtOH added to the mixture, obtained solution was stirred at room temperature for 0 – 4 h. the typical molar ratio of the starting solution were

LiNO$_3$·Mn(NO$_3$)$_2$·6H$_2$O·C$_{16}$TAC·EtOH·H$_2$O = 1:2:(0.2/0.4/0.8/1.6):0.007:8.3

and

Li(CH$_3$COO)·Mn(CH$_3$COO)$_2$·4H$_2$O·C$_{16}$TAC·EtOH·H$_2$O = 1:2:0.2:0.4:0.8:1.6:0.007:8.3.

![Fig. 1 A schematic diagram of experimental apparatus](image-url)
The solvent was removed under a reduced pressure 40 hPa at 303 – 343 K using vacuum rotary evaporator. The resulting solid, a LiMn$_2$O$_4$-template composite, was vacuum dried at 363 K, 101.3 Pa for 10 h to remove a drop of solvent. The obtained powder was calcined at 473 – 1073 K for 2 – 8 h to remove the structure directing agents and sintering.

2.2 Characterization of LiMn$_2$O$_4$

The crystalline phase of as-prepared powders was examined by X-ray diffraction (XRD, Rigaku, Miniflex) for crystal analysis ranging from 10° to 90°. The average size of crystallites was estimated using Scherrer’s formula. The particle morphology was examined by field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6330F) operated at 15 kV. The surface structure of as-prepared particles was observed by using transmission electron microscopy (TEM, Philips, CM300-TWIN), and the specific surface area was determined by BET method (Bell Japan, BELSORP-mini). The N$_2$ adsorption/desorption isotherms were measured at a 77 K.

The electrochemical characterization of as-prepared powders was examined at room temperature in a three-electrode cell configuration, Li metal / electrolyte 1 mol/dm$^3$ LiPF$_6$- ethylcarbonate and diethylcarbonate (EC+DEC) / cathode material. The cathode materials consist of LiMn$_2$O$_4$ powders and Au wire as collector. The metallic lithium was used as a counter and reference electrodes. The charge and discharge characteristics of the cathode were evaluated at cyclic voltammograms. The cell assembly was conducted at room temperature in a glove box filled with high purity argon gas. The experiments were performed using a Hokuto-denko Model HAB-151 electrochemical interface controlled by a computer at a scanning rate of 10 mV/s.

3. RESULTS AND DISCUSSIONS

The experimental conditions are summarized in Table 1. Spinel LiMn$_2$O$_4$ particles were successfully synthesized by an solvent evaporation method from the precursor solutions. From SEM pictures of as-prepared LiMn$_2$O$_4$ particles confirmed that surface modification (Fig. 2). The specific surface area (SSA) and crystallite size (CS) of as-prepared
Fig. 3 XRD patterns of LiMn$_2$O$_4$ particles prepared from various starting solutions.

The XRD patterns of all samples were identified a single-phase spinel with a space group Fd3m in which the lithium ion occupied the tetrahedral (16d) site. All the samples were a secondary particle that was formed by cohesion of the primary particles with around a few ten nanometer sizes. The low temperature synthesis with C$_{16}$TAC is ascribed to removal by combustion of surfactant.

Fig. 4 shows the cyclic voltammograms of the surface modified (Run No. 2, 4) and conventional (Run No. 1, 3) LiMn$_2$O$_4$ particles between 3.0 – 4.5 V at a scan rate of 10 mV/s. As can be seen, two pair of gentle separated redox peaks were observed.
peaks, located at about 4.0 and 4.2 V (oxidation potential vs. Li/Li⁺) are observed. The presence of the two pair of redox peaks in cyclic voltammogram suggests that lithium-ion are extracted and inserted into the spinel phase by a two-step process. It can be clearly seen that the larger specific surface area, the better performance. This fact may indicated that the porous LiMn₂O₄ particles promotes the Li⁺ diffusion on the solid surface.

4. CONCLUSIONS

In this study the synthesis of the surface modification LiMn₂O₄ particles using solvent evaporation process was investigated. From SEM pictures of as-prepared LiMn₂O₄ particles confirmed that all samples were modified with surfactant micelles. All the samples had the spinel structures. To investigate the electrochemical characteristics of as-prepared LiMn₂O₄ particles, the assembly of electrochemical cells was made and the oxidation / redox performance were evaluated potentiostatically at room temperature. As the results, two pair of gentle separated redox peaks, located at about 4.0 and 4.2 V (oxidation potential vs. Li/Li⁺) were observed.

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