LiMn$_2$O$_4$ microspheres as high-performance cathode materials for Li-ion batteries

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Abstract. Spinel LiMn$_2$O$_4$ microspheres were prepared by lithiating MnCO$_3$ solid microspheres and MnO$_2$ hollow microspheres, respectively. Li$_2$CO$_3$ was used as lithium source. The spinel LiMn$_2$O$_4$ microspheres samples annealed at different temperatures were characterized by XRD, SEM, and galvanostatic charge/discharge profile measurement. The LiMn$_2$O$_4$ microspheres show an initial discharge capacity reaches 128 mAh/g at 1 C, more than 120 mAh/g of capacity is retained after 80 cycles and the best cycling stability. These results indicate that the LiMn$_2$O$_4$ microspheres could be a promising cathode material for lithium ion batteries.

1. Introduction

Spinel LiMn$_2$O$_4$ is an attractive candidate cathode material for Li-ion batteries and high theoretical capacity of 148mAh/g, because it has many advantages, such as low toxicity, cost efficiency, environmental friendliness [1–2]. However, spinel LiMn$_2$O$_4$ suffers from Mn-dissolution into the electrolyte (Mn$^{3+} \rightarrow$ Mn$^{2+}$ + Mn$^{4+}$) and Jahn-Teller distortion of Mn$^{3+}$ ions with high spin, leading to poor cycle life and storage performance, especially at high temperatures; restrict its commercial use. To address these issues, many strategies, such as surface coating and/or cations doping have been developed for preparing the LiMn$_2$O$_4$ with high performance [3]. Furthermore, the LiMn$_2$O$_4$ with special morphologies have been studied, such as nanoparticles, nanowires, nanorods, mesoporous materials, and microspheres. It is found the electrochemical performances are largely dependent on the morphology, the crystallinity and the porosity of the structures [4–5].

In this work, we have succeeded in designing and synthesis of unique microspheres of LiMn$_2$O$_4$ with nanoparticles-assembled ultrathin shell by a self-support template. As cathode materials for lithium ion batteries, the LiMn$_2$O$_4$ microspheres exhibit improved rate capability and good cyclic stability.

2. Experiment

All chemicals were of analytical grade and were used without further purification. Briefly, two stock solutions of MnSO$_4$ (4.84g of MnSO$_4$·H$_2$O in 100 ml of deionized water) and NH$_4$HCO$_3$ (22.57g of NH$_4$HCO$_3$ in 100 ml of deionized water) were first prepared. 10 ml ethanol was added in sequence to the MnSO$_4$ solution, after the NH$_4$HCO$_3$ solution was added to the MnSO$_4$ solution under stirring at room temperature. The mixture was maintained for 12 h at room temperature and the powders obtained were filtered and washed by distilled water several times and then dried in the air at 60°C for...
24 h. The obtained MnCO$_3$ microspheres were pre-calcined at 400 °C for 5 h; then, the as-prepared were mixed and ground with LiOH·H$_2$O with the stoichiometric molar ratio (Li: Mn = 1.05: 2) and then the mixtures were calcined at 700 °C for 12 h in air.

2.1. Characterization
Powder X-ray diffraction patterns of the samples were obtained with a Rigaku XRD diffractometer. The morphologies of the samples were observed by using a scanning electron microscope (SEM; LEO 1530VP, Germany).

2.2. Electrochemical measurement
The electrochemical properties of the products were measured via a model test cell system. The working electrodes were prepared by compressing a mixture of as-obtained (70 wt %), acetylene black (250 wt %) and polytetrafluoroethylene (PTFE) (10 wt %) onto a copper foil. Then the coated electrodes were dried at 110 °C for 24 h in a vacuum furnace. The counter and reference electrodes were Li foil. Between the anode and cathode, there was the electrolyte which was 1 M LiPF$_6$ dissolved in a 50/50 vol % mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The separator was Celgard 2400 porous polypropylene. The counter and reference electrodes were lithium foil. The model test cells were assembled in an argon-filled glove box. Charge-discharge tests were carried out at different current densities in the range of 3.0 V to 4.5 V.

3. Results and discussion
The structures of the as-synthesized LiMn$_2$O$_4$ samples was analysed by powder X-ray diffraction (XRD). The XRD patterns (Fig. 1a) of these samples are similar with the structure of spinel LiMn$_2$O$_4$. It can be found that all the diffraction peaks completely match with the standard diffraction peaks of LiMn$_2$O$_4$ under the Fd-3m space group (JCPDS No. 35-0782).

![Figure 1. XRD patterns of (a) LiMn2O4 microspheres; SEM image of (b) MnCO3, (c) MnO2 microspheres, and (d) LiMn2O4 microspheres.](image-url)
The morphologies of the MnCO$_3$, the as-prepared, and LiMn$_2$O$_4$ samples are shown in Fig. 1b-d. Fig.1b and c showed that MnO$_2$ faithfully retained the morphology and size of the precursor MnCO$_3$ particles, with both having a diameter of about 1.0-2.0 μm. The microspheres have a diameter of around 1.5μm in Fig. 1(d). We can observe that nanoparticles/plates are used as Nano blocks to assemble secondary microspheres.

It is generally known that the size and shape of the LiMn$_2$O$_4$ microspheres can have a greater influence on the electrochemical properties. Fig. 2a shows the cycling performance of the resulting LiMn$_2$O$_4$ microspheres at 1 C in the voltage range of 3.0-4.5 V. It can be seen that the LiMn$_2$O$_4$ microspheres with the initial discharge capacity of 128 mAh g$^{-1}$ can display good capacity retention of 93.8%, retains a reversible capacity of 120 mA g$^{-1}$ after 80 cycles. From the above analysis, it can be concluded that the LiMn$_2$O$_4$ microspheres can present good electrochemical performance due to the large surface-to-volume ratio and more efficient electron transport pathway, which benefits from the one-dimensional structure of the LiMn$_2$O$_4$ microspheres.

![Figure 2](image.png)

**Figure 2.** The cycle stability of LiMn$2$O$4$ microspheres at rate of (a)1C and (b) at different rates.

Fig. 2 b shown the rate capability of the LiMn$_2$O$_4$ microspheres electrode at various current densities. Apparently, the LiMn$_2$O$_4$ microspheres electrode displays good capacity retention at different current densities. the discharge capacity of the cathode is 129, 113, 102, and 86 mAh g$^{-1}$ at 1, 2, 4, and 5 C, respectively. It is notable that the discharge capacity reaches 119 mAh g$^{-1}$ at a rate of 1 C, up to 80% of the theoretical capacity (148 mAh g$^{-1}$).

4. **Conclusion**

In summary, LiMn$_2$O$_4$ microspheres have been prepared through a facile synergistic-effect promoted chemical reaction. When applied as cathode materials for rechargeable Li-ion batteries, the obtained LiMn$_2$O$_4$ microsphere materials exhibit a high electrochemical capacity of 128 mAh g$^{-1}$ at 1 C, excellent rate capability and outstanding cycling performances. The superior electrochemical performance suggests we will be able to use these obtained LiMn$_2$O$_4$ as cathode materials for high-power battery applications.

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