LiMn₂O₄ Microspheres: Synthesis, Characterization and Use As a Cathode in Lithium Ion Batteries

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ABSTRACT

Solid and hollow microspheres of LiMn₂O₄ have been synthesized by lithiating MnCO₃ solid microspheres and MnO₂ hollow microspheres, respectively. The LiMn₂O₄ solid microspheres and hollow microspheres had a similar size of about 1.5 μm, and the shell thickness of the hollow microspheres was only 100 nm. When used as a cathode material in lithium ion batteries, the hollow microspheres exhibited better rate capability than the solid microspheres. However, the tap density of the LiMn₂O₄ solid microspheres (1.0 g/cm³) was about four times that of the hollow microspheres (0.27 g/cm³). The results show that controlling the particle size of LiMn₂O₄ is very important in terms of its practical application as a cathode material, and LiMn₂O₄ with moderate particle size may afford acceptable values of both rate capability and tap density.

KEYWORDS

Cathode, LiMn₂O₄ microspheres, tap density, rate capability, particle size

1. Introduction

The spinel LiMn₂O₄ has been considered as a promising candidate for replacement of LiCoO₂ in lithium ion batteries (LIBs), on the basis of its low cost, low toxicity and high safety [1]. These merits make LiMn₂O₄ an ideal material, in principle, for use in large scale batteries for powering electric vehicles (EV) or hybrid electric vehicles (HEV) [2], but the energy density of LIBs is still too low to support their practical application. Fabrication of high energy density LIBs requires a cathode material with high specific capacity and high density [3]. Thus increasing the tap density of LiMn₂O₄ cathode materials will be helpful to increase the energy density of LIBs. It has been shown that the particle morphology is a very important factor affecting

the density of materials, and materials composed of spherical particles have higher tap density than that of irregular particles [3]. Indeed, there have been many reports of spherical particles of battery electrode materials showing high tap densities, including LiCoO₂ [3], LiMn₂O₄ [4], LiFePO₄ [5], and Li₄Ti₅O₁₂ [6, 7]. Here, we report a simple, template-free and high yield method for preparing solid and hollow spherical particles of LiMn₂O₄. As shown in Fig. 1, MnCO₃ solid microspheres and MnO₂ hollow microspheres as precursors were synthesized based on a modified version of a previous method [8, 9]. They were subsequently transformed into LiMn₂O₄ solid and hollow microspheres respectively. Furthermore, the electrochemical properties of LiMn₂O₄ solid and hollow microspheres have been evaluated and compared.

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Figure 1 Schematic illustration of the formation of LiMn_2O_4 solid microspheres and LiMn_2O_4 hollow microspheres

2. Experimental

2.1 Synthesis of MnCO_3 solid microspheres and MnO_2 hollow microspheres

0.169 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and 0.84 g of NaHCO_3 were separately dissolved in 70 mL portions of distilled water. 7 mL of ethanol was then added to the MnSO_4 solution under stirring, and the NaHCO_3 solution was then directly added. The resulting mixture was then maintained at room temperature for 3 h. The as-obtained MnCO_3 solid microspheres were washed several times with distilled water and absolute alcohol.

For MnO_2 hollow microspheres, 0.1 g of as-prepared MnCO_3 solid microspheres were dispersed in 20 mL of H_2O . Then 5 mL of 0.032 mol/L KMnO_4 solution was added under stirring. After 6 min, 5 mL of 0.01 mol/L HCl was added and the mixture stirred for 1 min. MnO_2 hollow microspheres were obtained after centrifugation, and washed several times with water.

2.2 Synthesis of LiMn_2O_4 solid and hollow microspheres

As-prepared MnCO_3 solid microspheres and MnO_2 hollow microspheres were separately mixed and ground with $\text{LiOH} \cdot \text{H}_2\text{O}$, with $\text{Li/Mn} = 1:2$. The two mixtures were calcined at 650°C for 3 h. Solid and hollow microspheres, respectively, of LiMn_2O_4 were obtained.

2.3 Characterization

X-ray diffraction (XRD) patterns were collected using a Rigaku D/max 2500Pc X-ray diffractometer with Cu

$\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The particle size and morphology of samples were investigated with a LEO 1530 field-emission scanning electron microscope (FESEM). Powders were dispersed in ethanol to prepare the SEM samples. The specific surface area of the powders was determined by the BET method using a Quantachrome Autosorb-1 analyzer. The tap density of the powders was measured as follows: A certain quantity of a powder was added into a dry measuring cylinder, and the measuring cylinder tapped until the volume of the powders did not change. The ratio of the mass to volume of the powder gives the tap density. The electrochemical properties of LiMn_2O_4 solid and hollow microspheres were evaluated using coin type cells with lithium metal as the counter electrode. The working electrode was fabricated by mixing the active material, acetylene black and polyvinylidene fluoride (PVDF) in the weight ratio 80:10:10. The electrolyte was a 1 mol/L solution of LiPF_6 in a 1:1 mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) and the separator was Celgard 2500. The cell was assembled in a glove box filled with highly pure argon gas. The galvanostatic charge/discharge experiments were performed between 3.0 and 4.3 V at different current densities.

3. Results and discussion

Figures 2(a) and 2(b) show the XRD patterns of the precursor MnCO_3 solid microspheres and MnO_2 hollow microspheres. Figures 2(c) and 2(d) show the XRD patterns of LiMn_2O_4 solid and hollow microspheres, which agree well with the standard pattern for spinel LiMn_2O_4 (JCPDS No. 35-0782), with no impurities detected.

The particle size and morphology of samples are shown in Fig. 3. Figures 3(a) and 3(b) show SEM images of MnCO_3 and solid LiMn_2O_4 microspheres, LiMn_2O_4 faithfully retained the morphology and size of the precursor MnCO_3 particles, with both having a diameter of about $1.5 \mu\text{m}$. Figure 3(c) shows a transmission electron microscope (TEM) image of the LiMn_2O_4 microspheres, suggesting they have a solid structure. The SEM images of MnO_2 and LiMn_2O_4 particles shown in Figs. 3(d) and 3(e), respectively, indicate that both are composed of microspheres with

Figure 2 XRD patterns of (a) MnCO_3 solid microspheres, (b) MnO_2 hollow microspheres, (c) LiMn_2O_4 solid microspheres and (d) LiMn_2O_4 hollow microspheres

Figure 3 (a) SEM image of MnCO_3 solid microspheres, (b) SEM image of LiMn_2O_4 solid microspheres, (c) TEM image of LiMn_2O_4 solid microspheres, (d) SEM image of MnO_2 hollow microspheres (the inset is a TEM image of MnO_2 hollow microspheres), (e) SEM image of LiMn_2O_4 hollow microspheres, and (f) TEM image of LiMn_2O_4 hollow microspheres

a diameter of about 1.5 μm . Figure 3(f) shows a TEM image of the LiMn_2O_4 , which indicates that the material is composed of hollow microspheres with a size of about 1.5 μm and shell thickness of about 100 nm, just like the precursor MnO_2 hollow microspheres (shown in the inset image in Fig. 3(d)).

As previously discussed, the tap density of the electrode materials is intimately related to the energy

density of a LIB. Higher tap densities will result in high volumetric specific capacities. The tap density of the solid microspheres was about four times of hollow microspheres (the measured values were 1.0 and 0.27 g/cm^3 , respectively). Although many reports have highlighted the many advantages of nanoelectrodes for use in LIBs, Scrosati and Armand have described some disadvantages of nanoelectrodes, the most important one being the poor packing density of the electrodes leading to lower volumetric energy densities [10, 11]. The tap density of the hollow microspheres, with their shell thickness of about 100 nm, was much lower than that of solid microspheres with size of about 1.5 μm . This suggests that using LiMn_2O_4 solid microspheres as a cathode will result in higher volumetric energy densities.

Subsequently, the electrochemical performances of as-prepared LiMn_2O_4 solid and hollow microspheres were investigated. The discharge capacities and cycle stability of LiMn_2O_4 solid and hollow microspheres are shown in Fig. 4(a), for a discharge rate of 100 mA/g . The solid and hollow microspheres exhibited almost the same discharge capacities of about 110 $\text{mA}\cdot\text{h}/\text{g}$, and low capacity fading, after 55 cycles. Thus at a discharge rate of 100 mA/g , the LiMn_2O_4 solid and hollow microspheres both have excellent cycle stability. In Fig. 4(b), the discharge capacities as a function of discharge rates of 50, 100, 200, 300, 400, and 500 mA/g are compared, where the charge/discharge cycle was carried out five times at every rate. At low discharge rates, from 50 to 300 mA/g , the discharge capacities and cycle stabilities of LiMn_2O_4 solid and hollow microspheres were quite similar. However, when the discharge rate was increased to 400 or 500 mA/g , LiMn_2O_4 solid and hollow microspheres showed quite different properties. For example, LiMn_2O_4 hollow microspheres displayed higher discharge capacity and better cycle stability than the solid microspheres. The discharge capacity of the solid microspheres only reached 60 $\text{mA}\cdot\text{h}/\text{g}$ at a rate of 400 mA/g , which was only two-thirds that of the value for the hollow microspheres.

The specific surface area of the LiMn_2O_4 hollow microspheres, determined by the BET method, was 17.5 m^2/g , higher than that of the solid microspheres (12.3 m^2/g). Larger surface areas can augment the

Figure 4 (a) The cycle stability of LiMn_2O_4 solid microspheres (■) and LiMn_2O_4 hollow microspheres (●) at rate of 100 mA/g, and (b) plots of discharge capacity vs. number of cycles for LiMn_2O_4 solid microspheres (■) and LiMn_2O_4 hollow microspheres (●) at different rates

interface between the electrode material and the electrolyte. As a result, LiMn_2O_4 hollow microspheres, with a shell thickness of about 100 nm, exhibited better rate capability than the solid microspheres with a size of about 1.5 μm . This can be attributed to the hollow microsphere structure giving shorter Li diffusion lengths and increased contact area between LiMn_2O_4 and the electrolyte; a similar phenomenon has been observed by Guo in the case of ZnFe_2O_4 hollow spheres [12]. The discharge capacity of LiMn_2O_4 solid microspheres is significantly reduced at high rate. Zaghbi and Goodenough explained that the decrease in capacity when discharging at a high rate may arise because the lithium ions do not have sufficient time to

enter into the core of the materials [13]. For example, Wan's group has calculated that a reduction of diffusion length from 10 μm (the typical particle size of commercial electrode materials) to 100 nm, results in a decrease in the mean diffusion time from 5000 to 0.5 s [14]. Many reports have also demonstrated that smaller particles of electrode materials have shorter diffusion lengths for Li^+ , higher electrode/electrolyte contact areas, and better accommodation of the strain than common micron-sized materials [15–19].

4. Conclusions

LiMn_2O_4 solid and hollow microspheres have been prepared and characterized. Although LiMn_2O_4 hollow microspheres exhibited better cycle stability than that of solid microspheres, the tap density of the solid microspheres was much higher than that of the hollow microspheres. This suggests that cathode materials with moderate particle size offer acceptable values of both rate capability and tap density. We suggest that the controlling particle size of cathode materials will be very important in developing practical applications of these materials.

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