LiMn$_2$O$_4$ Microspheres: Synthesis, Characterization and Use As a Cathode in Lithium Ion Batteries

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ABSTRACT
Solid and hollow microspheres of LiMn$_2$O$_4$ have been synthesized by lithiating MnCO$_3$ solid microspheres and MnO$_2$ hollow microspheres, respectively. The LiMn$_2$O$_4$ 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 LiMn$_2$O$_4$ solid microspheres (1.0 g/cm$^3$) was about four times that of the hollow microspheres (0.27 g/cm$^3$). The results show that controlling the particle size of LiMn$_2$O$_4$ is very important in terms of its practical application as a cathode material, and LiMn$_2$O$_4$ with moderate particle size may afford acceptable values of both rate capability and tap density.

KEYWORDS
Cathode, LiMn$_2$O$_4$ microspheres, tap density, rate capability, particle size

1. Introduction
The spinel LiMn$_2$O$_4$ has been considered as a promising candidate for replacement of LiCoO$_2$ in lithium ion batteries (LIBs), on the basis of its low cost, low toxicity and high safety [1]. These merits make LiMn$_2$O$_4$ 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 LiMn$_2$O$_4$ 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 LiCoO$_2$ [3], LiMn$_2$O$_4$ [4], LiFePO$_4$ [5], and Li$_4$Ti$_5$O$_12$ [6, 7]. Here, we report a simple, template-free and high yield method for preparing solid and hollow spherical particles of LiMn$_2$O$_4$. As shown in Fig. 1, MnCO$_3$ solid microspheres and MnO$_2$ hollow microspheres as precursors were synthesized based on a modified version of a previous method [8, 9]. They were subsequently transformed into LiMn$_2$O$_4$ solid and hollow microspheres respectively. Furthermore, the electrochemical properties of LiMn$_2$O$_4$ solid and hollow microspheres have been evaluated and compared.

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2. Experimental

2.1 Synthesis of MnCO₃ solid microspheres and MnO₂ hollow microspheres

0.169 g of MnSO₄·H₂O and 0.84 g of NaHCO₃ were separately dissolved in 70 mL portions of distilled water. 7 mL of ethanol was then added to the MnSO₄ solution under stirring, and the NaHCO₃ solution was then directly added. The resulting mixture was then maintained at room temperature for 3 h. The as-obtained MnCO₃ solid microspheres were washed several times with distilled water and absolute alcohol.

For MnO₂ hollow microspheres, 0.1 g of as-prepared MnCO₃ solid microspheres were dispersed in 20 mL of H₂O. Then 5 mL of 0.032 mol/L KMnO₄ 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. MnO₂ hollow microspheres were obtained after centrifugation, and washed several times with water.

2.2 Synthesis of LiMn₂O₄ solid and hollow microspheres

As-prepared MnCO₃ solid microspheres and MnO₂ hollow microspheres were separately mixed and ground with LiOH·H₂O, with Li/Mn = 1:2. The two mixtures were calcined at 650 °C for 3 h. Solid and hollow microspheres, respectively, of LiMn₂O₄ were obtained.

2.3 Characterization

X-ray diffraction (XRD) patterns were collected using a Rigaku D/max 2500Pc X-ray diffractometer with Cu Ka radiation (λ = 1.5418 Å). 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 LiMn₂O₄ 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 LiPF₆ 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 MnCO₃ solid microspheres and MnO₂ hollow microspheres. Figures 2(c) and 2(d) show the XRD patterns of LiMn₂O₄ solid and hollow microspheres, which agree well with the standard pattern for spinel LiMn₂O₄ (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 MnCO₃ and solid LiMn₂O₄ microspheres, LiMn₂O₄ faithfully retained the morphology and size of the precursor MnCO₃ particles, with both having a diameter of about 1.5 μm. Figure 3(c) shows a transmission electron microscope (TEM) image of the LiMn₂O₄ microspheres, suggesting they have a solid structure. The SEM images of MnO₂ and LiMn₂O₄ 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$_2$O$_4$ solid microspheres and (d) LiMn$_2$O$_4$ hollow microspheres

Figure 3  (a) SEM image of MnCO$_3$ solid microspheres, (b) SEM image of LiMn$_2$O$_4$ solid microspheres, (c) TEM image of LiMn$_2$O$_4$ 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$_2$O$_4$ hollow microspheres, and (f) TEM image of LiMn$_2$O$_4$ hollow microspheres

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$_2$O$_4$ solid microspheres as a cathode will result in higher volumetric energy densities.

Subsequently, the electrochemical performances of as-prepared LiMn$_2$O$_4$ solid and hollow microspheres were investigated. The discharge capacities and cycle stability of LiMn$_2$O$_4$ 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 mA·h/g, and low capacity fading, after 55 cycles. Thus at a discharge rate of 100 mA/g, the LiMn$_2$O$_4$ 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$_2$O$_4$ solid and hollow microspheres were quite similar. However, when the discharge rate was increased to 400 or 500 mA/g, LiMn$_2$O$_4$ solid and hollow microspheres showed quite different properties. For example, LiMn$_2$O$_4$ hollow microspheres displayed higher discharge capacity and better cycle stability than the solid microspheres. The discharge capacity of the solid microspheres only reached 60 mA·h/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$_2$O$_4$ 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
interface between the electrode material and the electrolyte. As a result, LiMn$_2$O$_4$ 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$_2$O$_4$ and the electrolyte; a similar phenomenon has been observed by Guo in the case of ZnFe$_2$O$_4$ hollow spheres [12]. The discharge capacity of LiMn$_2$O$_4$ solid microspheres is significantly reduced at high rate. Zaghib 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$_2$O$_4$ solid and hollow microspheres have been prepared and characterized. Although LiMn$_2$O$_4$ 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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