Facile synthesis of porous Mn$_2$O$_3$ microsphere as an anode material for lithium ion batteries

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Abstract. The precursors of Mn$_2$O$_3$ was synthesized through co-precipitation method using MnAc$_2$·4H$_2$O, NaHCO$_3$ as raw materials. The precursors were heat-treated at 400 °C, 500 °C, and 600 °C, respectively. The samples were characterized by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The electrochemical properties of the samples were investigated also. The test results showed that the Mn$_2$O$_3$ (heat-treated at and 600 °C) featured higher reversible capacity and better cycling performance than that of other samples. The specific capacity of the Mn$_2$O$_3$ samples (heat-treated at and 600 °C) was 745 mAh/g respectively after 100 cycles at a constant current of 100 mA/g in the voltage range of 0.01-3 V. The preparation principle for the formation of the Mn$_2$O$_3$ samples and its electrochemical process of Mn$_2$O$_3$ were discussed also.

1. Introduction
Lithium-ion batteries (LIBs) is a fast-developing technology in electric energy storage, are the dominant power source for a wide range of the communications, transportation and renewable-energy sectors [1, 2]. The current choice of anode materials for LIBs is graphite due to its long cycle life, abundant material supply and relatively low cost. However, graphite, the anode material currently used in commercial LIBs, has a relatively low Li storage capacity of 370 mAh/g [3].

Recently, a variety of metal oxides has been investigated as potential electrode materials for LIBs. Among the numerous candidates as LIB anodes, three representative types of metal oxides stand out with distinct lithium storage mechanisms and characteristics, namely tin dioxide, titanium dioxide, and many transition metal oxides (Fe$_2$O$_3$, Fe$_3$O$_4$, NiO, Co$_3$O$_4$, CoO, and MnO$_x$). Compared with the currently commercialized graphite anode, these metal oxide materials have been demonstrated with various advantages, such as very high capacity (high reversible capacities between 500 and 1000 mAh/g), widespread availability, good stability, and environmental benignity. Mn$_2$O$_3$ has a high specific theoretical capacity (1018 mAh/g) as an anode material for LIBs [4], but previous reports that the application of manganese oxide-based anodes is challenging because of their poor electrical conductivity and large volume change during cycling. Much attention has been paid to improve the cycling performance of Mn$_2$O$_3$ and reduce the irreversible capacity [5-7]. It is well known that the different morphologies and different particle sizes of the electrode materials have very important effects on the electrochemical performance of the LIBs.
In this work, we report a facile precipitation method for the large-scale synthesis of MnCO$_3$ microspheres and their transformation into porous Mn$_2$O$_3$ microspheres by controlling the calcination processes. This method is simple, inexpensive and suitable for mass production. The electrochemical performances of the as-prepared porous Mn$_2$O$_3$ microspheres as anode materials of LIBs were also investigated.

2. Experimental
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 1000 ml of deionized water) and NH$_4$HCO$_3$ (22.57g of NH$_4$HCO$_3$ in 1000 ml of deionized water) were first prepared. 100 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. Then the solution turned milky white, which indicated the initial formation of MnCO$_3$ sphere. 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 ℃ for 24 h. The obtained MnCO$_3$ powders were heated in air at 400-600 ℃ to synthesize Mn$_2$O$_3$ microspheres (denoted as MO-1, MO-2, and MO-3, respectively).

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).

The electrochemical characterization was performed using CR2032 coin-type test cells. The cell consisted of a cathode with the composition of 70 wt.% active materials, 20 wt.% carbon black, and 10 wt.% PVDF, a lithium metal anode separated by a Celguard 2400 microporous film. The electrolyte was 1 molL$^{-1}$ LiPF$_6$/(EC) and (DEC) (1:11:1 by volume). The counter and reference electrodes were lithium foil. The model test cells were assembled in a glove box filled with argon gas. Charge-discharge tests were carried out at different current densities in the range of 0.01 V to 3.0 V.

3. Results and discussion
Figure 1 illustrates the XRD patterns of the three Mn$_2$O$_3$ samples obtained at different annealing temperature. All diffraction lines in Fig.1a can be indexed to the pure cubic phase of Mn$_2$O$_3$ (JCPDS card No. 78-0390). No impurity phase was detected on the XRD patterns.
The surface morphological features of the samples were investigated by SEM (Fig. 2). Figure 2(a) shows the SEM images of the precursor MnCO$_3$. As shown in Figure 2a, MnCO$_3$ powder is composed of well-dispersed spherical particles with a size of about 0.5–1 μm. Figures 2(b-d) showed the SEM images of the Mn$_2$O$_3$ microsphere samples, the porous spherical morphology with the same diameter as the precursor MnCO$_3$ is formed. It is well known that the particle size, particle size distribution and morphologies of the samples will directly influence the electrochemical performance of the electrode materials. Fig.2d showed the SEM images of the Mn$_2$O$_3$ microsphere sample obtained from the thermal decomposition of MnCO$_3$ microspheres in air at 600 °C for 4 h. Apparently, the porous spherical morphology is formed when the annealing time is 4 h. It is well known that the particle size, particle size distribution and morphologies of the samples will directly influence the electrochemical performance of the electrode materials. Considering its mesoporous structure favoring the diffusion of Li$^+$ ions and electrode–electrolyte contacts during the electrochemical reaction, the porous Mn$_2$O$_3$ microspheres are expected to improve the electrochemical performance.

![Figure 2. SEM images of (a) precursor MnCO$_3$, (b) MO-1, (c) MO-2, and (d) MO-3.](image)

The electrochemical performances of Mn$_2$O$_3$ were measured via coin cell testing. Figure 3 showed the typical discharge/charge cycles of the as-prepared MO-1, MO-2, and MO-3 electrodes cycled between 0.01 and 3.0 V with a current density of 100 mA/g at room temperature, respectively. The initial discharge capacities of the as-prepared MO-1, MO-2, and MO-3 were 1092, 1231, and 1285 mAh/g, but the reversible discharge capacities drop to 374, 448, and 627 mAh/g, respectively. In the first discharge curves, two voltage plateaus near at 1.25 and 0.25 V is clearly observed in all samples, and the peak shifts to higher potential at 0.5 V in the following cycles, while the charge curves of the three samples show a deinsertion plateaus at about −1.3 V.
Figure 3. (a) 1st and (b) 100th charge-discharge voltage profiles and (c) cycling performance of the MO-1, MO-2, and MO-3; (d) cycling performance of the MO-3 electrode at various current densities.

To better understand the electrochemical behavior of the MO-3 mesoporous microspheres, we also investigated its rate performance as shown in Figure 3. The MO-3 electrode was cycled at various current densities (100−1600 mA/g). The cell shows good rate capability with average discharge capacity of 1238, 663, 496, 444, 339, and 293 mAh/g when the current density increased stepwise to 100, 200, 400, 800, 1200, and 1600 mA/g, respectively. Upon altering the current density back to 100 mA/g, an average discharge capacity as high as 620 mAh/g could be recovered. Large surface area and the short diffusion length of spherical porous structured electrode can improve the kinetic properties of the lithium-ion during intercalation and easily delivers high discharge capacity even under extremely high currents. These results demonstrate that the mesoporous structure Mn2O3 has great potential as high-rate anode material in lithium-ion batteries.

Fig. 4 illustrates the electrochemical impedance spectra of the samples which were recorded in the fresh cell. Two depressed semicircles are observed for both electrodes, the one located in high frequency ranges assigned to surface film resistance and the one located in medium frequency ranges assigned to charge transfer impedance. The kinetics difference of the electrodes was further investigated by modeling AC impedance spectra based on the Randles equivalent circuit. In this equivalent circuit, Rs represents the ohmic resistance of the electrolyte solution, Rct is the resistance of the charge transfer reaction, Cdl is the capacitance of the electrode–electrolyte double layer, and Zw is the Warburg impedance. Analysis of the experimental data was performed by fitting equivalent circuits. The charge transfer resistance Rct was significantly lower for the MO-3 electrode (143 Ω) compared to that the MO-1 and MO-2 electrodes (151 and 264 Ω). Obviously, the diameters of the
The semicircle for the MO-3 electrodes are smaller than that the other samples, and the semicircle was the smallest for the MO-3 electrodes, revealing lower charge transfer impedance. The remarkably improved rate properties of the carbon-coated samples are due to the suppression of the solid electrolyte interfacial (SEI) layer development and faster kinetics of both the Li\(^+\) diffusion and the charge transfer reaction. These facts support that the MO-3 electrodes sample has good electrochemical properties suitable for electrode material in lithium ion battery.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{EIS of MO-1, MO-2, and MO-3.}
\end{figure}

4. Conclusion
In summary, Mn\(_2\)O\(_3\) mesoporous microspheres have been synthesized by a facile method. The mesoporous MO-3 microspheres exhibited a high reversible capacity of 925 mAh/g, it still retains a high capacity of 565 mAh/g, even after 100 cycles at a current density of 100 mA/g. These results clearly demonstrate that the Mn\(_2\)O\(_3\) mesoporous microspheres have better electrochemical performance with high specific capacity, long cycle life, and good rate capability, indicating that they are promising candidates for LIB anodes. Besides, our facile strategy has made it possible to optimize the electrode conjuration of future energy storage devices and can also be extended to synthesize other anode materials with excellent performance.

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