Cryptomelane-type manganese oxide (KMn₈O₁₆) nanorods cathode materials synthesized by a rheological phase for lithium ion batteries

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Abstract. Cryotolerance-type manganese oxide (KMn₈O₁₆) nanorods were prepared for the first time by a rheological phase reaction method. The KMn₈O₁₆ samples were characterized by X-ray diffraction, scanning electron microscopy, the effects of different annealed temperatures on the morphologies and electrochemical properties of the final products were systematically investigated. The result that the annealed samples exhibit the superior electrochemical performances compared to the unannealed sample. The KMn₈O₁₆ nanorods annealed at 400 ℃ show the highest reversible discharge capacity (147.9 mAh/g even after 80 cycles) at current density of 50 mA/g and the best cycling stability. These results indicate that the KMn₈O₁₆ nanorods could be a promising cathode material for lithium ion batteries.

1. Introduction
Cryptomelane-type manganese oxide octahedral molecular sieves (OMS-2) are microporous materials. The OMS-2 materials are made of edge-shared MnO₆ octahedra that form 2 × 2 tunnels with a pore size of about 4.6 Å. Manganese in OMS-2 are Mn⁴⁺ and Mn³⁺ located in octahedral sites. In the tunnels, cations (Li⁺, K⁺, Na⁺, Rb⁺, Cs⁺, NH₄⁺, etc.,) reside with a small amount of water to stabilize the tunnel structure. Potassium ions have been taken as the ideal cation templates to form and stabilize the 2 × 2 tunnel structure in synthetic cryptomelane materials, because the dimensions of the tunnel sizes of OMS materials were believed to be controlled directly by the sizes of the templates used. The study on the use of metal cations other than K⁺ as tunnel templates to synthesize OMS-2 materials has been left as an open field for OMS materials.

In this work, we report the preparation of KMn₈O₁₆ nanorods via the rheological phase reaction method and successive annealing procedure. The crystal structure, morphology and electrochemical properties of the KMn₈O₁₆ nanorods were investigated. We find that the annealing procedure plays important roles in improving the electrochemical performance of the electrodes for LIBs.

2. Experimental
All chemicals were of analytical grade and were used without further purification. The KMn₈O₁₆ was synthesized by using KMnO₄, Mn(CH₃COO)₂·4H₂O, and KNO₃ as reactants. KMnO₄, Mn(CH₃COO)₂·4H₂O, and KNO₃ were mechanically mixed in the molar ratio of 2:3:0.05 in an agate mortar and an appropriate amount of water was added to the mixture to obtain a rheological phase.
The rheological phase mixture was heated at 100 °C for 12 h. The mixture was cooled down to room temperature and washed with distilled water for several times. A precursor was obtained. Then, the precursor was heated at 300, 400, and 500 °C for 4 h in air, respectively (designated as KMO-300, KMO-400, and KMO-500, respectively).

The structure and crystallinity of the samples were characterized using an X-ray diffractometer (XRD, Rigaku X-ray diffractometer). The morphologies of the samples were observed using a transmission electron microscope (TEM; Tecnai G2 F30, FEI company).

Electrochemical measurements were carried out using a 2032-type coin cell. The working electrode was fabricated in the ratio of 70:20:10 (w/w) active material/carbon black/polyvinylidene difluoride, while lithium foil served as counter and reference electrode. The electrolyte was 1 M LiPF₆ dissolved in 1:1 ethylene carbonate (EC) and dimethyl carbonate (DMC). Constant current charge/discharge cycling was conducted on a Newware battery tester in the voltage range between 4.0 and 1.5 V.

3. Results and discussion

The XRD patterns of all the KMn₈O₁₆ are shown in Fig. 1a. All diffraction lines can be indexed to the cryotolerance phase with tetragonal symmetry (JCPDS file No. 20-090), which were well consistent with the previous reports in the literature and no impurity phase was detected on the XRD patterns. The KMO-300 sample shows significantly broadened peaks compared to the other samples synthesized at higher temperatures, indicating that the KMO-300 sample has the smallest crystallinity. The surface morphological features of KMn₈O₁₆ were investigated by TEM of the three samples. As given in Fig. 1(b-d), The transmission electronmicroscope (TEM) images of the KMO-300, KMO-400 and KMO-500 are all mainly composed of nanorods with a diameter around 5–20 nm and a length of around 100–300 nm. The aspect ratio of these nanorods is in the range of 10–60.

![Figure 1. XRD patterns (a) of the three samples; TEM images of (b) KMO-300, (c) KMO-400, and (d) KMO-500.](image-url)
The electrochemical performances of KMn$_8$O$_{16}$ samples were measured via coin cell testing. Fig. 2 shows the cycling performances of the KMO-300, KMO-400 and KMO-500 electrodes cycled between 1.5 and 4.0 V with a current density of 50 mA g$^{-1}$ at room temperature, respectively. As can be seen, all KMn$_8$O$_{16}$ electrodes showed excellent cycling stabilities. KMO-400 exhibits the best performance for Li insertion, an initial discharge capacity of 143.9 mAh g$^{-1}$, corresponds to about 4 Li atoms. The initial discharge capacities of KMO-300 and KMO-500 electrodes were 120.4, 144.3, and 135 mAh g$^{-1}$, respectively. After 50 cycles, the discharge capacities of KMO-300, KMO-400 and KMO-500 drop to 134.8, 145.3, and 125.8 mAh g$^{-1}$, respectively. After 80 cycles, the discharge capacities can retain 133.2, 147.9, and 126.8 mAh g$^{-1}$. For the KMO-300 and KMO-500 electrodes, the capacity retentions were 92.3, and 93.4 % after 80 cycles, respectively. The capacity retention was above 100 % for the KMO-400 electrode. The capacities of the KMO-300, KMO-400, and KMO-500 electrodes kept rising at the initial stage, except for the first few cycles. These facts support that the annealed KMn$_8$O$_{16}$ samples have the good electrochemical properties suitable for electrode material in lithium ion battery.

![Figure 2](image)

**Figure 2.** (a) cycling performance of the three samples, (b) KMO-400 electrode at various current densities.

In order to investigate possible application in high power density devices, the rate capability of the KMn$_8$O$_{16}$ nanorod electrode was studied, as shown in Figure 2b. Apparently, the KMO-400 electrode displays good capacity retention at different current densities. When the current densities are 50, 100, 200, 400, and 800 mA g$^{-1}$, the specific capacities are 144.2, 125.2, 112.3, 97.3, and 84.5 mAh g$^{-1}$, respectively. When the current density is reduced to 50 mA g$^{-1}$ after the rate performance testing, the KMO-400 cell can provide the formerly measured value (147.5 mAh g$^{-1}$), indicating its good reversibility and high rate capability.

4. Conclusion

KMn$_8$O$_{16}$ were successfully synthesized by rheological phase reaction and following annealing treatment. The annealed temperature affected the electrochemical properties of the KMn$_8$O$_{16}$ nanorods. The annealed samples exhibited higher discharge capacities and better cycling performances compared to the unannealed sample. Especially, the sample KMO-400 showed the highest discharge capacity, best electrochemical performance, and high rate capability. After 80 cycles, the KMO-400 electrode exhibited a reversible discharge capacity up to 147.9 mAh g$^{-1}$ with a current density of 50 mA g$^{-1}$. The present results suggest that the annealed KMn$_8$O$_{16}$ nanorods are promising cathode materials for lithium ion batteries.
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