Synthesis and Electrochemical Properties of Li$_{0.33}$MnO$_2$ Nanorods as Positive Electrode Material for 3 V Lithium Batteries

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In this study, one-dimensional Li$_{0.33}$MnO$_2$ nanorods were synthesized by a solid state reaction using γ-MnO$_2$ as a precursor. γ-MnO$_2$ was prepared under different reaction times by a redox process. The HR-TEM results showed that the diameter and length of the Li$_{0.33}$MnO$_2$ nanorods are 5–20 nm and about 200 nm, respectively. The Li$_{0.33}$MnO$_2$ nanorods delivered a discharge capacity of 157 mA h g$^{-1}$ at 1 C, and retained 97% of their initial capacity over 30 cycles. Good rate performance was also observed, with discharge capacities of 201 and 133 mA h g$^{-1}$ at 0.1 C and 2 C, respectively. The morphology of the nanorods could increase their electrochemical properties, resulting in higher capacity and rate performance.

Keywords: Lithiated Manganese Dioxides, Nanorods, Redox Process, Lithium Batteries.

1. INTRODUCTION

3 V positive materials are efficient energy storage devices for small size memory back-up sources for various electrical devices. Lithiated MnO$_2$, Li$_{0.33}$MnO$_2$, is such a materials, and it shows a capacity of 140–190 mA h g$^{-1}$ with a flat potential of 2.9 V versus Li/Li$^+$. Several research works have documented the structural stability and the electrochemical properties of Li$_{0.33}$MnO$_2$. This compound exhibited a tendency for the capacity to fade during repeated charge/discharge processes and has shown poor rate stability.$^{1-3}$

Recently, nanostructured electrodes have been widely investigated for enhancing the performance of lithium ion batteries. Among them, low-dimension nanostructures, nanorods, are the most attractive morphology. Nanorod materials can generally provide high specific surface areas, short ion diffusion pathways and efficient one-dimensional electron transport pathways.$^{4-8}$

This study aims to improve the rate capability of Li$_{0.33}$MnO$_2$ by using nanorod morphology in the synthesis. We report the electrochemical performance of Li$_{0.33}$MnO$_2$ nanorods synthesized by heating LiNO$_3$ and γ-MnO$_2$ at a low temperature. γ-MnO$_2$ was synthesized under two different reaction times by a redox process. The crystal structures of the materials were studied, and their electrochemical properties were investigated. The influences of the precursor reaction time on the morphology of the Li$_{0.33}$MnO$_2$ were investigated. The correlation between the nanorod morphology and the improved electrochemical performance was also discussed.

2. EXPERIMENTAL DETAILS

Nanorods of γ-MnO$_2$ were prepared from MnSO$_4$ and MnCO$_3$ using NaClO$_3$ as an oxidizing agent. Stoichiometric amounts of MnSO$_4$, MnCO$_3$, and NaClO$_3$ were dissolved in distilled water and sulfuric acid was added. The mixture was heated at 80 °C for two different reaction times of 1 and 2 h. After the reaction was complete, the dark-brown products were filtered, washed several times, and dried at 60 °C. Li$_{0.33}$MnO$_2$ nanorods were synthesized by a solid state reaction using the prepared γ-MnO$_2$ with LiNO$_3$ (Li/Mn molar ratio of 0.33) and preheated at 280 °C for 5 h, and finally calcined at 350 °C for 12 h. The crystalline phases were identified by X-ray diffraction (XRD, D/Max 2500PC, Rigaku, Japan). Morphological studies were conducted using high resolution-transmission electron microscopy (HR-TEM,
JEOL, JEM-2000EX, Japan). The nitrogen adsorption/desorption isotherms and specific surface area of the materials were measured with Belshor-Mini II equipment (Bel Inc., Japan). X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, ULVAC-PHI, Japan) measurements were also performed.

The electrochemical performances of the samples were investigated with a two-electrode coin-type cell with lithium foil as the counter electrode. The working electrode was composed of 80 wt% active material, 10 wt% carbon black, and 10 wt% polyvinylidene fluoride binder. The electrolyte was a solution of 1.0 M LiPF$_6$ with ethylene carbonate/ethyl-methyl carbonate (EC/EMC = 1/1 vol%). The galvanostatic charge and discharge cycle tests of the cells were carried out at room temperature between 2 and 4 V.

3. RESULTS AND DISCUSSION

Figures 1(b), (d) show the XRD patterns of the Li$_{0.33}$MnO$_2$ nanorods made with the two different reaction times of the $\gamma$-MnO$_2$ (Figs. 1(a), (c)). The patterns of the Li$_{0.33}$MnO$_2$ appear at $2\theta$ = 17.6°, 21.6°, 37.0°, 41.7°, 49.3°, 52.8°, 53.3°, and 66.1°, which are very different from the features of the $\gamma$-MnO$_2$. The positions of the diffraction peaks and their relative intensities agree well with those of previous reports.$^9,10$

Figure 2 shows the morphology of the as-prepared Li$_{0.33}$MnO$_2$ nanorods. It can be seen that the reaction time of the precursor has a large effect on the morphology of the nanorods. With the increase in the reaction time, nanorods with higher aspect ratios were observed. As can be seen from Figure 2(a), nanorods with a reaction time of 1 h were 15–20 nm in diameter and 40–120 nm in length. When the reaction time was prolonged to 2 h (Fig. 2(b)), the nanorods were longer. They had diameters of 5–20 nm and lengths of 150–200 nm.

Figure 3 shows the nitrogen adsorption–desorption isotherms of the samples. The samples have a specific surface area of 34.1 m$^2$ g$^{-1}$ for Li$_{0.33}$MnO$_2$-1 h and 37.5 m$^2$ g$^{-1}$ for Li$_{0.33}$MnO$_2$-2 h, depending on the reaction time of precursors. The high specific surface area of the samples could increase the electrode–electrolyte contact area and thus decrease the current density per unit surface area, leading to its high electrochemical properties.$^1,11$

Figure 4 shows the Mn XPS core spectra for the samples. The binding energy was calibrated with reference to the C1s level of carbon (284.5 eV). There are two peaks in the Mn 2p core level spectrum, which are ascribed to the spin-orbit splitting of the components Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$. The major peak for Mn 2p$_{3/2}$ is centered at 642.2 eV and corresponds to the Mn$^{4+}$ ions in the compound.$^{12}$ The XPS results show that the predominant oxidation states of Mn in the samples are 4. In particular, the Mn 2p$_{3/2}$ peak position for Li$_{0.33}$MnO$_2$-2 h shifts towards higher binding
energies, owing to the (+4) oxidation state of the Mn cations.13

Figure 5 shows voltage profiles of the rate capabilities of the samples at different charge–discharge rates. The first discharge capacities of Li0.33MnO2-1 h and Li0.33MnO2-2 h are 189 and 201 mA h g⁻¹, respectively. The discharge capacity of the Li0.33MnO2-1 h nanorods decreases to 146, 123, 105, 80, and 61 mA h g⁻¹ as the current rate increases to 0.5, 1, 2, 5, and 10 C, whereas the discharge capacity of the Li0.33 MnO2-2 h nanorods is 182, 156, 133, 105, and 83 mA h g⁻¹ at these same current rates. The Li0.33MnO2-2 h nanorods exhibit higher initial discharge capacity and rate capability than Li0.33MnO2-1 h. The BET surface area of the Li0.33MnO2-2 h nanorods is lower than that of the Li0.33MnO2-2 h nanorods, and thus, the reduced electrolyte contact area leads to a decrease in the capacity decay at a higher C rate. This advantage results from the one-dimensional efficient electron transport of the Li0.33MnO2-2 h along the length of each rod. In addition, the small diameters the Li0.33MnO2-2 h nanorods contribute to improving the rate capability owing to the short lithium ion diffusion distance.14 15 The initial discharge capacity of the nanorods synthesized in this study was higher than that of previously synthesized Li0.33MnO2 (194 mA h g⁻¹) and Li0.33MnO2 nanorods (199 mA h g⁻¹).2 4 In addition, our present results were superior to He et al.’s work with respect to the rods’ rate capability. Apparently, the nanorod morphology of Li0.33MnO2 benefits from the shorter lithium diffusion path and larger contact area between active material and electrolyte, which promises higher discharge capacity.

Figure 6 shows the cycling behaviors of the samples for 30 cycles. The initial discharge capacity of the Li0.33MnO2-2 h nanorods is 157 mA h g⁻¹, which is higher than that of Li0.33MnO2-1 h (128 mA h g⁻¹). Li0.33MnO2-2 h has a high capacity retention of 97% after 30 cycles, compared with 93% for Li0.33MnO2-1 h. This is because the oxidation state of Mn in Li0.33MnO2 indicates 4+ with the increase in the reaction time of the precursor, as revealed by XPS.16

4. CONCLUSION

In summary, γ-MnO2 nanorods were used to successfully synthesize Li0.33MnO2 nanorods at 350 °C. Morphology control of the Li0.33MnO2 nanorods was demonstrated
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using precursors with 1-h and 2-h reaction times. Nanorods with a precursor reaction time of 1 h had diameters of 15–20 nm and lengths of 40–120 nm. When the reaction time was increased to 2 h, the nanorods obtained had diameters of 5–20 nm and lengths of 150–200 nm. The Li$_{0.33}$MnO$_2$-2 h nanorods exhibited a discharge capacity of 157 mA h g$^{-1}$ with capacity retention of 97% over 30 cycles. They also showed good rate capability. The improved electrochemical performance comes from the nanorods, which decreased the diffusion lengths of both the lithium and the electrons.

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References and Notes


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