



Effects of the starting materials of Na_{0.44}MnO₂ cathode materials on their electrochemical properties for Na-ion batteries



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ABSTRACT

Na_{0.44}MnO₂ is one of the most promising cathode materials in the development of sodium ion batteries (SIBs). Here, a solid-state method is described for the synthesis of regular Na_{0.44}MnO₂ nanorods about 200 nm in size at a low temperature without further annealing being required. In this work, we have investigated effects of different precursors on preparation of Na_{0.44}MnO₂ and found that the size and width of the Na_{0.44}MnO₂ nanorods were influenced by the MnCO₃ precursors. The electrochemical properties for SIBs of Na_{0.44}MnO₂ nanorods synthesized from three different preparation methods were thoroughly researched. Na_{0.44}MnO₂ nanorods prepared by hydrothermal synthesis of MnCO₃ (HS-Na_{0.44}MnO₂) produced a superior cathode material than other Na_{0.44}MnO₂ which uses commercial MnCO₃ (C-Na_{0.44}MnO₂) and co-precipitation synthesis of MnCO₃ (CP-Na_{0.44}MnO₂) as precursors. The HS-Na_{0.44}MnO₂ exhibits high discharge capacity (about 139.6 mAh g⁻¹), good cycling stability (98.2% after 40 cycles at the current density of 20 mA g⁻¹) and excellent rate performance, which is a much better performance than those in previous reports. The superior electrochemical performance of HS-Na_{0.44}MnO₂ is mainly due to the relatively smaller size, uniform morphology and excellent crystallinity. Furthermore, the electrochemical impedance spectroscopy (EIS) showed that the surface film resistance and charge transfer resistance of the HS-Na_{0.44}MnO₂ is smaller than others, which leading to the better electrochemical performance.

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1. Introduction

Lithium-ion batteries (LIBs) are widely used in consumer electronics and electric vehicles. The study for LIBs have also aroused widely concern and achieved great achievements [1–8]. Sodium ion (Na-ion) based battery system is an alternative option of LIBs for large scale energy storage and portable applications due to the abundance and low cost of sodium source and similar intercalation behavior with Li-ion [9–13]. The larger radius of Na-ion (1.02 Å, relative to Li-ion 0.69 Å) would cause more difficult and complicated extraction and insertion than Li-ion [14,15]; moreover sodium prefers 6-coordination in octahedral or prismatic arrangement, whereas Na4-coordination is quite limited in inorganic materials [16]; this property makes it challenging to find favorable cathode materials with suitable diffusive tunnels and structure for sodium storage. G. Ceder, et al. [15] research shows that open

structures, such as the layered structures, that are both able to accommodate the Na and Li ion; moreover, attributed to the weaker Na-O than Li-O bonding resulting the Na⁺ migration can potentially be easier than that for Li⁺ migration. For the close-packed structures, such as AMPO₄, show that Na generally prefers the maricite structure, whereas Li prefers the olivine structure. Thus far, various potential cathode materials for SIBs have been reported [17–19], such as layered sulfides (Ni₃S₂) [20], olivine structure NaFePO₄ [21], Prussian blue crystals [22] and sodium transition-metal oxides [23–27].

Especially, Na_xMnO₂ (x = 0.2, 0.40, 0.44, 0.70, 1) compounds [28] with layered or tunnel structures have attracted particularly extensive attention due to the larger ionic size difference between sodium and transition metals. Among these, the orthorhombic Na_{0.44}MnO₂ (i.e. Na₄Mn₉O₁₈) shows excellent electrochemical performance [28–33] because it possesses large S-shaped tunnel structure which is suitable for sodium incorporation. The Na_{0.44}MnO₂ has a theoretical specific capacity of about 122 mAh g⁻¹ between 2.0V and 4.0V and can provide relatively high capacity in literatures. The researchers have done a series of

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reports on the synthesis methods of influence on structure and properties [34,35]. For example, recent research shows that the capacity of $\text{Na}_{0.44}\text{MnO}_2$ nanowires can reach 128 mAh g^{-1} at 0.1C, and the capacity also maintained 77% after 1000 cycles at 0.5C [36]. Single phase $\text{Na}_{0.44}\text{MnO}_2$ nanorods obtained through a classic solid-state reaction delivers a reversible capacity of 140 mAh g^{-1} in 3.8–2.0 V at a cycling rate of C/200 [37]. Moreover, $\text{Na}_{0.44}\text{MnO}_2$ is successfully applied in aqueous electrolyte which means that the cost battery could be further reduction [29]. In spite of all the favorable properties of $\text{Na}_{0.44}\text{MnO}_2$, the efficiency and capacity of the nanoscale $\text{Na}_{0.44}\text{MnO}_2$ are restricted by their poor electrical conductivity ($\sim 10^{-6} \text{ S cm}^{-1}$ at 20°C) [36,38]. In addition, the $\text{Na}_{0.44}\text{MnO}_2$ prepared by directly solid state method usually contained Mn_2O_3 -bixbyite impurity and the acidic treatment to remove the Mn_2O_3 would induces sodium leaching [39]. In this case, developing simple route to synthesize high performance $\text{Na}_{0.44}\text{MnO}_2$ is noteworthy. Furthermore, the effect of the reactant MnCO_3 on the electrochemical performance of the final product is also needed to be thoroughly exploit for further commercial application of this material.

In this report, we successfully applied three types MnCO_3 obtained by different methods (hydrothermal synthesis, co-precipitation method and commercial products) as Mn source to fabricate $\text{Na}_{0.44}\text{MnO}_2$ nanorods. The size and morphology of the $\text{Na}_{0.44}\text{MnO}_2$ nanorods were affected by the MnCO_3 reactant; the $\text{Na}_{0.44}\text{MnO}_2$ fabricated by hydrothermal synthesis MnCO_3 shows better crystallizability and more uniform particle size. Furthermore, we have investigated the electrochemical properties of $\text{Na}_{0.44}\text{MnO}_2$ cathode materials for SIB; the $\text{Na}_{0.44}\text{MnO}_2$ fabricated by hydrothermal synthesis MnCO_3 delivers highest discharge capacity (about 139.6 mAh g^{-1}) and cycling stability (98.2% after 40 cycles at the rate of 20 mA g^{-1}) among three $\text{Na}_{0.44}\text{MnO}_2$ electrodes. The diffusion behavior of three $\text{Na}_{0.44}\text{MnO}_2$ materials is further researched by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

2. Experimental

All reagents were analytical grade and used were not further purified.

2.1. MnCO_3 synthesis

For hydrothermal synthesis of MnCO_3 (HS- MnCO_3): In detail, 1.5 mmol KMnO_4 were dissolved in 25 ml deionized water, then 0.075 g potassium sodium tartrate and 0.3 g glucose were added to the above solution, and the mixture were dispersed into a uniform solution by magnetic stirring. The final solution was placed in Teflon-lined autoclaves (30 mL) and heated at 160°C for 6 h. After the reaction solution was cooled to room temperature, the final product was filtered, washed by absolute alcohol and deionized water repeatedly. Finally, the products were dried in a vacuum freeze-drier and collected for further characterization.

For co-precipitation method preparation of MnCO_3 (CP- MnCO_3): 0.250 g polyvinyl pyrrolidone (M.W = 30,000), 0.212 g Na_2CO_3 and 0.338 g MnSO_4 were added to 50 ml of deionized water. The mixture was stirred at room temperature for 12 hours. The product were filtered, washed and then vacuum freeze-dried.

2.2. $\text{Na}_{0.44}\text{MnO}_2$ synthesis

$\text{Na}_{0.44}\text{MnO}_2$ was synthesized by solid-phase reaction using three kinds of MnCO_3 (hydrothermal synthesis, co-precipitation method and commercial products) and Na_2CO_3 as raw material with the Na_2CO_3 to MnCO_3 ratio 0.23:1. The reagents were grounded with ethanol by Ball mill for 5 hours. The resulting

homogenous mixture precursor was preheated at 300°C for 8 h and then calcined at 800°C for 9 h at the heating rate of 2°C min^{-1} . For convenience, the final products were noted as C- $\text{Na}_{0.44}\text{MnO}_2$ (synthesized by commercial MnCO_3), CP- $\text{Na}_{0.44}\text{MnO}_2$ (synthesized by CP- MnCO_3), and HS- $\text{Na}_{0.44}\text{MnO}_2$ (synthesized by HS- MnCO_3) respectively.

2.3. Crystal and morphology structure characterization

The X-ray diffraction (XRD) analysis was performed with a Bruker D8 advanced X-ray diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Diffraction data were collected by step scanning over an angular range of $5\text{--}80^\circ$ with a step width of 0.02° (35 KV, 30 mA). The size and the morphology of the obtained samples were performed on a Hitachi S-4800 scanning electron microscope (SEM).

2.4. Electrochemical characterization

The $\text{Na}_{0.44}\text{MnO}_2$ electrodes for electrochemical measurements were prepared by dispersing a mixture of 10% polyvinylidene fluoride (PVDF), and 10% conductivity carbon black, and 80% active materials ($\text{Na}_{0.44}\text{MnO}_2$) in N-methyl pyrrolidone (Fluka Inc., St. Louis, MO, USA) onto a Al foil current collector. And the typical loading amount of the active material was about 2.0 mg/cm^2 . The liquid electrolyte consisted of 1 M NaClO_4 in a mixture of isometric diethyl carbonate (DEC) and ethylene carbonate (EC) (volume ratio 1:1, Guotaihuarong Co., Zhangjiagang, China). The CR-2025 type coin cell were assembled in an argon glove box with the concentrations of moisture and oxygen below 1 ppm, using Na foil as a counter electrode and glass fiber (GF/D) of Whatman separator. The galvanostatic charge-discharge and cyclic voltammetry (CV) experiments were tested in CR2025 coin cell, over a range of 4.0–2.0 V (vs. Na/Na^+). The EIS measurements were utilizing a three-electrode system and performed at room temperature on an electrochemical work station (CHI760E, Chenhua Ltd Co., Shanghai, China) with an amplitude of 1 mV s^{-1} , the frequency range was between 10^{-2} and 10^5 Hz .

3. Results and Discussion

3.1. XRD and SEM studies

XRD patterns of MnCO_3 compounds obtained by three methods are shown in Fig. 1. The strong and sharp diffraction peaks reflect that the products are all well crystallized. The diffraction peaks (Fig. 1a) can be well indexed as the MnCO_3 (rhomb-centered hexagonal phase with the cell parameters of $a = 4.79 \text{ \AA}$, $c = 15.69 \text{ \AA}$ and $\beta = 106.31^\circ$, space group $R3c$ (167), JCPDS No: 44–1472). Fig. 1b and c showed the same diffraction peaks with Fig. 1a, which indicated that MnCO_3 were successfully prepared by hydrothermal

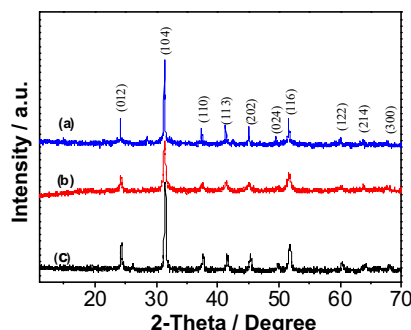


Fig. 1. XRD patterns of MnCO_3 (a) HS- MnCO_3 ; (b) CP- MnCO_3 ; (c) C- MnCO_3 .

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