



Low-cost birnessite as a promising cathode for high-performance aqueous rechargeable batteries



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ABSTRACT

A highly reversible aqueous rechargeable battery system is assembled by using a Zn anode, a room-temperature synthesized MnO₂-birnessite cathode and a mild ZnSO₄-based aqueous electrolyte with MnSO₄ as an additive. Structural analysis reveal that MnO₂-birnessite undergoes a structural transformation to poorly crystalline MnO₂. It offers an operating voltage of 1.39 V, an energy density of 364 Wh kg⁻¹ (cathode only) at 200 mA g⁻¹ and shows a capacity retention of 100% over 400 cycles at 500 mA g⁻¹. This low-cost battery system is a promising candidate for large-scale energy storage.

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1. Introduction

Due to the ever-increasing energy demands and concerning on global warming, advanced renewable energy technologies have received much attention [1–4]. With the development of clean and sustainable energy sources such as wind, solar and tide, large-scale stationary energy storage systems (ESSs) are critical for the utilization of renewable energy sources [5]. Among various options, lithium-ion batteries (LIBs) have emerged as a leading candidate for digital and mobile devices [6]. Although LIBs show high energy density and efficiency [5], some intrinsic properties hinder their large-scale applications in stationary ESSs, where the cost, safety and durability become relatively more important [7]. Therefore, the promising alternatives for large-scale stationary ESSs are the low-cost and safe aqueous rechargeable batteries (ARBs).

To date, a variety of ARBs have been investigated, such as lithium-ion batteries [8], sodium-ion batteries [9], potassium-ion batteries [10], magnesium-ion batteries [11], nickel-ion batteries [12], aluminium-ion batteries and mixed-ion batteries [13,14]. Development of aqueous zinc-ion batteries employing a cheap metallic Zn as anode have attracted much interest [15–17]. A

cation-defected ZnMn₂O₄ spinel has lately been studied as a cathode material for Zn-ion ARBs. Whereas, this cathode exhibits relatively low capacity (about 90 mAh g⁻¹ at 500 mA g⁻¹) [18]. Meanwhile, Prussian blue analogues with finite capacity have been reported as zinc intercalation cathodes in Zn-ion ARBs [19,20]. Also, porous amorphous iron phosphate has been shown as a potential host for Zn ion [10]. Unfortunately, inferior capacity make this cathode less feasible for large-scale stationary ESSs. Additionally, cobalt oxide (Co₃O₄) [21] and Nickel oxide hydroxide (NiOOH) [2] have been exploited as cathodes, which showed high reversible capacity, good rate performance and high stability. The discharge capacity of Co₃O₄ cathode was 78 mAh g⁻¹ at 10 A g⁻¹ [21]. More than 54,000 cycles were achieved by using a rechargeable nickel-Zn battery [2]. Nevertheless, the use of Ni and Co raise the cost and causes significant environmental concerns [22,23]. On the other hand, manganese-based materials show some promise as cathodes for large-scale stationary ESSs because the elemental abundance in the Earth's crust [24], but the manganese oxides cathodes suffer poor rate-performance and significant capacity fading, more must be done to improve performance [25–29].

In this work, we demonstrate an aqueous rechargeable battery based on Zn and poorly crystalline MnO₂-birnessite with high reversible capacity and long-cycle stability. More importantly, poorly crystalline MnO₂-birnessite can be synthesized at room temperature. The low energy consumption cathode exhibited an

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average discharge voltage of 1.39 V at 0.67C (1C corresponding to 300 mA g^{-1}) and was cycled at 100% coulombic efficiency at both low (0.67C) and high (10C) rates. This study provides greener and more sustainable batteries for large-scale electrical energy storage.

2. Material and methods

2.1. Synthesis of layered MnO_2 -birnessite

All chemical reagents were purchased from Aladdin Reagent Company (Shanghai, China) and used without any further purification. The synthetic procedure was conducted as follows: first, 2.535 g of manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) was dissolved in 50 ml of deionized water (denoted as solution A). 2.16 g of sodium hydroxide (NaOH) and 10 ml of hydrogen peroxide (H_2O_2 , 30 wt%) were dissolved in 90 ml of deionized water (denoted as solution B). Then, solution B was dropwise added to solution A under vigorous stirring. The mixed solution was kept stirring for 1 h and aged overnight at room temperature. The precipitate was collected by filtration, washed with water and ethanol, and dried at 50°C .

2.2. Materials characterization

X-ray diffraction (XRD) patterns of the samples were recorded on an Empyrean X-ray diffractometer using filtered $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA. The morphologies of the samples were characterized by SEM using a field emission scanning electron microscope (FE-SEM, JEOL, JSM-7500F). Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images were obtained using a ZEISS LIBRA-200FE field emission transmission electron microscope operating at 200 kV. Thermogravimetric analysis (TGA) was carried out under air flow with a temperature ramp of $10^\circ\text{C min}^{-1}$.

2.3. Electrochemical measurements

The electrochemical tests were carried out in coin-type cells (CR2032). The working electrodes were prepared as follows: the as-prepared MnO_2 -birnessite was mixed with carbon black (Super P) and polymer binder (polytetrafluoroethylene, PTFE) in a weight ratio of 70:20:10 with the help of ethanol. After drying, the mixture was pressed into a film and cut into disk (diameter 10 mm, thickness $\sim 70 \mu\text{m}$, see Fig. S1 in Supplementary). The mass of cathode was measured by an electronic balance (Sartorius BSA124S, 0.1 mg resolution). Several cathode were weighed and then used. The MnO_2 -birnessite mass loading is $3\text{--}5 \text{ mg cm}^{-2}$. The coin cells were assembled in open air atmosphere using a MnO_2 -birnessite electrode as the cathode, a glass fibre (GF/D, Whatman) as the separator and a zinc foil (Alfa Aesar) as the anode. 1 M ZnSO_4 with 0.1 M MnSO_4 as an additive in H_2O was used as the electrolyte without oxygen removal [30]. All of the cells were aged for 6 h before any electrochemical processes. The charge–discharge (1.0–1.85 V vs. Zn/Zn^{2+}) tests were conducted on a LANHE battery tester (Wuhan, China) at room temperature. All of the cells were initially charged/discharged five cycles at 0.33C before further tests. The cells were cycled at various current densities. For the current densities higher than 0.67C, a two-step charge process is employed. That is, the constant current charge step is followed by an additional constant voltage charge step till the current drops to two fifths of its initial value. The cyclic voltammetry (CV) tests were carried out using an AUTOLAB PGSTAT302 N potentiostat.

3. Discussion

3.1. Structure and morphology

Layered MnO_2 -birnessite was synthesized via a facile precipitation method at room temperature. Fig. 1a shows the XRD pattern of the as-synthesized sample, which can be indexed to a layer hexagonal unit cell of the birnessite framework (JCPDS: 23-1046). Based on the (002) diffraction peak, the manganese layer-to-layer distance is approximately 0.727 nm, which is consistent with previous reports [31,32]. The (212) diffraction peak located at 24.6° hints the interplanar spacing is 0.361 nm, which is corresponding to the interplanar separation between manganese oxide layers and water/ Na^+ ion. The morphology of MnO_2 -birnessite was confirmed by using a field emission scanning electron microscope (FE-SEM). As shown in Fig. 1b and Fig. S2 (see Supplementary), the as-synthesized MnO_2 -birnessite particles consist of thin sheets of size 10 nm. The MnO_2 -birnessite sheets are agglomerated to each other, forming several micrometre-sized secondary particles. In addition, the ratio of Na and Mn was approximately determined using energy-dispersive spectroscopy, and the value is 0.32 (Fig. S3, see Supplementary). A thermogravimetric analysis (TGA) result reveals that the weight loss between 120°C and 300°C was about 6.4% (Fig. S4, see Supplementary), which can be ascribed to the removal of the crystal water [31,32]. According to the above results, the chemical formula of as-synthesized MnO_2 -birnessite is $\text{Na}_{0.32}\text{MnO}_2 \cdot 0.34\text{H}_2\text{O}$.

3.2. Electrochemical performance

The electrochemical properties of MnO_2 -birnessite in aqueous rechargeable ion batteries was examined using coin-type cells. Based on the previous result, MnSO_4 was used as additive to improve the cycling performance of the MnO_2 -birnessite electrode [15]. Cyclic voltammetry (CV) curves of MnO_2 -birnessite and Zn were scanned at 0.1 mV s^{-1} in the potential range of 1.0–1.85 V vs. Zn/Zn^{2+} . As shown in Fig. 2a, two separated reversible redox peaks located at 1.17/1.59 and 1.34/1.65 V can be clearly identified in the initial cycle. After several cycles, the CV curves are well repeated with two pairs reduction/oxidation peaks located at 1.25/1.53 and 1.39/1.60 V, which are in accordance with plateaus of the discharge/charge curves (see below, Fig. 2c), corresponding to a two-step reaction. The remarkable difference in CV profiles between the initial and following cycle suggests phase transition.

In addition to the rate capability test, the MnO_2 -birnessite were cycled at various charge/discharge current rates ranging from 0.33C to 10C over a potential window of 1.0–1.85 V, and 1C rate was set to 300 mA g^{-1} . The MnO_2 -birnessite electrode shows an excellent rate capability (see Fig. 2b), delivering high specific charge and discharge capacities of 266, 242, 208, 169, 129 and 113 mAh g^{-1} at 0.33, 0.67, 1.67, 3.33, 6.67 and 10C, respectively. After being cycled at high rate, a high discharge capacity of about 259 mAh g^{-1} can be recovered at 0.33C.

The charge and discharge curves are shown in Fig. 2c. For the charge rate $>0.67\text{C}$, a constant voltage charge step was added till the charge current dropped to two fifths of its initial value. A small fraction (less than 10%) of the total charge capacity was corresponding to the constant voltage step. Interestingly, with the increase in current density, the capacity drops in the first voltage plateau (denoted as region I, see Fig. 2c) are small, whereas capacity in the second voltage plateau (denoted as region II, see Fig. 2c) dramatically dropped. As claimed by Wang et al., the above

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