Low-temperature performance of aqueous electrochemical capacitors based on manganese oxides

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ABSTRACT

This paper involves preparation of four different crystal phases (δ, γ, α and λ) of MnO_2 by redox, solid reaction, hydrothermal routes and delithiation of $LiMn_2O_4$, respectively. The obtained MnO_2 samples have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and the Brunauer–Emmett–Teller (BET) method for micro-structural, morphological and porosity studies. Cyclic voltammetric and galvanostatic tests were carried out to evaluate their capacitive properties in an anti-freezing aqueous electrolyte at different operating temperatures ranging from 25 to $-35\,°C$. The δ-MnO_2 prepared by a redox method exhibits the best electrochemical performances when conducted either in the single electrode tests (from 174.7 to $148.6\,F\,g^{-1}$) or in the capacitor measurements (from 47.4 to $42\,F\,g^{-1}$) as the operating temperature decreased from $25\,°C$ down to the low temperature of $-35\,°C$. Moreover, electrochemical impedance spectroscopy has been investigated and the activation energy values of different impedance components have been analyzed. It has been discovered that the operation temperature has more effect on the charge transfer resistance than diffusion resistance. To some degrees, these results have guiding significance for the low-temperature applications of manganese oxides-based electrochemical capacitors.

1. Introduction

With the sharply growth of global population, there is a much higher demand for energy in future years. Fossil fuel shortage and climate change have triggered significant word-wide interest in developing sustainable and clean energy products [1,2].

Owing to the excellent performance in the terms of high power density and long cycle life, electrochemical capacitors are now attracting extensive research interest as electric energy storage devices [2–4]. There are generally two criteria to classify electrochemical capacitors. One is the charge storage mechanism of electrode materials, and the other is the type of electrolyte. According to the former standard, electrochemical capacitors can be grouped into electrical double-layer and pseudo-capacitors [3]. Based on the latter benchmark, electrochemical capacitors can be divided into aqueous, non-aqueous or solid-state capacitors. Whatever an electrochemical capacitors is ascribed, it will at last be evaluated by the practical needs from different respects,

including electrochemical performance, environmental benignity as well as low cost, etc. In this sense, aqueous electrochemical capacitors using manganese oxides-based electrode material are quite promising. The merits are apparent. Firstly, the electrolyte solutions are aqueous solutions dissolving neutral salts, which are safe, cheap and easy to be handled. Secondly, manganese oxides possess many virtues like their abundant resources, reasonable price, low toxicity, wide electrochemical window, rich redox chemistry, and high theoretical specific capacitance (1100–$1300\,F\,g^{-1}$) [5–10] as well as their flexible and multiple structures or morphologies. Most of the previous studies on manganese oxides-based aqueous capacitors focus on the performance at room temperature.

Very little attention has been paid to the operation of these capacitors in cold environments [37]. This fact actually originates from the lack in suitable aqueous electrolyte solutions for low-temperature utilizations. Recently, we have developed anti-frozen aqueous electrolytes for the electric double-layer capacitors consisting of two porous carbon electrodes [20,36]. We found that the capacitive behavior of porous carbon electrodes at low temperatures is quite different from that at room temperature. So it can be estimated that the charge storage mode of

manganese oxides at low temperatures may be a new challenge for research.

On the other hand, the electrochemical characteristics of a manganese dioxide are strongly dependent upon its crystal structure and morphology [10–13]. Among the crystallographic forms of manganese oxides frequently encountered, α-, β-, γ-, ε-, and ρ-MnO_2 have one-dimensional (1D) tunnel structures, while δ-MnO_2 has an open 2D layered structure, and λ-MnO_2 has an interconnected 3D networks structure [14,15]. Their pseudo-capacitive manners have big differences even at room temperature. Therefore, their respective pseudo-capacitive response towards the drop in temperature is worthy of attention.

In this paper, we report our investigation of these items. Manganese oxides with four kinds of crystallographic forms were synthesized. The electrochemical performance of these electrode materials and the corresponding electrochemical capacitors were tested from room temperature (about 25 °C) to −35 °C.

2. Experimental

2.1. Preparation of manganese oxides

All chemicals were of analytical grade and were used without further treatment. Samples of MnO_2 with different crystal structures were synthesized by the following procedures.

δ-MnO_2 was prepared by a redox method [16]. Briefly, 30 mL of 0.6 M $KMnO_4$ solution was mixed with 30 mL of 0.45 M $MnSO_4 \cdot H_2O$ solution and stirred continuously for 6 h. The precipitate was washed several times with distilled water, centrifuged, and dried at 70 °C in air for 12 h. The as-synthesized MnO_2 was denoted as sample A.

γ-MnO_2 was prepared by a solid reaction [17]. $Mn(OAc)_2 \cdot 4H_2O$ and $(NH_4)_2C_2O_4 \cdot H_2O$ with a mole ratio of 1:1.2 were mixed and well ground in a mortar. After being ground for 40 min, the mixture was placed in a water bath of 80 °C for 4 h. The dry mixture was washed with distilled water, dried in an oven at 110 °C for 10 h, and then the white MnC_2O_4 precursor was obtained. The precursor was air-calcined at 600 °C in a muffle furnace for 10 h. The calcined product was subjected to acid-treatment in 2 M H_2SO_4 solution at 80 °C for 2 h under magnetic stirring. The products were washed with distilled water, filtered, and dried at 70 °C, and the final product was denoted as sample B.

α-MnO_2 was prepared by a hydrothermal method [18]. 1.185 g $KMnO_4$ were dissolved in 45 mL 0.2 mol L^{-1} HNO_3 aqueous solutions under continuous stirring. Then the solution was loaded into a Teflon-lined stainless-steel autoclave and heated at 180 °C for 24 h. The autoclave was cooled slowly to room temperature. The precipitate was washed several times with distilled water, centrifuged, and dried at 50 °C in air for 24 h. The as-synthesized MnO_2 was denoted as sample C.

λ-MnO_2 was prepared by delithiation of $LiMn_2O_4$ [19]. The spinel $LiMn_2O_4$ was synthesized by high temperature solid-state reaction. Electrolytic MnO_2 (EMD) and Li_2CO_3 with the molar 4:1 were ground with 5 mL ethanol as dispersant in an agate mortar .The mixture was extensively ground and then calcined at 800 °C for 4 h. Then the obtained $LiMn_2O_4$ was stirred in 0.5 mol L-1 aqueous sulfuric acid solution for 45 min. The aqueous solution was decanted, and the remaining solid material was filtered and dried in air at 70 °C. The as-synthesized λ-MnO_2 was denoted as sample D.

2.2. Characterization of manganese oxides

X-ray diffraction (XRD) patterns were recorded on a Rigaku-Dmax 2500 diffractometer equipped with graphite monochromatized Cu Kα-radiation source (λ = 1.5406 Å) at a scanning speed of 4° min^{-1} in the range of 10–80°. Scanning electron microscopy (SEM) images were performed using Philips XL 30 and JEOL JSM-6700F microscopes. The detailed morphology observation of the samples was performed using a transmission electron microscopy (TEM) JEOL JEM-2010. The Brunauer-Emmett-Teller (BET) surface area was determined by an nitrogen sorption at 77 K on a Micromeritics ASAP 2020 Analyzer, prior to analysis, samples were heated at 120 °C for 2 h in air, whereas the pore size distribution and pore volume data were calculated from the desorption branches based on the Barrett-Joyner-Halenda (BJH) equation.

2.3. Fabrication of electrodes and assembly of asymmetric capacitors

An electrode was fabricated by pressing the homogenized mixture of 66.7 wt.% active material and 33.3 wt.% conductive binder (TAB, teflonized acetylene black with a PTFE and AB mass ratio of 1:2) on a piece of stainless steel mesh with the area of 1 cm^2. Active electrode materials included the MnO_2 samples or a commercial activated carbon (AC) with the B. E. T. surface area of 1800 $m^2 g^{-1}$ (Heda Carbosino Material CO., Ltd. Shanghai). The mass loading of active material on each electrode was 3 mg cm^{-2}.

AC/MnO_2 asymmetric capacitors were assembled into two-electrode coin cells (type CR2032), where an AC electrode, a MnO_2 electrode and a layer of filter paper served as the negative electrode, the positive electrode and the separator, respectively.

The anti-freezing electrolyte used in this study was 5 M $NaClO_4$ dissolved in the methanol-water binary solvent (16.11 wt.% methanol to 83.89 wt.% water) [20].

2.4. Electrochemical measurements

Electrochemical characterizations were analyzed by electrochemical impedance spectroscopy, cyclic voltammetric and galvanostatic tests, respectively. Electrochemical tests for MnO_2 electrodes were carried out in a three-electrode cell equipped with a MnO_2 working electrode, a graphite sheet ($3 \times 4 cm^2$) counter electrode, and a heavy AC reference electrode. The mass loading of active materials was 15 mg cm^{-2}.
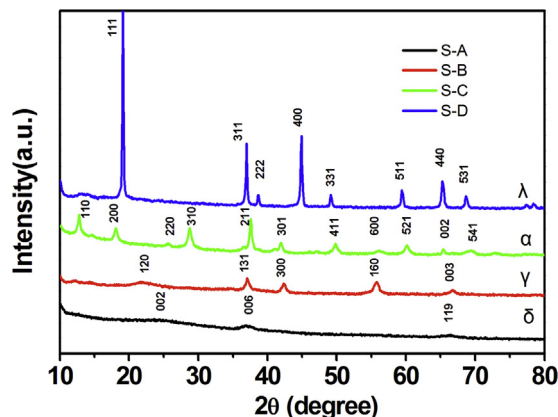

Fig. 1. XRD patterns of MnO_2 samples A(s-A), B(s-B), and C(s-C).