

## Regular Article

# Facile synthesis of birnessite-type manganese oxide nanoparticles as supercapacitor electrode materials



Lihu Liu<sup>a</sup>, Yao Luo<sup>a</sup>, Wenfeng Tan<sup>a</sup>, Yashan Zhang<sup>b</sup>, Fan Liu<sup>a</sup>, Guohong Qiu<sup>a,\*</sup>

<sup>a</sup> College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, PR China

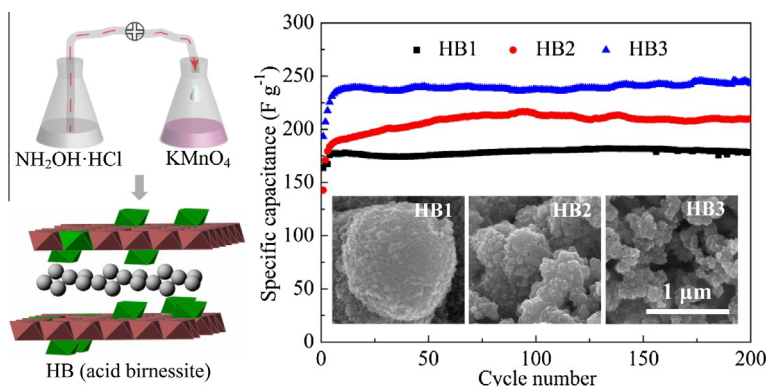
<sup>b</sup> Department of Chemistry, University of Connecticut, Storrs, 55 North Eagleville Road, Storrs, CT 06269, USA

## HIGHLIGHTS

- Acid birnessite is prepared by adding dropwise  $\text{NH}_2\text{OH}\cdot\text{HCl}$  to  $\text{KMnO}_4$  solution.
- Chemical composition, specific surface area and pore volume can be adjusted.
- The as-prepared birnessite shows the highest capacitance of  $245 \text{ F g}^{-1}$ .
- Capacitive performance is mainly affected by surface area and pore volume.

## GRAPHICAL ABSTRACT

Birnessite was facilely prepared by adding dropwise  $\text{NH}_2\text{OH}\cdot\text{HCl}$  to  $\text{KMnO}_4$  solution under ambient temperature and pressure. The as-prepared nanostructured birnessite shows high specific capacitance and excellent cyclic stability, and the capacitive performance is mainly affected by specific surface area and pore volume.



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## ABSTRACT

Manganese oxides are environmentally benign supercapacitor electrode materials and, in particular, birnessite-type structure shows very promising electrochemical performance. In this work, nanostructured birnessite was facilely prepared by adding dropwise  $\text{NH}_2\text{OH}\cdot\text{HCl}$  to  $\text{KMnO}_4$  solution under ambient temperature and pressure. In order to fully exploit the potential of birnessite-type manganese oxide electrode materials, the effects of specific surface area, pore size, content of  $\text{K}^+$ , and manganese average oxidation state (Mn AOS) on their electrochemical performance were studied. The results showed that with the increase of  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , the Mn AOS decreased and the corresponding pore sizes and specific surface area of birnessite increased. The synthesized nanostructured birnessite showed the highest specific capacitance of  $245 \text{ F g}^{-1}$  at a current density of  $0.1 \text{ A g}^{-1}$  within a potential range of 0–0.9 V, and excellent cycle stability with a capacitance retention rate of 92% after 3000 cycles at a current density of  $1.0 \text{ A g}^{-1}$ . The present work implies that specific capacitance is mainly affected by specific surface area and pore volume, and provides a new method for the facile preparation of birnessite-type manganese oxide with excellent capacitive performance.

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\* Corresponding author.

E-mail address: [qiugh@mail.hzau.edu.cn](mailto:qiugh@mail.hzau.edu.cn) (G. Qiu).

## 1. Introduction

With the gradual depletion of fossil fuels and growing energy consumption, the demand for clean and efficient energy has become increasingly prominent [1–3]. Electrochemical supercapacitors, which are characterized by long cycle life, reasonably high energy densities, and ultra-fast charge-discharge rate, have become a versatile solution to various emerging energy applications [2,4,5]. Double-layer capacitance and pseudo-capacitance are the two energy storage mechanisms for supercapacitors. The common electrode materials for double-layer capacitor are carbon materials, and likewise, transition metal oxides are most common for pseudo-capacitors [6–8].

Transition metal oxides, including  $\text{RuO}_2$  [9],  $\text{MnO}_2$  [10–12],  $\text{NiO}$  [13],  $\text{Co}_3\text{O}_4$  [14],  $\text{Fe}_2\text{O}_3$  [15], and  $\text{VO}_x$  [16], are able to improve the energy density of supercapacitors by storing more charge through redox reaction compared with carbon materials. Among different transition metal oxides,  $\text{MnO}_2$  has greater potential owing to its high theoretical specific capacitance ( $1380 \text{ F g}^{-1}$ ) [17,18], low raw material cost and environmentally friendly characteristics. Moreover, birnessite, a layered manganese oxide, has been widely studied as supercapacitor electrode materials due to the rapid intercalation-deintercalation of  $\text{H}^+$  and alkali metal cation.

There are two types of birnessite, namely acid birnessite and alkaline birnessite. In acid birnessite, systematic  $\text{MnO}_6$  octahedral vacancies result in an overall negative charge on the layers of  $\text{MnO}_6$  octahedra [19]. This charge is compensated by  $\text{Mn(II)/Mn(III)}$  in the interlayers above or below the vacancies in the layers of  $\text{MnO}_6$  octahedra, and the  $\text{Mn(II)/Mn(III)}$  content increases with the decrease of Mn AOS. However, few  $\text{MnO}_6$  octahedral vacancies are present in alkaline birnessite and almost all of  $\text{Mn(III)}$  is located in the layers of  $\text{MnO}_6$  octahedra (Fig. 1) [19]. Compared with alkaline birnessite, acid birnessite shows higher specific capacitance and adsorption capacity of heavy metal ions as a result of the existence of more  $\text{MnO}_6$  octahedral vacancies in the layers of  $\text{MnO}_6$  octahedra [18,19].

Different methods have been explored for the synthesis of acid birnessite besides the classic way using the reduction of boiled  $\text{KMnO}_4$  solution by  $\text{HCl}$  [20]. Microwave-assisted hydrothermal method was conducted on the basis of traditional one [21]. Birnessite-type manganese oxides with large specific surface area were prepared by the hydrothermal treatment of a mixed solution of  $\text{KMnO}_4$  and cetyltrimethylammonium hydroxide [11] and  $(\text{NH}_4)_2\text{SO}_4$  [22] at  $90^\circ\text{C}$  for 12 and 24 h, respectively. The reduction of  $\text{KMnO}_4$  solution was also performed by alcohol to obtain acid birnessite at  $60^\circ\text{C}$  [23]. Sol-gel technique was applied to synthesize birnessite with the calcination of the precursor at  $450^\circ\text{C}$  for 2 h [24]. Birnessite was rapidly obtained by adding lactate to the

$\text{KMnO}_4$  solution at ambient atmosphere [25]. A simple redox reaction involving hydroxylamine and permanganate in alkaline medium was applied to prepare layered birnessite-type manganese oxide with the calcination of the precursor at  $400^\circ\text{C}$  [26]. Graphite disk electrode was immersed in the acidic solution of  $\text{KMnO}_4$  at room temperature to obtain  $\alpha\text{-MnO}_x\cdot n\text{H}_2\text{O}$  on the electrode surface [27]. Birnessite particles with large specific surface area were synthesized in an ice-water bath using ascorbic acid to reduce  $\text{KMnO}_4$  [28]. However, most of the currently available methods for synthesizing birnessite are usually conducted under high temperature and pressure with long reaction time. Therefore, it is highly necessary to develop a facile synthesis method for shape-controlled birnessite under mild conditions.

As previously reported, the capacitance performance of manganese oxides is affected by specific surface area, pore size, content of  $\text{K}^+$ , and Mn AOS [7,29]. Large specific surface area and pore volume facilitate the transport of electrolyte ions to the electrode surface. The high content of  $\text{K}^+$  in the interlayers facilitates the rapid transport of ions in birnessite during the charge-discharge processes. Taguchi et al. reported that the decrease of Mn AOS resulting from the increase of  $\text{Mn(III)}$  content led to the attenuation of the specific capacitance due to the lower conductivity of birnessite [30]. However, the decrease of specific capacitance with the increase of Mn AOS of manganese oxides was also reported [31,32]. Thus, the influence of  $\text{Mn(III)}$  content on the supercapacitor performance of manganese oxides remains elusive.

In this work, acid birnessites with different morphologies and particle sizes were fabricated by adding  $\text{NH}_2\text{OH}\cdot\text{HCl}$  to  $\text{KMnO}_4$  solution at ambient temperature and pressure. The influences of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  concentration on the micro-morphologies, Mn AOS, and the corresponding electrochemical properties were systematically investigated.

## 2. Experimental section

### 2.1. Materials synthesis

Birnessite was prepared through reducing  $\text{KMnO}_4$  by  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution at room temperature.  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solutions of 200 mL were first prepared at the concentrations of 0.03, 0.05, 0.07, and  $0.09 \text{ mol L}^{-1}$ , and were respectively added dropwise to  $\text{KMnO}_4$  solution ( $200 \text{ mL}$ ,  $0.1 \text{ mol L}^{-1}$ ) at a speed of  $0.7 \text{ mL min}^{-1}$  with vigorous stirring. Black-brown suspension was soon formed with the addition of  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . After the addition of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution, the suspension was soon filtered and washed with deionized water until the filtrate conductivity was below  $20.0 \mu\text{S cm}^{-1}$ . The as-prepared products were subsequently dried in an oven at  $60^\circ\text{C}$ . The samples were designated as HB1, HB2, HB3, and HB4

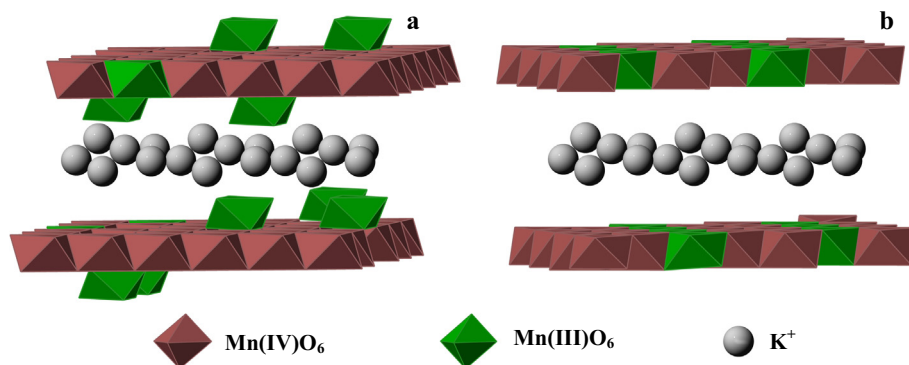


Fig. 1. Schematic illustration for the crystal structures of acid birnessite (a) and alkaline birnessite (b).

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