Colloids and Surfaces A: Physicochem. Eng. Aspects 457 (2014) 94–99

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Electrochemical properties of manganese ferrite-based supercapacitors in aqueous electrolyte: The effect of ionic radius

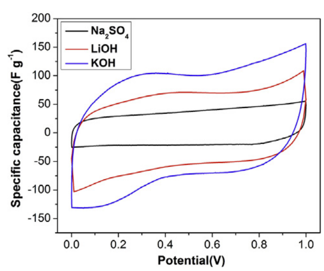
Rongyue Wang [a,b], Qun Li [a,b], Lulu Cheng [a,b], Hongliang Li [a,b], Baoyan Wang [a,b], X.S. Zhao [a,b,c], Peizhi Guo [a,b,*]

[a] *Laboratory of New Fiber Materials and Modern Textile, the Growing Base for State Key Laboratory, Qingdao University, Qingdao 266071, PR China*
[b] *School of Chemistry, Chemical Engineering and Environment, Qingdao University, Qingdao 266071, PR China*
[c] *School of Chemical Engineering, The University of Queensland, St Lucia 4072, QLD, Australia*

HIGHLIGHTS

- The capacitance of $MnFe_2O_4$ colloidal nanocrystal clusters can be adjusted by the electrolytes.
- The assembly of colloidal nanocrystals should be important for their electrocapacitive features.
- The size of hydrated ions plays the key roles in determining the electrocapacitive features.
- The capacitance of the electrode was the largest when using the potassium hydroxide electrolyte.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 March 2014
Received in revised form 20 May 2014
Accepted 23 May 2014
Available online 2 June 2014

Keywords:
$MnFe_2O_4$
Colloidal nanocrystal cluster
Supercapacitor
Electrolyte

ABSTRACT

The electrochemical performances of symmetric supercapacitors assembled by $MnFe_2O_4$ colloidal nanocrystal clusters (CNCs) in aqueous electrolytes were investigated by using cyclic voltammetry, galvanostatic charge–discharge, cycle stability and electrochemical impedance spectroscopy. Results showed that the capacitance of $MnFe_2O_4$ CNCs can be easily adjusted by the controlled electrolytes. It was found that the specific capacitances of CNCs-based electrodes were 97.1, 93.9, 74.2 and 47.4 $F\,g^{-1}$ for the electrolytes (2 M) containing KOH, NaOH, LiOH and Na_2SO_4, respectively, at the current density of 0.1 $A\,g^{-1}$. The capacitance of the electrode was increased from 56.9 to 152.5 $F\,g^{-1}$ with aqueous KOH electrolytes changed from 0.5 M to 6 M. The $MnFe_2O_4$ CNCs-based supercapacitor using aqueous KOH (6 M) electrolyte displayed the best cycle stability among all the supercapacitors. Based on the experimental results, the enhancement mechanism of electrochemical performances for the CNCs-based supercapacitors was proposed.

1. Introduction

Nano-scale materials can show unique optical, electronic and catalytic properties compared with those bulk materials due to their small size effect and surface effect. Recently, magnetic spinel ferrites nanomaterials have received increasing interest due to their important applications, especially in energy, catalysis and biomedicine [1,2]. The synthesis and physicochemical properties of ferrite nanomaterials have been made great progress. Ferrite

* Corresponding author at: Qingdao University, Ningxia Road 308#, Qingdao, PR China. Tel.: +86 532 859 51290/+86 532 859 55529; fax: +86 532 859 55529.
E-mail addresses: pzguo@qdu.edu.cn, guopz77@yahoo.com (P. Guo).

http://dx.doi.org/10.1016/j.colsurfa.2014.05.059
0927-7757/

nanostructures with tunable sizes and morphologies including nanocrystals [3,4], hollow spheres [5], nanorods/nanowires [6] and nanotubes [7] have been successfully synthesized by using various synthetic techniques, such as hydrothermal/solvothermal method [8], thermolysis [9], template [10], sol–gel technique [11], coprecipitation [12] and electrochemical synthesis [13], etc. For example, size-tunable manganese ferrite nanocrystals can be synthesized controllably by solution phase strategies through adjusting the nature of the solvents [14–16]. MnZn ferrite nanocubes with a core–shell structure have been prepared with the assistance of mixed surfactants via a reflux method in benzyl ether systems [17].

It is well-accepted that magnetic nanocrystals with the size larger than a critical size (usually ~20 nm) show ferromagnetic behavior [5,18]. Recently, submicrometer superparamagnetic colloidal nanocrystal clusters (CNCs) of ferrites have been synthesized based on the solvothermal method through tuning the synthetic microenvironments [5,18,19]. The superparamagnetic nature of ferrite CNCs could be ascribed to the highly-preferred orientations of the primary nanocrystals, which attributed to their excellent photocatalytic or electrocatalytic properties. $MnFe_2O_4$, as a kind of spinel ferrite materials, is face-centered and cubic lattice structure. The ions of transition metal Mn and Fe which were distributed in the tetrahedral and octahedral gap, have the same intensity of ionic bonds with oxygen ion [12]. The energy storage properties of ferrites nanomaterials should be expected due to their unique composite nature and tunable-structural features.

As one type of the best energy storage devices, supercapacitor (namely electrochemical capacitor) has attracted great interest in recent years due to their excellent properties [20,21]. Compared with batteries, supercapacitors have the greater potential for providing good cyclability and high power density [22–24]. Supercapacitors mainly composed of four parts: electrode material, collector, separator and electrolyte. The synthesis of advanced electrode materials is the key issue in the development of supercapacitors. The first discovered electrode material for pseudocapacitor (one type of the supercapacitor, the other is the electric double layer capacitor) is RuO_2 [25]. Successive multielectron transfer at Ru ions, from Ru^{4+} to Ru^{3+}, then to Ru^{2+}, lead to the capacitor behavior [26]. For the further development of affordable electrode materials, various oxide materials were investigated, such as cobalt oxide [27], nickel oxide [28] and manganese oxide [29]. Recently, ferrites have been found to exhibit good electrochemical performances either in organic Li-ion electrolyte [30] or in aqueous electrolytes [26]. In our previous reports, the effect of surfactants added into the electrolytes has been studied based on the $MnFe_2O_4$ CNCs-based supercapacitor with aqueous $LiNO_3$ electrolytes [31]. However, the electrocapacitive performances of ferrite-based electrodes still need to be further clarified.

Herein, the capacitive features of $MnFe_2O_4$ CNCs-based supercapacitor have been investigated by adjusting aqueous electrolytes. Recently, we had found that $MnFe_2O_4$ colloidal nanocrystal clusters electrode displayed a higher capacitance than $MnFe_2O_4$ hollow spheres [31]. The aim of this work is to elucidate the size effect of electrolyte ions on the electrochemical properties of CNCs-based supercapacitors and the used compounds were KOH, NaOH, LiOH, Na_2SO_4 and $LiNO_3$ [31]. Furthermore, the electrocapacitive variation of the supercapacitors with the concentration of the electrolytes has been investigated. The electrochemical performances of $MnFe_2O_4$ CNCs-based supercapacitors were evaluated by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), cycle stability and electrochemical impedance spectroscopy (EIS). It is found that the capacitances of CNCs electrodes were 47.4, 51.1, 74.2, 93.9 and 97.1 $F\,g^{-1}$ for the electrolytes (2 M) containing Na_2SO_4, $LiNO_3$, LiOH, NaOH and KOH, respectively, at the current density of 0.1 $A\,g^{-1}$. The capacitance of CNCs electrodes increased from 56.9 to 152.5 $F\,g^{-1}$ with the KOH concentration increased from 0.5 M to 6 M at the current density of 0.1 $A\,g^{-1}$.

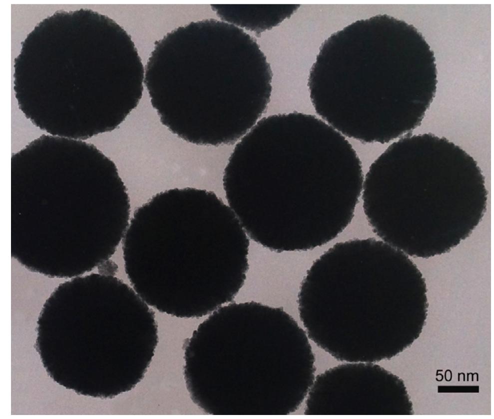


Fig. 1. Typical TEM image of $MnFe_2O_4$ colloidal nanocrystal clusters.

2. Experiments

2.1. Materials

All chemicals such as $Mn(CH_3COO)_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, CH_3COONa, KOH, NaOH, LiOH, Na_2SO_4, iso-propyl alcohol and ethylene glycol were of analytical grade and purchased from Sinopharm Chemical Reagent Company. Acetylene carbon black (99.99%) and polytetrafluoroethylene latex (PTFE 60 wt.%) were procured from Strem Chemicals and Aldrich, respectively. Double distilled water was used in all the experiments.

2.2. Synthesis of $MnFe_2O_4$ and characterization

Hydrothermal method was being applied to synthesize $MnFe_2O_4$ CNCs. Details were described in our literature [5]. Transmission electron microscopy (TEM) images were recorded by a JEM-2000EX transmission electron microscope operated at 160 kV [5].

2.3. Electrochemical measurements

The electrodes were composed of 5 wt.% PTFE, 15 wt.% acetylene carbon black and 80 wt.% active materials. All the materials need to mix uniformity and were pressed onto a nickel foam substrate (1 cm^2) at 1.0 MPa, followed by drying in a vacuum oven at 110 °C for 12 h. Each electrode was about 5 mg. Two electrodes were isolated by a porous membrane based on aqueous KOH (NaOH, LiOH or Na_2SO_4) electrolyte, thus form a two-electrode cell. CV, GCD, EIS and cycle stability measurements were performed by a CHI760E electrochemical workstation (CH Instrument, USA). All measurements were conducted at room temperature.

3. Results and discussions

$MnFe_2O_4$ CNCs were selected to investigate the effect of electrolytes on the electrochemical properties of the as-made supercapacitors because CNCs were composed of small primary nanocrystals with highly-preferred orientations. This led to a large surface area of sample CNCs that the electrolyte ions can access [31]. As depicted in Fig. 1, spherical CNCs were well-dispersed with the size of about 160 nm. The unique ordered assembly of primary nanocrystals in CNCs was ascribed to its superparamagnetic behavior with an unusually large magnetization saturation value. Because of the structural feature of the materials, $MnFe_2O_4$ CNCs-based