Journal of Colloid and Interface Science 512 (2018) 758–766

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

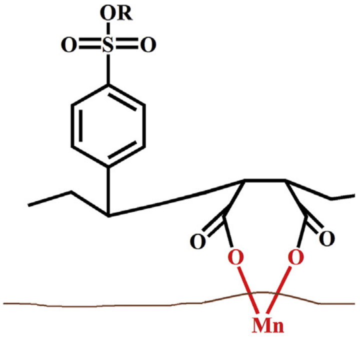
Regular Article

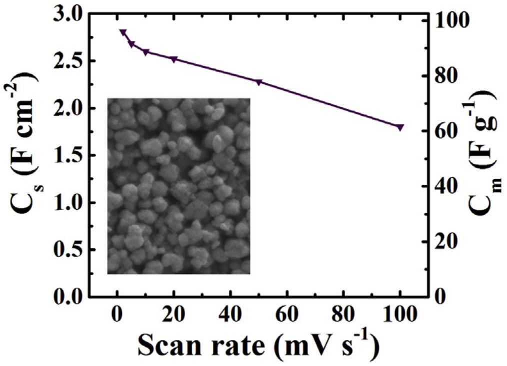
Fabrication of Mn_3O_4–carbon nanotube composites with high areal capacitance using cationic and anionic dispersants

M.S. Ata, J. Milne, I. Zhitomirsky *

Department of Materials Science and Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4L7, Canada

GRAPHICAL ABSTRACT





ARTICLE INFO

Article history:
Received 25 July 2017
Revised 29 October 2017
Accepted 30 October 2017
Available online 31 October 2017

Keywords:
Manganese oxide
Supercapacitor
Carbon nanotube
Composite
Capacitance
Impedance

ABSTRACT

Mn_3O_4-multiwalled carbon nanotube (MWCNT) electrodes for supercapacitors with high active mass loadings have been fabricated with the goal of achieving a high area normalized capacitance (C_S) and enhanced capacitance retention at high charge-discharge rates. Poly(4-styrenesulfonic acid-*co*-maleic acid) sodium salt P(SSA-MA) was used as a charging and dispersing agent for the fabrication of Mn_3O_4. The unique bonding properties of the MA monomers allowed efficient P(SSA-MA) adsorption on Mn_3O_4, whereas SSA monomers imparted a negative charge. Cationic ethyl violet (EV) and pyronin Y (PY) dyes were used for dispersion and charging of MWCNT. Good dispersion of the individual components and their electrostatic heterocoagulation facilitated efficient mixing, which allowed enhanced capacitive behavior at mass loadings of 28.4 mg cm^{-2}, which meet requirements for practical applications. The highest capacitance of 2.8 F cm^{-2} was obtained at a scan rate of 2 mV s^{-1} for the composites, prepared using PY. However, the composites, prepared using EV showed better capacitance retention of 88% in the scan rate range of 2–100 mV s^{-1} and the capacitance of 2.1 F cm^{-2} was obtained at a scan rate of 100 mV s^{-1}. The composites showed activation behavior during cycling, which resulted in a capacitance increase and electrical resistance reduction. The results of this investigation showed that Mn_3O_4–MWCNT composites, prepared by new colloidal methods are promising materials for practical applications in electrochemical supercapacitors.

1. Introduction

Manganese oxides, such as MnO_2 and Mn_3O_4 are under intensive investigation for charge storage applications in

---

* Corresponding author.
E-mail address: zhitom@mcmaster.ca (I. Zhitomirsky).

https://doi.org/10.1016/j.jcis.2017.10.110

electrochemical supercapacitors and batteries [1–3]. The interest in manganese oxides for the development of supercapacitor electrodes is attributed to their high theoretical capacitance, nearly ideal capacitive charge-discharge behavior in a relatively large voltage window and low cost [4–6]. Many investigations were focused on the analysis of charge-discharge mechanisms and study of specific capacitance at different experimental conditions [7–10]. Relatively high gravimetric capacitance (C_m, F g^{-1}) was achieved at low active mass loadings [5,10–14] in the range of 0.005–1 mg c m^{-2}. Such active mass loadings usually result in relatively low ratios (<1–2%) of active material mass to the current collector mass. Significantly higher active mass loadings above 10 mg cm^{-2} are necessary for practical applications [15]. However, C_m decreased drastically [16] with increasing mass of the active material, especially at high charge-discharge rates due to poor electrolyte access to the active material and low electronic conductivity. For practical applications, high C_m must be achieved at high mass loadings. Areal capacitance (C_S, F cm^{-2}) is an important parameter for the characterization of supercapacitor electrodes with high active mass loadings.

Investigations [17–20] have shown that the specific capacitance does not correlate with the BET surface area, since some very small pores are inaccessible by the electrolyte. However, the preparation of non-agglomerated particles with small size is critical for the fabrication of advanced electrodes. The synthesis of nanoparticles in the presence of dispersing agents offers a way to reduce particle size and avoid agglomeration. Particles of MnO_2 are usually prepared by the reduction of Mn^{7+} species in $KMnO_4$ solutions [21,22]. However, the use of organic dispersing agents during synthesis presents difficulties, because $KMnO_4$ is a strong oxidant, which reacts with organic dispersants. In contrast, the synthesis of Mn_3O_4 can be achieved from Mn^{2+} salt solutions and various dispersants and colloidal strategies can be used for the control of particle size and morphology during Mn_3O_4 synthesis and fabrication of composite electrodes with advanced microstructures. The Mn_3O_4 synthesis in the presence of organic dispersants is a promising strategy for the fabrication of Mn_3O_4 electrodes with enhanced performance.

Electrochemical [23] and chemical [24] techniques can be used for the fabrication of Mn_3O_4. Recent studies showed that particle shape and growth rate during synthesis can be controlled by glucose adsorption [24]. It was demonstrated [25] that cationic polyelectrolytes, containing amino groups, such as chitosan and polyethylenimine, promoted room temperature crystallization of Mn_3O_4 nanoparticles. Moreover, particle size can be controlled by variation of the polymer concentration in the solutions [25]. Porous Mn_3O_4 particles with high surface area were obtained for supercapacitor applications using a surfactant as a microstructure controlling agent [26]. In another investigation [27] tunable microstructures were obtained using a block copolymer template (Pluronic F127) as a dispersant.

Nanostructured Mn_3O_4 thin film electrodes showed interesting activation phenomena, related to capacitance increase [5,23,28,29] during initial cycling with corresponding changes in the film morphology and oxidation of manganese ions to a higher oxidation state. Advanced Mn_3O_4 based composites were developed [30–36], containing various conductive components, such as carbon nanotubes, graphene, graphite and RuO_2. Typical C_S [7,37–40] of Mn_3O_4 electrodes were in the range of 0.02–0.6 F cm^{-2}.

Despite the impressive progress achieved in the materials synthesis and microstructure design, further investigations are necessary for the preparation of Mn_3O_4 based composites for advanced supercapacitor electrodes with high active lass loading. New strategies must be developed for the fabrication of well dispersed Mn_3O_4 nanoparticles and their efficient mixing with carbon nanotubes in order to achieve high C_S and good capacitance retention at high charge-discharge rates.

The objective of this investigation was the development of efficient Mn_3O_4-multiwalled carbon nanotube (MWCNT) electrodes with high active mass loading and high areal capacitance. In order to realize this objective, we prepared Mn_3O_4-MWCNT electrodes with active mass loading of 28.4 mg cm^{-2}. The approach was based on the use of poly(4-styrenesulfonic acid-*co*-maleic acid) sodium salt P(SSA-MA) as a dispersing agent for Mn_3O_4 synthesis. The unique feature of P(SSA-MA) is that this polyelectrolyte exhibits strong adsorption on Mn_3O_4 due to the bonding properties of the maleic acid monomers, which provide multiple bonding sites. The use of P(SSA-MA) during synthesis allowed the fabrication of non-agglomerated nanoparticles, which were negatively charged and well dispersed. Another important finding was the possibility of efficient dispersion of MWCNT using small cationic dispersants, such as ethyl violet (EV) or pyronin Y (PY) dyes, which imparted a positive charge to MWCNT. It was found that the electrostatic heterocoagulation of the negatively charged Mn_3O_4, dispersed using P (SSA-MA), and positively charged MWCNT, dispersed using EV or PY, allowed good mixing of the individual components. The use of the electrostatic heterocoagulation techniques facilitated the fabrication of electrodes with high active mass loading, which showed enhanced capacitive properties. The highest capacitance C_S of 2.8 F cm^{-2} at a scan rate of 2 mV s^{-1} and good capacitance retention at a scan rate of 100 mV s^{-1} were achieved. Cyclic voltammetry and impedance spectroscopy methods were used for the analysis of the electrode activation process.

2. Experimental procedures

Poly(4-styrenesulfonic acid-*co*-maleic acid) sodium salt P(SSA-MA) (M_W = 20,000, SSA:MA = 1:1), ethyl violet (EV), pyronin Y (PY), $Mn(NO_3)_2$, NaOH, poly(vinyl butyral-*co*-vinyl alcohol-*co*-vinyl acetate) (PVB, average Mw = 50,000–80,000) (Aldrich), multiwalled carbon nanotubes (MWCNT, ID 4 nm, OD13 nm, length 1–2 µm, Bayer, Germany) were used. Ni foams with 95% porosity were provided by Vale Limited Company.

The synthesis of Mn_3O_4 particles was performed using 0.5 M $Mn(NO_3)_2$ solutions, containing 0.5 g L^{-1} P(SSA-MA). The pH of the solutions was adjusted to pH = 10 by NaOH. The solution was ultrasonicated for 5 min during synthesis and then stirred for 4 h. The precipitates were washed with water, dried in air and then used for X-ray diffraction and electron microscopy analysis.

MWCNT were dispersed in the aqueous solutions of dispersing agents, such as EV or PY. The mass ratio of MWCNT: dispersant was 2:1. The suspensions were ultrasonicated for 15 min. The suspensions of 4 g L^{-1} Mn_3O_4, dispersed using 0.5 g L^{-1} P(SSA-MA) were mixed with 1 g L^{-1} MWCNT suspension, containing 0.5 g L^{-1} EV or PY. The obtained mixture was filtrated, washed and dried in air. The PVB solution in ethanol was added to the mixture. The PVB content in the slurry was 3% of the total mass of Mn_3O_4 and MWCNT. The obtained slurry was used for the impregnation of Ni foam current collectors and fabrication of electrodes with area of 1 cm^2. The active mass loading was 28.4 mg cm^{-2} (±3%). Composites 1 and 2 were prepared using EV and PY, respectively.

Scanning electron microscopy (SEM) investigations were performed using JEOL JSM-7000F microscope. X-ray diffraction (XRD) studies were carried out using a powder diffractometer (Nicolet I2, monochromatized CuK_α radiation). XPS analysis was performed using Quantera II Scanning XPS instrument (Physical Electronics Inc.). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) investigations were carried out using a potentiostat (PARSTAT 2273, Princeton Applied Research,