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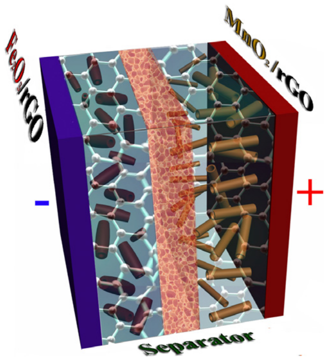
Asymmetric supercapacitor based on MnO_2 and Fe_2O_3 nanotube active materials and graphene current collectors

Y. Liu, D. Luo, K. Shi, X. Michaud, I. Zhitomirsky [*]

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

GRAPHICAL ABSTRACT



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ABSTRACT

Asymmetric electrochemical supercapacitors, containing MnO_2 nanotube positive electrodes and Fe_2O_3 nanotube negative electrodes in 0.5 M Na_2SO_4 electrolyte were fabricated and tested. The nanotubular electrode materials were prepared by hydrothermal synthesis methods. A chelating polyelectrolyte was used for electrosteric dispersion and electrophoretic deposition (EPD) of MnO_2 and Fe_2O_3 nanotubes. The individual chelating monomers of the polyelectrolyte created multiple bonds with Mn and Fe atoms on the nanotube surfaces and allowed for strong adsorption, efficient dispersion and EPD. Electrochemical testing results were compared for electrodes formed by EPD on reduced graphene oxide aerogel (rGO) and stainless steel (SS) current collectors. The MnO_2/rGO and Fe_2O_3/rGO electrodes, showed significantly higher areal capacitances and gravimetric capacitances, normalized by active mass or by total mass of the electrode material and current collector, compared to MnO_2/SS and Fe_2O_3/SS electrodes. The difference was attributed not only to capacitive properties and light weight of rGO, but also to better utilization of capacitive properties of the nanotubes and lower impedance. The use of rGO allowed for significant reduction of the ratio of active material mass to current collector mass, which offers benefits for the development of light weight devices. The capacitive properties of Fe_2O_3/rGO in the negative potential range closely matched the capacitive properties of MnO_2/rGO in the positive potential range. Such matching was beneficial for the fabrication of asymmetric devices, which showed good electrochemical performance in a voltage window of 1.8 V.

1. Introduction

Electrochemical supercapacitors [1–3] are currently under intensive investigations for energy storage due to their high

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

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capacitance, fast charging, high power and long cycle life. Nanostructured materials are increasingly being explored as electrode materials for supercapacitors [4–6]. Of particular interest are 1-D nanomaterials, such as nanofibers, nanowires and nanorods, which allow the fabrication of electrodes with reduced binder content and improved electrolyte access to the active material [7–11]. Moreover, 1-D nanomaterials are beneficial for the fabrication of flexible devices [12,13].

MnO_2 is a promising material for the fabrication of positive electrodes of electrochemical supercapacitors [2,14–16]. The interest in MnO_2 is related to high theoretical specific capacitance of this material and a relatively large voltage window. Many investigations were focused on the use of MnO_2 nanotubes and nanowires for the fabrication of advanced electrodes [13,14,17]. Due to the low electronic conductivity of MnO_2, significant research activity was focused on the development of nanocomposites, containing nanostructured MnO_2 and conductive additives, such as carbon nanotubes, graphene and carbon black [2,3,15,18]. The fabrication of nanostructured materials and nanocomposites requires the use of efficient dispersants [19–21]. The interest in dispersion of MnO_2 nanoparticles has driven the development of advanced dispersants with strong adsorption on MnO_2 surface. Various molecules were investigated [22,23], which provided enhanced bi-dentate or tridentate bonding to the MnO_2 particle surface, including chelating anionic and cationic molecules from catechol, salicylic, phosphonic and chromotropic acid families. It was found that polyaromatic molecules, such as pyrocatechol violet [18,22] allow efficient dispersion of nanoparticles. However, the dispersion of larger MnO_2 particles, such as nanotubes and nanowires requires the development of more advanced dispersants with stronger adsorption on the MnO_2 surface.

It is known that voltage window of supercapacitors can be increased in asymmetric devices, containing different electrode materials [2,3,17,24,25]. Various materials were investigated as negative electrodes in a combination with positive MnO_2 electrodes, including carbon nanotubes, graphene, activated carbon, V_2O_5, MoO_3, Fe_2O_3, Fe_3O_4 and composites [2,3,15,26–31]. However, the specific capacitances of materials for negative electrodes were lower than the specific capacitance of MnO_2 for positive electrodes. Therefore, further investigations are necessary in order to match the capacitances of positive and negative electrodes and optimize the total capacitance of supercapacitor devices.

The goal of this investigation was the fabrication of an asymmetric supercapacitor device, containing MnO_2 nanotubes as positive electrodes and Fe_2O_3 nanotubes as negative electrodes. Good dispersion of the nanotubes was achieved using a chelating polyelectrolyte as a dispersant. In this strategy, chelating monomers provided multiple bonds to the metal atoms on the MnO_2 and Fe_2O_3 nanotube surfaces and allowed strong adsorption, which facilitated good electrosteric dispersion. The use of the chelating polyelectrolyte as a charged dispersant allowed the fabrication of advanced electrodes by electrophoretic impregnation of graphene aerogel current collectors. The capacitance of the negative electrode closely matched the capacitance of the positive electrodes at similar active mass loadings, which was beneficial for the device performance. The use of graphene aerogel as a current collector instead of stainless steel foil offered benefits of higher capacitance, lower impedance and high ratio of active material mass to the current collector mass.

2. Experimental procedures

Poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO), $KMnO_4$ and $NaNO_3$ (Aldrich Canada), HCl, $NH_4H_2PO_4$, H_2SO_4, H_2O_2 and NH_4OH (Caledon Laboratories, Canada), $FeCl_3$ (Anachemia Canada), graphite (Fisher Scientific, USA) were used as starting materials.

MnO_2 and Fe_2O_3 nanotubes were prepared by hydrothermal methods. For the synthesis of MnO_2 nanotubes [32], 0.321 g of $KMnO_4$ was dissolved in 29 mL of deionized water, followed by adding 0.7 mL of HCl aqueous solution (37 wt%). After vigorous stirring for 0.5 h, the solution was transferred to a 50 mL teflon-lined stainless steel autoclave for hydrothermal synthesis at 120 °C for 12 h. The obtained precipitate was collected, washed with deionized water and ethanol and then dried in an oven at 60 °C overnight. The procedure for the Fe_2O_3 nanotubes [33] synthesis involved mixing of 1.6 mL of aqueous 0.5 M $FeCl_3$ solution and 1.4 mL of aqueous 0.02 M $NH_4H_2PO_4$ solution. Deionized water was then added in order to achieve a final volume of 40 mL. After stirring for 20 min, the mixture was transferred to the autoclave for the hydrothermal synthesis at 220 °C for 48 h. The powders were collected and washed with deionized water and ethanol several times, and dried in an oven at 80 °C overnight.

Graphene oxide (GO) was synthesized from graphite powder using a modified Hummer's method [34]. In a typical procedure, 1 g of graphite powder was mixed with 0.5 g $NaNO_3$ and 23 mL H_2SO_4 (98%), the mixture was cooled to 0 °C. Then, 3 g $KMnO_4$ was added slowly to keep the temperature of the suspension in the range of 0–5 °C and the mixture was stirred for 1 h. The reaction system was transferred to 35 °C water bath and stirred for about 2 h, forming a thick paste. Then, 46 mL distilled water was added slowly to the mixture, and stirring was performed for 30 min at 95 °C. The mixture was further diluted with 140 mL distilled water, treated with 10 mL H_2O_2 (30%), washed with 50 mL HCl (1:10) and distilled water 2 times and then re-suspended in distilled water and obtained precipitate was dried at 50 °C.

Reduced graphene aerogel (rGO) was prepared by a hydrothermal method [35]. In a typical procedure, 4 mL of NH_4OH solution (28 wt%) was added to 18 mL of aqueous GO dispersion (2.5 mg mL^{-1}), then the mixture was sealed in a Teflon-lined stainless-steel autoclave. Black hydrogels were formed after the mixture was heated at 180 °C for 12 h. After washing 3–5 times by distilled water, rGO was obtained by freeze-drying at −20 °C for 12 h under vacuum. The rGO thin layers with a mass of 1 mg cm^{-2} were used as current collectors for electrodes of supercapacitors.

Electron microscopy investigations were performed using a JEOL JSM-7000F scanning electron microscope (SEM) and FEI Tecnai Osiris transmission electron microscope (TEM). A powder diffractometer (Bruker D8, monochromatized CuK_α radiation) was used for X-ray diffraction (XRD) studies. UV–Vis spectroscopy analysis was performed using a spectrometer Cary-50 (Agilent Technologies). The samples for UV–Vis spectroscopy were prepared by electrophoretic deposition of nanotubes from the suspensions, containing PAZO. The deposited material, containing adsorbed PAZO, was removed from the substrates and washed with water. In this case only adsorbed PAZO was included in the samples.

The suspensions for electrophoretic impregnation of rGO contained 0.5 g L^{-1} PAZO and 2 g L^{-1} of MnO_2 or Fe_2O_3 nanotubes in a mixed water–ethanol solvent (25% water). The electrochemical cell for impregnation contained rGO substrate and Pt counter electrode. The distance between the electrodes was 1.5 cm, the applied voltage was 50 V.

Electrochemical performance of single electrodes and coin cells was tested by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronopotentiometry methods, using a potentiostat (PARSTAT 2273, Princeton Applied Research) and charge–discharge analyzer (BST8, MTI Corporation).

Electrochemical testing was performed using 0.5 M Na_2SO_4 aqueous electrolyte. The capacitive behavior of individual electrodes was studied in three-electrode cells. The area of the working electrode was 1 cm^2. The counter electrode was a platinum gauze, and the reference electrode was a standard calomel electrode (SCE). The individual electrodes and a porous polymer membrane

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