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Asymmetric supercapacitor, based on composite MnO_2-graphene and N-doped activated carbon coated carbon nanotube electrodes

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Manganese dioxide nanotubes and activated carbon coated multiwalled carbon nanotubes (AC-MWCNT) are prepared by hydrothermal methods. MnO_2-graphene positive electrodes with good dispersion of individual components are fabricated using poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) as a co-dispersant. The unique structure of PAZO, containing chelating aromatic monomers allows for efficient adsorption of this polyelectrolyte on MnO_2 and graphene, which is a prerequisite for their efficient electrosteric co-dispersion. The MnO_2-graphene electrodes with active mass loading of 30 mg cm^{-2} show a capacitance of 3.3 F cm^{-2} at a scan rate of 2 mV s^{-1} and a capacitance retention of 64% is achieved with increase of scan rate from 2 to 100 mV s^{-1}. The use of AC-MWCNT with thick AC coating allows the fabrication of negative electrodes, which closely match the capacitive performance of the positive electrodes. The asymmetric supercapacitors containing MnO_2-graphene positive electrodes and AC-MWCNT negative electrodes show capacitance of 1.42 F cm^{-2} at a scan rate of 2 mV s^{-1}, capacitance retention of 52% in the scan rate range of 2–100 mV s^{-1} in a voltage window of 1.8 V.

1. Introduction

Despite the impressive progress [1–4] achieved in the development of new electrode materials for electrochemical supercapacitors (ES), MnO_2 remains the most promising charge storage material for positive electrodes [5–7]. The interest in application of MnO_2 for supercapacitors [8–10] resulted from high theoretical specific capacitance (1370 F g^{-1}) of this material. Nearly ideal box shape cyclic voltammograms (CVs) were observed [11–13] in a voltage window of ~0.9 V in mild aqueous electrolytes. The charge-discharge mechanism of MnO_2 involved the reaction [8]:

$$MnO_2 + C^+ + e^- \leftrightarrow MnO_2C \qquad (1)$$

where $C^+ = H^+, Na^+, K^+$. Small particle size and electrode porosity were important for good access of the electrolyte ions (C^+) to the capacitive MnO_2 material. In order to increase the electronic conductivity, MnO_2 was mixed with conductive additives [14–16]. The major difficulties were attributed to poor utilization of capacitive [11] properties of MnO_2. At low charge-discharge rates, the gravimetric capacitance decreased by an order of magnitude with increase of electrode mass [16–19] due to low electronic conductivity and poor electrolyte access to the active material. Moreover, the gravimetric capacitance decreased drastically with increasing charge-discharge rate, especially at high active material mass [14].

Many investigations were focused on the development of MnO_2–graphene composites, utilizing high capacitance of MnO_2 and high electronic conductivity of graphene. Relatively high gravimetric capacitances were reported for thin composite films [20–26], fibers [27], MnO_2 clusters on graphene layers [28], laminates [29], nanoflowers [30], nanocables [31], foams [32] and other MnO_2-graphene composite structures with low active mass loadings [33–40]. The areal electrode capacitance [41–44] was typically below 1.5 F cm^{-2}. Recent studies highlighted the importance of the fabrication of composites with higher active mass loadings [45]. It was pointed out [45] that for practical applications the active mass loading must be above 10 mg cm^{-2}. The important challenge faced by the researchers was to increase mass loading of the MnO_2-graphene composites and achieve high areal capacitance.

One of the major problems in the development of MnO_2-graphene composites was inefficient mixing of the individual

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components. This problem was addressed by the use of a redox reaction [46–52] of $KMnO_4$ and graphene, which promoted the synthesis of MnO_2 nanoparticles on the graphene surface:

$$4KMnO_4 + 3C + H_2O \rightarrow 4MnO_2 + K_2CO_3 + 2KHCO_3 \quad (2)$$

In this approach graphene was used as a sacrificial reducing agent for the synthesis of MnO_2. Therefore, reaction (2) resulted in the degradation of the graphene structure and properties. It is extremely important to avoid the graphene degradation and utilize its high electrical conductivity in the composite electrodes. An alternative approach is therefore needed to synthesize MnO_2-graphene composite structures with good mixing of the individual components. Colloidal processing is an important strategy for the fabrication of advanced nanocomposites. However, this method requires the development of efficient co-dispersants for graphene and MnO_2.

The asymmetric devices, containing MnO_2 based positive electrode and AC negative electrode offered the advantage of enlarged voltage windows and improved power-energy characteristics, compared to symmetric devices [15]. However, AC electrodes typically exhibited significantly lower specific capacitance, compared to the capacitance of MnO_2. Recent advancements in the development of efficient AC materials have been described in review papers [53,54]. AC was mixed with conductive additives in order to increase electrical conductivity. The fibrous AC materials [53] offered an advantage of high surface area and improved contact with conductive additives and current collectors.

The synthesis of AC coated CNT is a promising approach to the development of efficient electrodes with improved conductivity and high capacitance. This strategy requires the development of thick and uniform AC coatings on CNT. The goal of our investigation is the fabrication of asymmetric supercapacitors, based on MnO_2-graphene positive electrodes and AC-MWCNT negative electrodes. Our target is to produce electrodes and devices with high active mass loading, avoid graphene degradation and achieve high areal capacitances and good capacitance retention at high charge-discharge rates for positive and negative electrodes. Using AC-MWCNT with thick AC coatings as an active material for negative electrodes we match capacitance of the negative electrode with the capacitance of MnO_2-MWCNT positive electrode at the same active mass loadings. The experimental results presented below show that our strategies in materials processing allow for enhanced capacitive behavior of the individual electrodes and asymmetric devices.

2. Experimental procedures

$KMnO_4$, glucose, sodium dodecyl sulfate (SDS), poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) and melamine (Aldrich), HCl and HNO_3 (Caledon Laboratories, Canada), graphene (single layer, ACS Material LLC, USA), multiwalled carbon nanotubes (MWCNT, ID 4 nm, OD 13 nm, length 1–2 μm, Bayer, Germany) and Ni foam current collectors (Vale, Canada) were used.

For the synthesis of MnO_2 nanotubes [55], 0.32 g of $KMnO_4$ was dissolved in 29.3 mL of deionized water with vigorous stirring, then 0.7 mL of HCl aqueous solution (37 wt%) was added. After stirring for 0.5 h, the mixed solution was transferred to a 50 mL autoclave for synthesis at 120 °C for 12 h. The prepared powders were washed with deionized water and ethanol and dried under vacuum at 80 °C for 12 h.

For the fabrication of AC-MWCNT [56], 40 mg MWCNT were ultrasonically dispersed in 20 ml of aqueous solution containing 1.6 g glucose and 20 mg SDS. The black suspension was then transferred to a 50 mL autoclave and heated at 180 °C for 15 h. After the reaction, the powder was collected and washed with deionized water and ethanol, and then dried at 60 °C overnight. The as-obtained product and melamine were mixed in a mass ratio of 1: 9. This mixture was then placed into a quartz tube under argon atmosphere and heated to 700 °C at a rate of 10C min^{-1}. After the annealing at 700 °C for 2 h, the final product was cooled down to room temperature and used for characterization and electrochemical tests.

The limitations of the zeta potential concept for the analysis of electrokinetic properties of nanoparticles, containing adsorbed polyelectrolytes, were described in the literature [57,58]. Therefore, the charging mechanism and electrokinetic behavior of the particles were investigated by the deposition yield measurements in electrophoretic deposition (EPD) experiments. Moreover, the use of EPD provided a possibility of investigation of dispersant adsorption by analysis of particles, removed from the substrate after deposition. EPD was performed from 0.5 g L^{-1} PAZO solutions in a mixed ethanol-water solvent (60% ethanol), containing dispersed MnO_2, graphene or their mixture. The suspensions were ultrasonically agitated before the EPD. The electrochemical cell for the deposition of films contained a stainless steel substrate and Pt counter electrode (30 × 50 × 0.1 mm). The deposition voltage was 30 V. The distance between the electrodes was 15 mm.

The microstructure of materials was studied by scanning electron microscopy (SEM, JEOL JSM-7000F) and transmission electron microscopy (TEM, FEI Tecnai Osiris). UV–vis spectroscopy

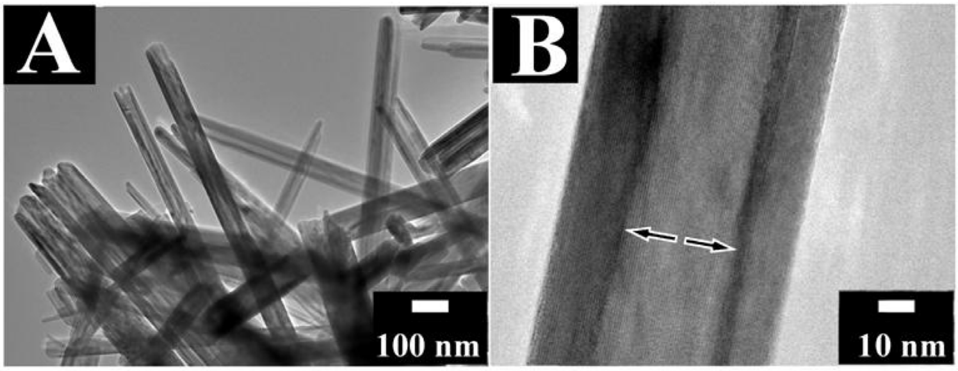

Fig. 1. (A,B) TEM images at different magnifications of MnO_2 tubular particles, arrows in B show inner diameter.