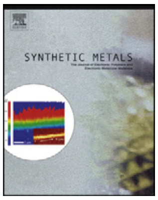
Synthetic Metals 160 (2010) 94–98

Contents lists available at ScienceDirect

Synthetic Metals

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



Preparation and enhanced stability of flexible supercapacitor prepared from Nafion/polyaniline nanofiber

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ARTICLE INFO

Article history:
Received 1 September 2009
Accepted 5 October 2009
Available online 25 November 2009

Keywords:
Polyaniline Nanofiber
Flexible
Nafion
Supercapacitor

ABSTRACT

Polyaniline nanofibers were used to produce a flexible supercapacitor electrode with a specific capacitance of 235 F g^{-1}. Cycle life and energy density were enhanced after encapsulating the polyaniline nanofiber electrode in Nafion. A specific capacitance of 195 F g^{-1} was obtained over 10,000 charge–discharge cycles.

A fully flexible, stand alone capacitor comprising two polyaniline nanofiber based electrodes and a PVDF separator was constructed. An initial specific capacitance of 125 F g^{-1} (100 mV s^{-1}) was obtained. This decreased to 95 F g^{-1} over 10,000 cycles.

1. Introduction

The development of flexible electronic devices including capacitors is of interest for a number of applications including the field of wearable electronics [1–3] or other textile based structures such as tents or blankets. The realization of flexible stand alone capacitor structures may also provide new opportunities for application in more traditional fields such as memory protection in computer electronics, electric vehicles and devices such as cellular telephones [4–6].

Most reports to date on redox supercapacitors have considered polymer or metal oxide materials supported by rigid metal electrode substrates used as current collectors. The capacitance arises mainly from the redox reactions occurring on/within the electrode materials [7–9]. Conducting polymers including polyaniline (PAN), polypyrrole (PPy) and polythiophene (PTh) have been shown to exhibit high capacitance due to contributions of both capacitive and faradaic current in the charge storage process. Among the conducting polymers available, PAN provides some attractive features, due to the existence of several oxidation states, the high conductivity available and the ease of synthesis [10–12]. Synthesis approach of particular interest is the production of high surface area polyaniline nanotubes [13]. The electrochemical deposition of conducting polymers on robust yet more flexible substrates such as carbon paper, textiles and carbon nanotubes has also been investigated [14–16].

It has been recognized previously that conducting polymer based capacitors are susceptible to rapid degradation in performance upon repetitive cycling (charging/discharging) [17–19]. In studies aimed at alleviating this limitation, combinations of conducting polymers with insulating polymers that display good mechanical properties such as poly-N(vinyl alcohol) and polystyrene [18,20] have been explored.

In this study, we demonstrate that flexible PAN nanofiber electrodes on a gold-coated porous PVDF substrate provide a specific capacity of 235 F g^{-1}. We have also investigated the effect of encapsulating this high surface area electrode in Nafion. The use of Nafion in combination with conducting polymers has previously been shown to improve the stability of the latter material [16,21] and is attributed to the ability of Nafion to stabilize the radical cations formed during charging of the conducting polymer material.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich. Aniline was vacuum distilled before use. Triple-distilled water of 18 MΩ was obtained from an aqua MAX water system (Younglin, Korea) and used to prepare the solutions of Nafion 117 (Merck, 5 wt.% in lower aliphatic alcohols and water). Polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF) was purchased from Aldrich.

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doi:10.1016/j.synthmet.2009.10.011

2.2. Preparation of polyaniline nanofibers

Aniline was polymerized in 1 M $H_2SO_{4(aq)}$ by the rapid addition of the oxidant ammonium persulfate. The aniline-to-oxidant ratio was approximately 4:1, with the aniline concentration being 0.5 M. Due to the immediate reaction between the monomer and the oxidant, the primary reaction product obtained was nanofibers. The product was purified by extensive washing in 1.0 M H_2SO_4.

2.3. Preparation of flexible PAN electrode

PVDF membranes were coated with gold using a Dynavac Magnetron Sputter Coater (Model SC100 MS) and sputtering at 30 mA for 30 min to give a thickness of 100 nm. Acid doped PAN nanofiber dispersions (0.1 g/ml) were drop cast onto the active area (1 cm × 1 cm) of the gold-coated PVDF using a micropipette. They were then left to dry for 2 h, prior to use for capacitance measurements. In order to determine the effect of Nafion on the capacitive behaviour of the polyaniline nanofibers, they were coated by casting Nafion (2 μl) from an ethanolic solution (0.25 wt%).

2.4. Cyclic voltammetry and impedance measurement

Cyclic voltammetry of the PAN coated electrodes was carried out in a single compartment 3 electrode cell using an EG&G potentiostat/galvanostat (Model 273A). The 3-electrode cell consisted of a PAN/Au/PVDF working electrode (1 cm^2 surface area), Pt plate counter electrode and Ag/AgCl (3.0 M NaCl) reference electrode. Capacitance values were calculated based on only the weight of active electrode materials without Au/PVDF.

Impedance measurements were carried out in a 3-electrode, single compartment cell using an Auto lab/FRA instrument over the frequency range 100 kHz–0.1 Hz with an AC perturbation of 5 mV.

3. Results and discussion

3.1. Polyaniline nanofibers were cast onto the gold-coated PVDF membrane.

Scanning electron micrographs (SEMs) confirmed that the porous nature of the PVDF membrane is retained after being sputter coated with gold (Fig. 1(a)) and the subsequent deposition of PAn nanofibers resulted in a three-dimensional open porous electrode structure (Fig. 1(b)). Deterioration of the PAN/Au/PVDF without the Nafion coating after repeated redox cycling was observed while the Nafion-coated PAN/Au/PVDF electrode was mechanically robust.

These electrodes were subjected to cyclic voltammetry in 1.0 M H_2SO_4 using potential scan rates over the range 10–200 mV s^{-1} (Fig. 2a). The specific capacitance was obtained from the cyclic voltammograms using Eq. (1) and the discharge capacitance using Eq. (2):

$$C = \frac{q_a + q_c}{2m\Delta V} \tag{1}$$

$$C = \frac{q_c}{m\Delta V} \tag{2}$$

where, q_a, q_c, m and ΔV are anodic and cathodic charges on the anodic and cathodic scans, mass of the electroactive material and the potential window of the cyclic voltammogram, respectively.

With cyclic voltammetry, a pair of broad redox peaks attributed to the transition of polyaniline from the polyleucoemraldine (yellow) to the polyemeraldine (dark blue) state was observed (Fig. 2a). These responses were clearly visible over the scan rate range considered (10–200 mV s^{-1}) with the current magnitude increasing linearly. The capacitance values (Fig. 2b) were calculated from the cyclic voltammograms; a value of 250 F g^{-1} was obtained at lower scan rates. This compares favourably with other reports on polyaniline based capacitors with values of 264 F g^{-1} [22] and 180 F g^{-1} [23] being reported. The decreases in capacitance at faster scan rates is typical of the behaviour observed with conducting polymers [24].

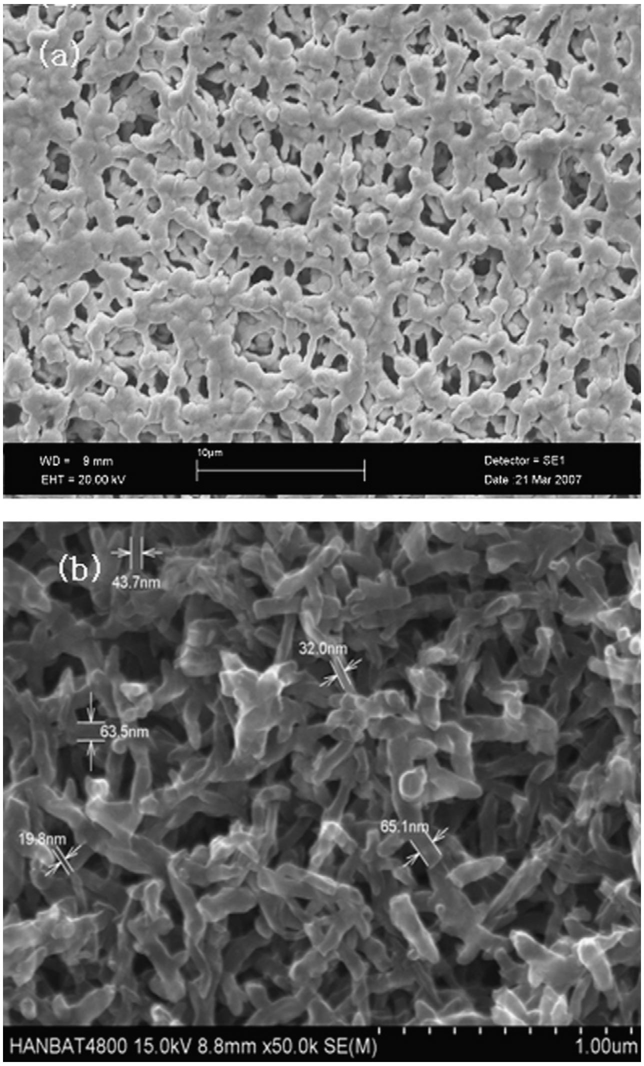

Fig. 1. SEM of (a) Au coated PVDF membrane and (b) dried PAN on Au coated PVDF membrane.

PAN nanofiber electrodes were then encapsulated in Nafion using the procedure described in Section 2. The redox responses observed for the encapsulated material were still clearly visible, however the initial capacitance values decreased slightly to 240 F g^{-1} at 100 mV s^{-1}.

3.2. Electrochemical stability

Stability to electrochemical cycling was investigated by carrying out experiments over 10,000 cycles in 1 M H_2SO_4 at a scan rate of 100 mV s^{-1} (Fig. 3). A decreasing capacitive current with increased number of cycles was observed for the PAN fiber electrodes both with and without Nafion. This decrease is attributed to electrochemical degradation of polyaniline at more anodic potentials [25] and also mechanical stresses induced by the acid doping/dedoping process of the polyaniline causing the polymer to expand/contract [26]. The shift in the redox potentials with and without the Nafion coating upon extended cycling is indicative of an increased resistance.