Short communication

A novel capacitor material based on Nafion-doped polypyrrole

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Abstract

The electrochemical characteristics of polypyrrole doped with either perchlorate or Nafion are determined. Polypyrrole doped with Nafion ions or perchlorate ions exhibits a specific capacitance of 344 or 355 $F\,g^{-1}$, respectively. Cycle life experiments reveal that the Nafion-doped material retains 98% of the original capacitance after 3000 cycles whereas that doped with perchlorate retains only 70% over this period. Scanning electron microscopy (SEM) before and after long-term cycling, reveals some mechanical degradation.
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1. Introduction

Supercapacitors are attracting attention due to their potential use as power sources in electronic equipment, medical devices, computer memory backup and electric vehicles [1–6]. Pursuit of high power and high energy density supercapacitors is therefore a vibrant field of research.

We have here developed an electrode material showing an energy density of 19.2 $Wh\,kg^{-1}$ and power density of 5.8 $kW\,kg^{-1}$ after 3000 cycles in aqueous media.

Supercapacitors may be divided into two sub-classes: electric double-layer capacitors (EDLCs) and electrochemical capacitors (ECs) [1]. ECs are capable of storing higher charge than EDLCs due to the availability of double-layer and faradaic pseudocapacitive sites. Numerous transition metal oxides [7–15] and conducting polymers [16–30] have been used as electrode materials in ECs. However, the demanding requirements of materials to be used as electrodes for ECs mean that the search for new formulations continues.

In the present paper, we have investigated the use of the performance of a well-known conducting polymer, polypyrrole, as an electrode material in ECs. Numerous reports have eval-

uated polypyrrole and composites containing this conducting polymer for supercapacitor applications [22–25,31–33]. Specific capacitance values as high as 290 $F\,g^{-1}$ have been reported with power and energy densities as high as 13 $kW\,kg^{-1}$ and 34.3 $Wh\,kg^{-1}$, respectively [40,41]. Such performance characteristics are indeed impressive, however, an intrinsic drawback of polypyrrole in particular, and conducting polymers in general is the limited stability observed with repeated cycling [42]. This is attributed to degradation in the mechanical strength [33–37], and the chemical reactions of the radical cations formed during oxidation of conducting polymer electrodes [9,25,38].

Numerous studies have investigated the use of conducting polymer composites containing carbon nanotubes in order to improve stability upon repeated cycling [33–37,39]. Capacities as high as 330 $F\,g^{-1}$ with an energy density of 6 $Wh\,kg^{-1}$ and an outstanding power performance of 20 $kW\,kg^{-1}$ have been reported [30,43].

Recently it was discovered that Nafion physically mixed with polypyrrole greatly improves performance by stabilizing the radical cations formed during polymer oxidation [44]. Here the use of Nafion as a molecular dopant has been investigated with a view to improving stability during the charge–discharge cycle. In addition to stabilizing the radical cations, Nafion is also expected to improve the mechanical properties of the conducting polymers produced.

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In the present study, we have prepared a Nafion-doped polypyrrole (PPy-Nf) by using a simple electropolymerisation process. Using this material as an electrode, the capacitance as well as the stability over a number of electrochemical cycles has been determined. The performance was compared with that obtained when perchlorate was used as the dopant ion.

2. Experimental

Nafion 117 (5 wt.% in lower aliphatic alcohols and water), tetrabutyl ammonium perchlorate (Bu_4NClO_4) and Na_2SO_4 were purchased from Fluka (Switzerland) and used without further purification. Pyrrole (Merck) monomer was distilled prior to use. Deionised water (18 MΩ) obtained from a Milli-Q water purifier was used. Pt electrodes were cleaned with piranha solution.

Using an acetonitrile solution containing 0.1 M pyrrole and 0.25 wt.% Nafion, PPy-Nf was galvanostatically deposited (0.3 mA cm^{-2} until $Q = 180$ mC) on a Pt (1 cm × 1 cm) working electrode. To prepare the perchlorate-doped polypyrrole (PPy-ClO_4), similar experimental conditions were employed with 0.1 M Bu_4NClO_4 used as the electrolyte instead of Nafion.

To evaluate the electrochemical performances, both kinds of electrodes (PPy-Nf and PPy-ClO_4) were subjected to cyclic voltammetry (CV) analysis (EDAQ 401 potentiostat, Australia) using a single compartment cell equipped with a Pt (2 cm × 2 cm) counter electrode and an Ag/AgCl (3.0 M NaCl) reference electrode in the voltage range of −0.8 to 0.5 V at various scan rates. An aqueous solution containing 1.0 M Na_2SO_4 and purged with pure nitrogen for at least 30 min, was employed as the electrolyte solution. During electrochemical cycling the electrolyte solution was covered with a nitrogen blanket. Impedance measurements (frequency range of 100 kHz to 10 mHz) were carried out using an Auto Lab/FRA instrument. An ac perturbation of 5 mV was applied using bias potentials of −0.8 or 0.5 V. Specific capacitance values were calculated based on the total mass of the electro-deposited material on the Pt working electrode. The morphology of the polymer electrodes was examined using a scanning electron microscope (HITACHI, S-4800). All the experiments were carried out at room temperature.

3. Results and discussion

Using the galvanostatic method described in Section 2, both PPy-Nf and PPy-ClO_4 polymers were obtained as adherent and continuous deposits on the platinum electrode substrate. PPy-Nf grew at a potential of 0.72 V while PPy-ClO_4 grew at a potential of 0.68 V.

After polymer growth, cyclic voltammograms were recorded at various scan rates (Fig. 1). Both polymers show distinct polymer oxidation–reduction processes and PPy-Nf (Fig. 1(a)) shows additional charge storage capabilities beyond the redox responses. However, the PPy-ClO_4 system was overall capable of greater charge storage.

The lower number of specific redox active sites (i.e. sites per g of composite) for PPy-Nf is understandably based on the fact
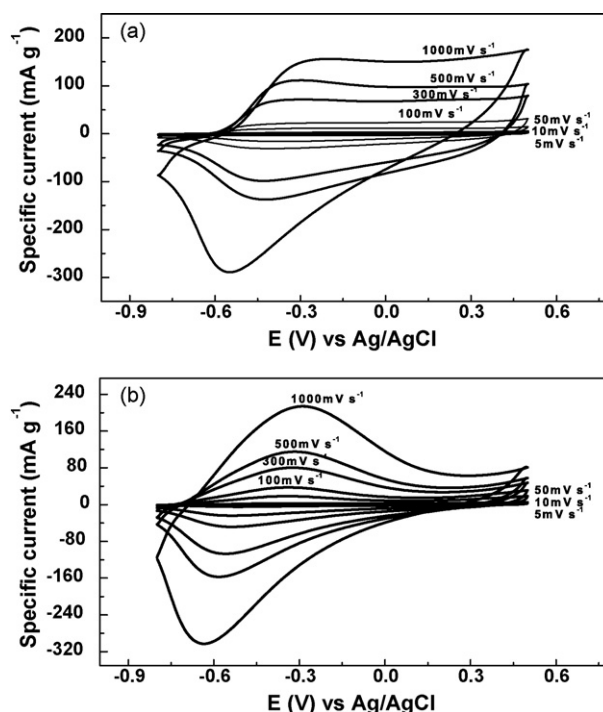

Fig. 1. Cyclic voltammograms of (a) PPy-Nf and (b) PPy-ClO_4 electrodes recorded in an electrolyte solution of 1.0 M Na_2SO_4 at various scan rates.

that the molecular weight of the Nafion dopant is much higher than the perchlorate dopant and not all of this contributes to charge storage. However, as indicated by the voltammograms obtained, the PPy-Nf discharges over a wide potential range unlike the charge available over just a narrow potential window for the PPy-ClO_4 material. The behavior observed for PPy-Nf is desirable in a capacitor electrode material.

The specific capacitance for both electrodes was calculated from the cyclic voltammograms obtained, using the following equation:

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

where q_a, q_c, m and ΔV are indicative of the sums of anodic and cathodic voltammetric charges on the anodic and cathodic scans, mass of the electro-deposited material and the potential window of the cyclic voltammogram, respectively.
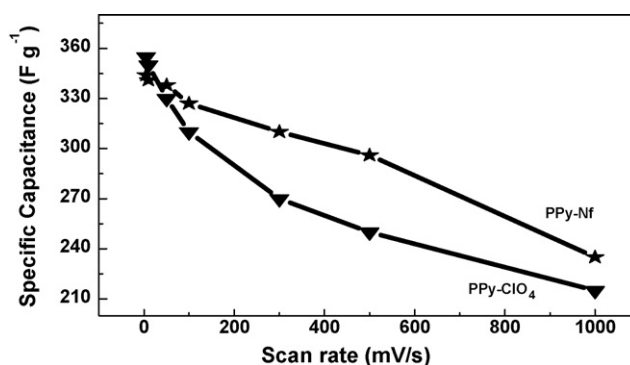

Fig. 2. Variation of specific capacitances of PPy-Nf (★) and PPy-ClO_4 electrodes (▲) as a function of scan rate. Electrolyte solution: 1.0 M Na_2SO_4.
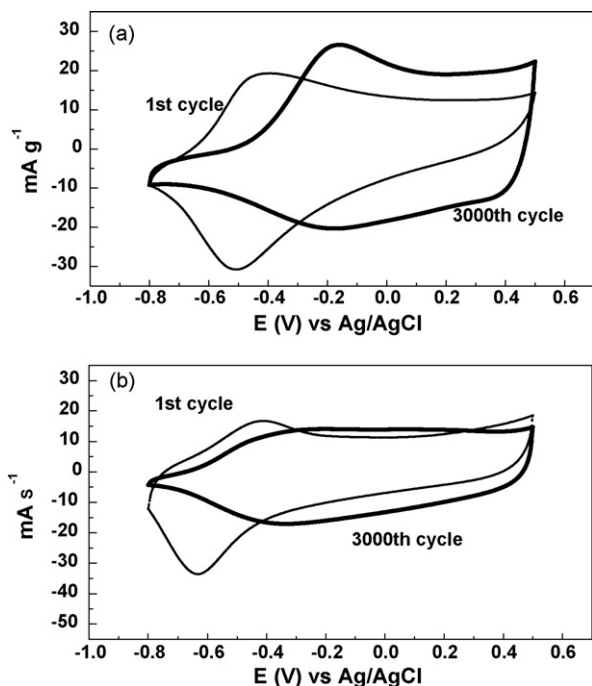
Fig. 4. Specific capacitance of PPy-Nf (■) and PPy-ClO$_4$ electrodes (●) as a function of cycle number.

Fig. 3. Representative cyclic voltammograms of (a) PPy-Nf and (b) PPy-ClO$_4$ electrodes in electrolyte solution containing 1.0 M Na$_2$SO$_4$. Responses observed after the 1st and 3000th cycle are shown. Scan rate: 100 mV s^{-1}.

These specific capacitance values are plotted as a function of scan rate in Fig. 2. At the lowest measured scan rate of 5 mV s^{-1}, the specific capacitance obtained for PPy-ClO$_4$ was higher (355 F g^{-1}) than that observed for PPy-Nf (344 F g^{-1}),
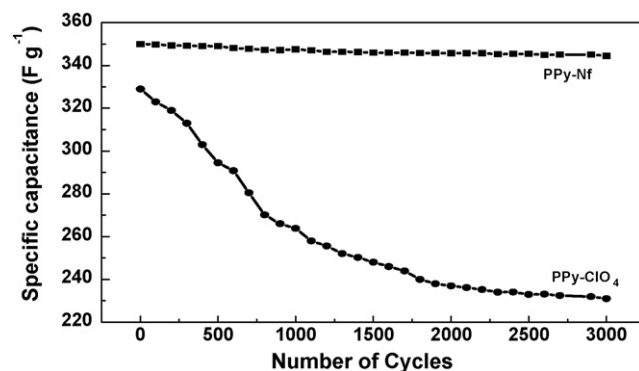
but at all higher scan rates, PPy-Nf showed a higher specific capacitance. Since the specific capacitance of PPy-ClO$_4$ mainly depends on the redox pseudocapacitance (see Fig. 1(b)), these values decrease at higher scan rates, possibly due to the diffusional limitations of the dopant anions inside the polymer matrix.

The improved performance at high scan rate for PPy-Nf is what is required for high energy and power density electrode materials.

It was observed that the energy density and power density of PPy-Nf at the scan rate of 1000 mV s^{-1} were 14.6 Wh kg^{-1} and 4.3 kW kg^{-1} whereas the values for PPy-ClO$_4$ were 12.3 Wh kg^{-1} and 3.7 kW kg^{-1}, respectively.
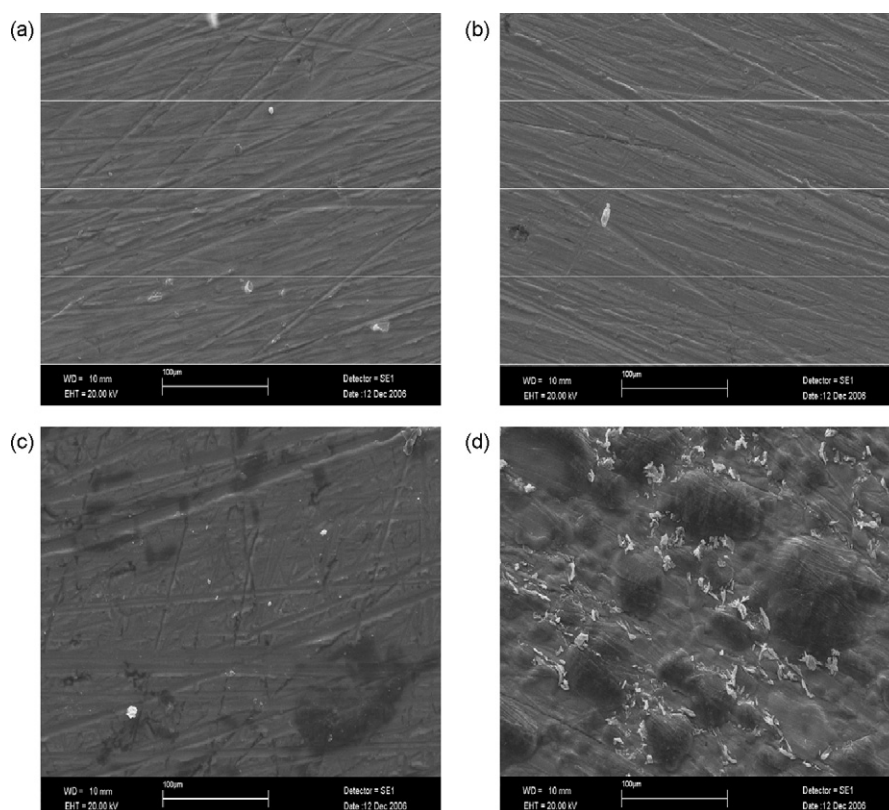

Fig. 5. SEM images of (a) PPy-Nf and (b) PPy-ClO$_4$ electrodes obtained before cycling; (c) PPy-Nf and (d) PPy-ClO$_4$ electrodes after 3000 cycles.

The stability to electrochemical cycling for both electrodes was investigated by carrying out CV experiments for over 3000 cycles between -0.8 and $0.5\,V$ at a scan rate of $100\,mV\,s^{-1}$ (Fig. 3).

After 3000 cycles, voltammograms obtained for PPy-Nf were even better defined than those observed in earlier potential scans. Higher capacitive currents were also obtained. The shift in the redox potentials of both electrodes (Fig. 3(a) and (b)) after extended cycling is attributed to the exchange of anions between the polymer and the supporting electrolyte. It is expected that polypyrrole prepared using either Nafion or perchlorate ions would gradually incorporate sulfate anions from the Na_2SO_4 electrolyte. The specific capacitance values estimated from the cyclic voltammograms as a function of cycle number are shown in Fig. 4. The PPy-Nf electrode shows excellent stability to electrochemical cycling. The capacity of the PPy-Nf and PPy-ClO$_4$ electrodes after the 3000th cycle had decreased to 98% and 70% of the initial values, respectively.

The remarkable stability of the PPy-Nf electrode is superior $(350\,F\,g^{-1}$ after 3000 cycles at $100\,mV\,s^{-1})$ to that reported previously for PPy-PEDOT composites with a 90% retention in capacity $(230\,F\,g^{-1}$ after 1000 cycles at $100\,mV\,s^{-1})$ [41].

Scanning electron micrographs were obtained before and after 3000 cycles for both polymers (Fig. 5). Both the as-prepared materials (Fig. 5(a) and (b)) show a smooth morphology. After 3000 cycles, there was not much difference in the morphology of PPy-Nf, however, the PPy-ClO$_4$ coating showed many "blisters" on top of the original morphology. This blistering occurs as the conducting polymer becomes delaminated from the platinum surface. The absence of this blistering indicates excellent adhesion.

4. Conclusions

A highly stable capacitor electrode material has been produced using Nafion as a molecular dopant. The presence of the Nafion influenced the nature of the current flow (increasing capacitance) and improved both the energy and power density.

The Nafion dopant also improved the mechanical robustness of the polymer coating; improving the stability to electrochemical cycling.

Acknowledgement

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