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Nafion-Doped Polypyrrole as a Supercapacitor Electrode in Ionic Liquid

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The supercapacitive properties of flexible Nafion-doped polypyrrole(PPy/Nafion) electrodes prepared using a flexible gold coated porous PVDF substrate were investigated in the presence of an ionic liquid, N-methyl-N-propylpyridinium trifluoromethanesulfonyl imide(P1,3TFSI), by means of cyclic voltammetry for supercapacitors. The PPy/Nafion showed capacitance values in the range of 350–450 F/g at the scan rates of 50–300 mV/s, indicating the ionic liquid is suitable for the electrolyte in supercapacitor.

Keywords Ionic liquid; polypyrrole; supercapacitor

1. Introduction

Conducting polymers can store charge throughout their entire volume as supercapacitor electrodes [1,2]. Among the most extensively studied conducting polymers, polypyrrole(PPy) is currently considered as one of the most promising materials for the supercapacitors due to the high conductivity and excellent stability attainable [3–6].

Recently many strategies have been adopted for the utilization of flexible conducting polymers as energy storage devices [7,8]. For example, wearable energy storage devices utilizing supercapacitors based on conducting polymers [9] have been developed. Electrochemical redox supercapacitors using polyvinylidene fluoride co-hexafluoropropylene (PVDF-HFP) based gel electrolytes with polypyrrole electrodes has been reported to show specific capacitances of $78 \sim 138\,\mathrm{F\,g^{-1}}$ of electrode materials [10]. Using PVDF membrane separators we have shown that efficient

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electrochemical cells (using electrochemical actuators) can be constructed by coating conducting polymer on each surface of the PVDF (Bender, actuator) [11]. Other investigators have prepared and utilized PPy/Nafion deposited on Pt or polypyrrole modified Nafion composite membranes for electrochemical applications [12,13].

In the present study the supercapacitive properties of a flexible PPy/Nafion electrodes were studied in the presence of an ionic liquid of N-methyl-N-propylpyridinium trifluoromethanesulfonyl imide(P1,3TFSI) to investigate whether the ionic liquid is suitable for the electrolyte in supercapacitors based on PPy electrode or not.

2. Experimental

Pyrrole monomer was distilled before use. Nafion 117 was obtained from Merck. Polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF) was purchased from Aldrich.

The PPy-Nafion was galvanostatically deposited ($0.3\,\mathrm{mA\,cm^{-2}}$, until 180 mC charge consumed) on the gold coated PVDF ($1 \times 1\,\mathrm{cm^2}$) membrane as working electrode from the aqueous solution containing 0.1 M pyrrole and 0.25 wt.% Nafion.

To evaluate the electrochemical performance, the PPy/Nafions were subjected to cyclic voltammetric analysis (E-corder 401 EA161 potentiostat, EDAQ, Australia) using a single compartment cell equipped with a Pt ($2 \times 2\,\mathrm{cm^2}$) counter electrode and an Ag/AgCl (3.0 M KCl) reference electrode in the voltage range of −0.8 to 0.5 V at various scan rates. P1,3 TFSI was employed as an electrolyte in the above experiment. During the long-term cycle life testing of the electrodes, the electrochemical cell was covered with a nitrogen gas blanket. Capacitance values were calculated based on the total mass of the electro-deposited materials.

3. Results and Discussion

Figure 1 shows the cyclic voltammograms of the flexible PPy/Nafion electrode which is obtained in the ionic liquid of P1,3TFSI as a function of scan rate. It can be observed from Figure 1 that there are the well-defined redox peaks, indicating that a pseudo capacitor electrode was obtained for the PPy/Nafion even at high

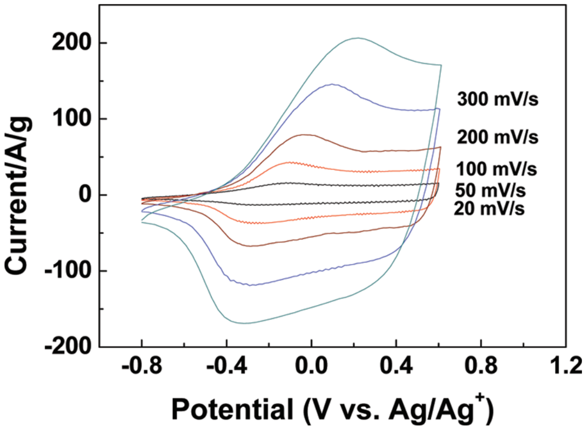
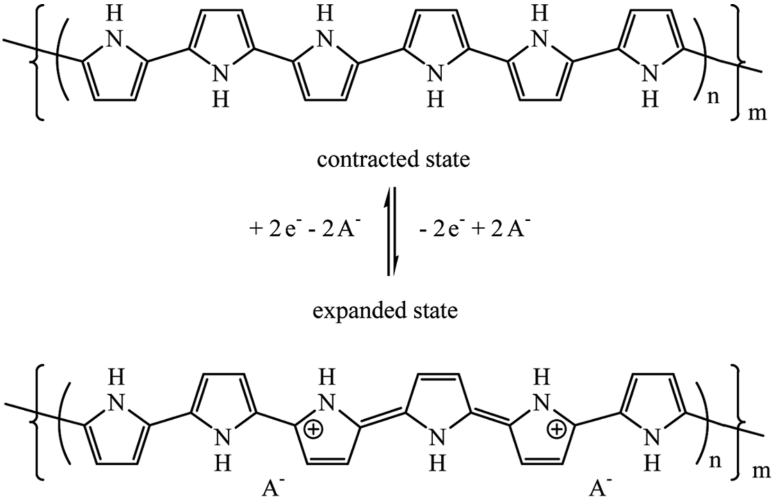


Figure 1. Cyclic voltammograms of the flexible PPy/Nafion electrode in the ionic liquid of P1,3 TFSI as a function of scan rate.

scan rates over 300 mV/s. The responses due to the oxidation/reduction of the PPy backbone that occur according to the below electrochemical reaction 1 are clearly discernible at all scan rates investigated. This electrochemical performance of the PPy/Nafion electrode may be attributed to the fast charge compensation from the ionic liquids to polymer backbone due to their high ionic conductivity.



[A^-represents anions, e^- electrons]
n determines degree of doping, m determines molecular weight (1)

The specific capacitance values were obtained from the cyclic voltammograms using Equation 2 and are shown in Figure 2.

$$C = (Q_a + Q_c)/(2\,m\,\Delta V) \tag{2}$$

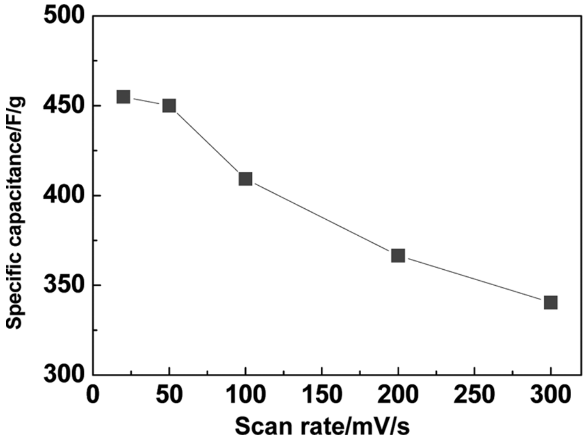


Figure 2. The specific capacitance values as a function of scan rate.

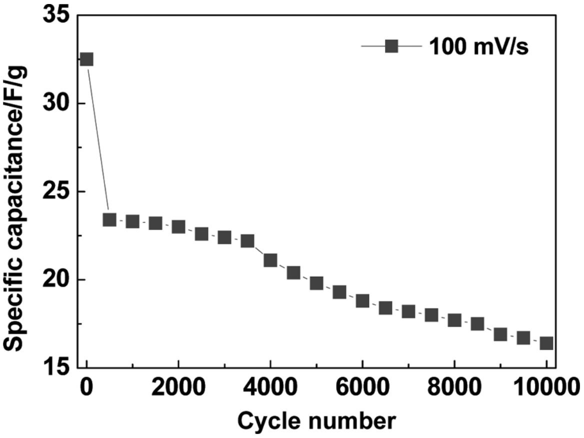


Figure 3. Cyclic number dependence of the capacitance values for the flexible PPy/Nafion electrodes in the ionic liquid, P1,3 TFSI.

where, Q_a, Q_c, m and ΔV are anodic and cathodic charges on the anodic and cathodic scans, mass of the electroactive materials and the potential window of the cyclic voltammogram, respectively. PPy/Nafion electrode maintained approximately 77% (350 F g^{-1}) of the low scan rate capacitance value (450 F g^{-1}) even at 300 mVs^{-1}.

Figure 3 shows capacitance values of the flexible PPy/Nafion electrodes as a function of cyclic number to investigate the electrochemical stability in the ionic liquid, P1,3TFSI.

It can be seen from the Figure 3 that the flexible PPy/Nafion electrodes maintained approximately 70% capacitance value of initial value after 4,000 cycles at 100 mVs^{-1}. The enhanced stability observed for the flexible PPy/Nafion electrode is likely due to the ionic liquid stabilizing the radical cations formed during the redox reaction. Moreover, the ability of the composite film to conduct both ions

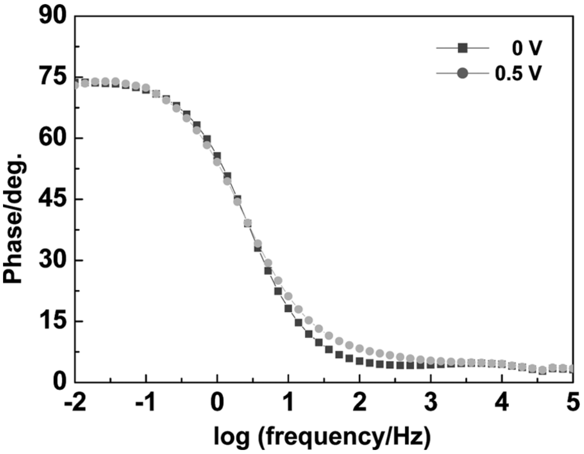


Figure 4. AC impedance spectra for the flexible PPy/Nafion electrodes in the ionic liquid, P1,3 TFSI.

and electrons may enable more effective charge transfer during the charge-discharge process in the ionic liquid.

In order to more clearly understand the above charge transfer process, AC impedance spectra as a bode plot were obtained as shown in Figure 4. It can be observed from Figure 4 that the PPy/Nafion electrode shows the phase angle of 75° at low frequency region, indicating pseudo capacitive behavior, not the ideal capacitance behavior. This behavior keeps until the frequency of less than 1 Hz, meaning the charge transfer process is not slow in the ionic liquld, which supports the cyclic voltammetric data.

Conclusion

The flexible PPy/Nafion electrode shows capacitance values in the range of 350–450 F/g in the ionic liquid, N-methyl-N-propylpyridinium trifluoromethanesulfonyl imide, indicating that it may be suitable for the supercapacitors based on PPy electrodes.

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