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Chemical Synthesis, Characterization, and Electrochemical Studies of Poly(3,4-ethylenedioxythiophene)/Poly(styrene-4-sulfonate) Composites

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Poly(3,4-ethylenedioxythiophene)/poly(styrene-4-sulfonate) (PEDOT/PSS) composites have been prepared from aqueous and aqueous acetonitrile solutions of EDOT and NaPSS by oxidation using Fe(III) salts. Powders with PEDOT to PSS ratios ranging from 0.3 to 4.2 and electronic conductivities as high as 10 S cm^{-1} have been obtained in good yields. The PEDOT/PSS blends are cation exchangers and exhibit facile eletrochemistry in both aqueous and acetonitrile media. Impedance measurements have shown that 30 μm thick PEDOT/PSS layers have proton conductivities as high as 0.03 S cm^{-1}.

Introduction

In recent years there has been increasing interest in the synthesis of conducting polymer particles by chemical oxidation.[1−5] This method is more suitable for mass production than the more commonly used electrochemical methods.[6]

Our interest in chemically prepared conducting polymer particles stems from their potential as catalyst support materials for proton exchange membrane (PEM) fuel cells. By polymerizing pyrrole in the presence of a proton-conducting polymer [poly(styrene-4-sulfonate), PSS][7] and subsequently depositing catalytic Pt particles,[8−10] we have been able to produce highly active catalysts. However, the poor long-term stability of polypyrrole (PPY) precludes its use in commercial fuel cells.

Poly(3,4-ethylenedioxythiophene)[11] (PEDOT) has been reported to exhibit greatly enhanced stability relative to polypyrrole[12] and appears to be the most stable conducting polymer currently available.[13] We have therefore used it to replace polypyrrole in our catalyst support.[14,15] PEDOT has been attracting growing interest since it was first reported in 1992[11] and is currently being marketed by Bayer. In most cases, electrochemically prepared films have been used, although there are a number of reports of the oxidative chemical polymerization of EDOT.[2,11,16]

Our interest in using PEDOT as a catalyst support in PEM fuel cells requires that they have good cation (proton) conductivity. To achieve this, a polyanion, PSS, is used as the counteranion during synthesis.[10,17] The anions then become fixed in place around the conducting polymer chains. Incorporation of an excess of the polyanion during synthesis, or partial reduction of the polymer (eq 1) will produce a cation exchanger with mobile cations.

$$(-\mathrm{EDOT}^{n+}-)n(\text{poly-A}^-) + n\mathrm{e} + n\mathrm{C}^+(\text{solution}) \rightleftharpoons (-\mathrm{EDOT}-)n(\text{poly-A}^-)n\mathrm{C}^+ \quad (1)$$

This strategy has been shown to be effective in the case of PPY/PSS composites, which exhibit proton conductivities as high as 25 mS cm^{-1}.[10] The PEDOT/PSS composites exhibit similarly high proton conductivities, and when catalyzed with Pt, they provide significantly better activity for oxygen reduction in PEM gas diffusion electrodes.[14,15]

This paper describes the synthesis, characterization, and electrochemical studies of chemically synthesized polymer blends of PEDOT and the polyanion PSS. The

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Table 1. Synthesis Conditions, Compositions, Yields, and Initial Conductivities

ID	solvent	oxidant[a]	PEDOT:PSS ratio initial	PEDOT:PSS ratio obtained[b]	reactn time	% yield	initial conductivity (S cm^{-1})
M2	AN/H_2O	×5	2.5	1.1	3 days	18	0.3
M3	AN/H_2O	×10	2.5	1.4	3 days	61	1.5
M4	AN/H_2O	×4	7.5	2.1	3 days	93	1.3
MB	AN/H_2O	×5	1.5	1.5	4 days	35	1.0
MS2	AN/H_2O	×10[c]	1	0.3	2 days	38	6×10^{-3}
MS1a	AN/H_2O	×10	1	1.0	2 days	39	2.5
MS1	H_2O	×10	1	0.5	2 days	50	0.3
Q1	H_2O	×5	5	0.4	2 h	62	0.4
Q2	H_2O[d]	×5	5	4.2[e]	2 h	100[f]	9.9

[a] $Fe(NO_3)_3{\cdot}9H_2O$ per mole of EDOT. [b] See the text. [c] $FeCl_3$. [d] Low-volume emulsion polymerization. See ref 14. [e] Estimated for $PEDOT^{0.5+}$/PSS/NO_3^- assuming 100% incorporation of PSS. [f] Assumed.

Table 2. Elemental Analyses

sample	formula		C	H	N	O	S	Fe[a]
M3	$PEDOT_{1.4}(NO_3)_{0.22}Fe_{0.18}PSS{\cdot}3H_2O$	expl	43.20	3.26	0.69	31.61	15.38	2.4
		calcd	43.0	3.89	0.68	33.2	16.8	2.2
M4	$PEDOT_{2.1}(NO_3)_{0.45}Fe_{0.13}PSS{\cdot}1.5H_2O$	expl	45.27	3.11	1.21	27.18	17.09	0.90
		calcd	45.8	3.41	1.17	29.8	18.4	1.4
MB	$PEDOT_{1.5}(NO_3)_{0.15}Fe_{0.14}PSS{\cdot}1.5H_2O$	expl	45.64	3.39	0.49	25.71	17.88	2.1
		calcd	46.6	3.67	0.49	29.2	18.3	1.8
Q1	$PEDOT_{0.42}Fe_{0.26}PSS{\cdot}1.5H_2O$	expl	45.46	3.78	0	27.68	14.50	4.8
		calcd	44.6	4.12	0	30.1	16.0	5.2

(Column group over C to Fe: elemental analysis and calculated values (% by mass))

[a] Determined from the %S by mass and the Fe:S ratio from EDX.

deposition of precious metal catalysts on these materials and the electrocatalysis of oxygen reduction, hydrogen oxidation, and methanol oxidation by the resulting supported catalysts are described elsewhere.[14,15] We are aware of only one previous report of the synthesis of PEDOT/PSS, and that described only the electrochemical formation of films on electrodes.[12]

The PEDOT/PSS blends described here are also attractive for applications in supercapacitors[18] and batteries.[19] Their high cation conductivities will produce large power densities and make them more compatible with lithium and lithium ion anodes than most other conducting polymers, including PEDOT itself. Results of a preliminary investigation of one of the PEDOT/PSS blends in Li^+ containing aqueous and acetonitrile solutions is therefore included.

Experimental Section

Synthesis of the PEDOT/PSS blends was carried out at ca. 22 °C in mixtures of water and acetonitrile (AN) as well as in neat aqueous solutions. One sample (Q2) was prepared from a dispersion of EDOT in NaPSS(aq), as previously described.[14] Details of the synthesis of each sample are given in Table 1. The mixed solvent system was used in most cases since the EDOT monomer (Bayer trial product) has a low solubility in water,[2] but conversely, sodium poly(styrene-4-sulfonate) (NaPSS, Aldrich, avg MW ≈ 70 000) is insoluble in AN. In a 1:1 (volume) mixture of H_2O and AN, NaPSS has a solubility (at 25 °C) of ca. 0.5 M, while that of the EDOT monomer is ca. 0.15 M. The appropriate amounts of EDOT and NaPSS were first dissolved individually in AN and H_2O, respectively, in proportions such that when mixed together a 1:1 solvent mixture resulted. The mixed solutions would often be turbid, but upon addition of more AN + H_2O they would become clear. After a few minutes of stirring to allow equilibration, a molar excess (up to 10:1 relative to EDOT) of the oxidant, in a small amount of water, was added. Oxidants used were $Fe(NO_3)_3{\cdot}9H_2O$ (BDH) and $FeCl_3$ (anhydrous, Fluka). After various reaction times (from 2 to 100 h) deep blue powders were collected by filtration, washed, and then dried overnight in a vacuum oven at 25−40 °C.

For synthesis of PEDOT/PSS in the absence of acetonitrile, the EDOT was first dissolved in warm NaPSS(aq). $Fe(NO_3)_3{\cdot}9H_2O$ in a small volume of water was then added to the cooled (room temperature) solution. EDOT dispersed much better in NaPSS(aq) than in pure water, and this assisted the formation of highly conducting PEDOT/PSS composites.[14]

The blend compositions given in Table 1 were determined from Fe:S ratios from energy-dispersive X-ray emission analysis (EDX) by using eq 2, which is based on a simple charge balance.

$$\mathrm{S{:}Fe} = n_{\mathrm{Fe}}(x + 1)/(1 + a - xd) \qquad (2)$$

where n_{Fe} is the average charge on the $Fe^{3+/2+}$ ions, a is the ratio of other anions (NO_3^-) to PSS, and d is the doping level of the polymer (average charge per EDOT ring). A doping level of 0.50 and an Fe oxidation state of 3 were assumed, since these values gave the best fit with elemental analyses (see below). The parameter a was determined from the %N from elemental analysis or assumed to be zero for samples that were not analyzed.

Elemental analysis was performed on selected samples on three separate occasions by two different companies (Canadian Microanalytical Service Ltd., Vancouver, Canada, and CE Instruments, Calgary, Canada). The most complete data set (Canadian Microanalytical Service) is given in Table 2. Repeat determinations of both carbon and sulfur differed by as much as 3%, making the C:S ratios unreliable for estimation of PEDOT:PSS ratios. The analyses gave unaccounted for masses ranging from 3.2 to 8.5%, and since all elements that could possibly be in the samples were quantified (only He, Li, Be, B, F, and Ne would not be detected by the combination of elemental and EDX analysis), these residuals must be due to errors in the analyses. The origin of these errors is unclear, but they are not due to inhomogeneity of the samples, because replicate elemental analyses performed at the same time gave good precision (<1% rsd for C and S).

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To evaluate the electrochemistry of the polymer powders, electrodes were fashioned in the following manner. The dry polymer was mixed with 20% PTFE [poly(tetrafluoroethylene) aqueous suspension, Dupont] as a binder, agitated in an ultrasonic bath for 5 min, and then spread uniformly onto carbon fiber paper (CFP, Toray TGPH090) with a spatula to give a polymer loading of ca. 2.5 mg cm^{-2}. For most experiments in H_2SO_4(aq), a Nafion 117 membrane (Dupont) was hot-bonded to the polymer layer under an applied load of 180 kg cm^{-2} for 90 s at ca. 125 °C. The application of a Nafion membrane ensures that cations (protons) are the predominant mobile species in the polymer layer and more closely represents conditions in a PEM fuel cell. Experiments without the Nafion layer gave very similar results, indicating that anions and liquid electrolyte are not important in the electrochemistry of the PEDOT/PSS composite under acidic hydrated conditions.

Disks (1 cm^2) were cut from the membrane electrode assemblies (MEA) and tested in a plexiglass cell described elsewhere.[7] A controlled flow of nitrogen was passed over the back of the electrode while the membrane side faced the solution (1 M H_2SO_4). This configuration reproduces conditions required for a further study on the electrocatalytic properties of these polymer powders modified with catalyst particles.[15] For work in aqueous and nonaqueous $LiClO_4$ and $NaClO_4$ solutions, a metal (Pt disk) contact was made on the back of the polymer-coated carbon fiber paper disk (1 cm^2) and the polymer layer was exposed directly to the electrolyte solution in a standard three-electrode cell.

Cyclic voltammetry was carried out in a three-electrode configuration with a Pt wire as the counter electrode and a saturated sodium chloride calomel electrode (SSCE) as the reference electrode in a Luggin tube positioned close to the surface of the polymer electrode. All potentials are quoted with respect to the SSCE reference electrode (0.236 V vs NHE). Voltammetric measurements were made using a Solartron 1286 potentiostat/galvanostat. AC impedance was conducted with a Solartron 1250 frequency response analyzer coupled to the above potentiostat controlled by a PC and commercial software (ZPLOT2, Scribner). Electrodes were prepolarized for 30 s and then scanned with a perturbation amplitude of 5 mV RMS between 65 kHz and 0.1 Hz.

Conductivity measurements were obtained with a four-point probe assembly described elsewhere.[7] The probe permits the powders to be pressed into a pellet in situ, where the applied pressure is controlled by the torque on a screw. A pressure of 120 kg cm^{-2} was used for all measurements reported here.

Scanning electron microscopy and semiquantitative analyses were obtained with an Hitachi S-570 scanning electron microscope with an energy-dispersive X-ray (EDX) analyzer (Tracor Northern 5500). Relative elemental concentrations were calculated by fitting and correcting the EDX spectra with commercial software (SQ, Tracor Northern). Analyses were carried out two or three times on different portions of the sample. Fe(III)(PSS)$_3$ and KPSS, both prepared from NaPSS by ion-exchange, were used as standards. The measured Fe:S ratio was found to be low by a factor of 0.83, while the K:S ratio was high by a factor of 1.04. Ratios measured for the composites were therefore corrected by these factors.

Results and Discussion

Composition. Determination of the compositions of the polymer blends prepared in this work was difficult because commercial elemental analysis gave variable and inaccurate results. PEDOT:PSS ratios calculated from the experimental C:S ratios showed considerable scatter and were negative in several cases. Average values, calculated by first averaging the replicate %C and %S values but omitting analyses that gave negative PEDOT:PSS ratios (this was done because it improved the agreement with the analyzed metal ion contents), are given in Table 3.

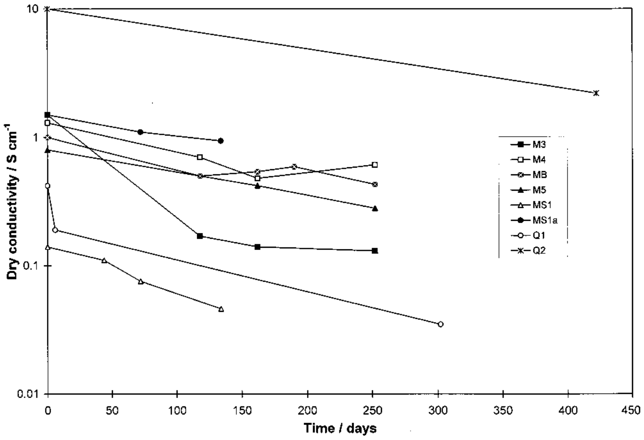

Figure 1. Electronic conductivities of PEDOT/PSS samples as a function of time stored in air.

Table 3. PEDOT:PSS Mole Ratios

sample	S:Fe mol ratio from EDX	PEDOT:PSS from S:Fe	PEDOT:PSS from C:S
M3	13	1.3	1.4
M4	34	2.4	1.9
MB	15	1.4	1.6
Q1	5.5	0.43	0.42

Because of the large uncertainties in the PEDOT:PSS ratios calculated from the experimental C:S ratios, and in order to find a more expedient way of determining these ratios, they were also estimated from S:Fe molar ratios from EDX by using eq 2. Values for n_{Fe} and d were adjusted by trial and error to give the best fit with the PEDOT:PSS ratios from the C:S ratios, while values of a (see Table 2) were estimated by approximately fitting the analytical %N. The optimum values of $n_{Fe} = 3$ and $d = 0.5$ are reasonable, given that the composites were prepared in the presence of a large excess of Fe^{3+}.

The PEDOT:PSS ratios given by the two methods (Table 3) are in acceptable agreement given the uncertainties in the data. Calculated elemental compositions, based on the average PEDOT:PSS ratios from the two methods, H_2O and NO_3^- levels adjusted for a reasonable global fit, and Fe levels required for charge neutrality are given along with the experimental values in Table 2. The agreement between the calculated and experimental elemental analyses is reasonable, given the poor precision and accuracy of the analytical data.

Examination of the PEDOT:PSS ratios for all of the polymers blends (Table 1) reveals that some control can be exercised over the composition of the polymer by changing the solvent, oxidant, and/or EDOT:NaPSS ratio in the reaction mixture. Use of $FeCl_3$ as the oxidant (sample MS2) decreases the PEDOT content of the resulting composite relative to using $Fe(NO_3)_3$ (sample MS1a). Using the AN + H_2O mixed solvent system, and consequently increasing the concentrations of the reactants by decreasing the amount of solvent, increases the PEDOT content of the composite (compare samples MS1 and MS1a). A further increase in PEDOT content can be realized by increasing the EDOT:NaPSS ratio in the reaction mixture, or by using an emulsion polymerization (Q2).

Cation Exchange. To demonstrate the cation exchange nature of the PEDOT/PSS composites, a number

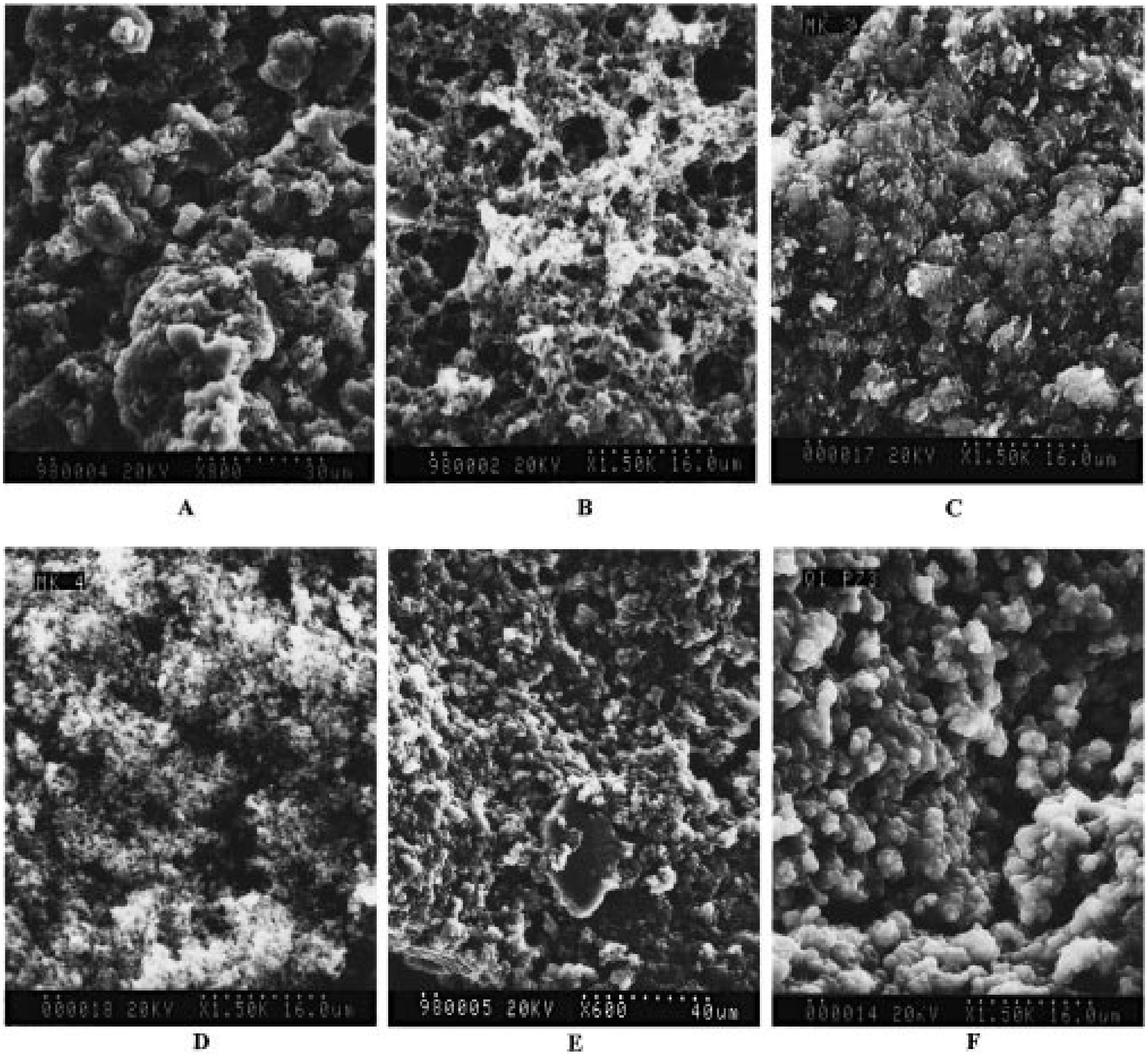

Figure 2. Scanning electron micrographs of PEDOT/PSS samples: (A) MS1, (B) MS1a, (C) M3, (D) M4, (E) Q1, (F) MS2.

of samples were ion exchanged with K^+ and then reanalyzed. Ion exchange was accomplished by stirring the polymer with saturated KCl(aq) for 30 min. The exchanged polymer was then collected by filtration, washed well with water, and dried in a vacuum oven at 25−40 °C. EDX indicated that 70−90% of the Fe was replaced by K^+ under these conditions.

Conductivity. Figure 1 shows pressed-pellet electronic conductivities of the polymer blends, determined by the four-point probe method, as a function of time over the course of ca. 9 months of storage in air. Initial conductivities (Table 1) were generally ca. 1 S cm^{-1}, but increased with increasing PEDOT content to as high as 10 S cm^{-1} for one sample (Q2). Conductivities were lower for the polymer prepared using $FeCl_3$ as the oxidant (MS2).

All samples lost conductivity with time. The conductivities of many samples seemed to plateau after about 4 months, at which time their conductivities had decreased by up to an order of magnitude.

Microscopy. Figure 2 shows representative scanning electron micrographs of some of the polymer blends. Particles are generally of irregular shape, tending to agglomerate and vary considerably in size. There appears to be a weak relationship between composition (or PSS fraction) and average particle size, with a tendency to smaller size with lower PSS content. However, the strong dependence of particle size on the concentration of the oxidant that was observed for PPY/PSS[7] is absent here. There is also a weak inverse correlation between the particle size and the polymer's bulk conductivity (Figure 1), which is consistent with our results for PPY/PSS.[7]

Cyclic Voltammetry. Figure 3 shows cyclic voltammograms of two CFP/(PEDOT/PSS)/Nafion MEAs in 1 M H_2SO_4(aq) at a sweep rate of 20 mV s^{-1}. These voltammograms show a highly reversible capacitive response at potentials more positive than −500 mV, which is characteristic of conducting polymers.[6] The broad cathodic and anodic peaks between −0.20 and

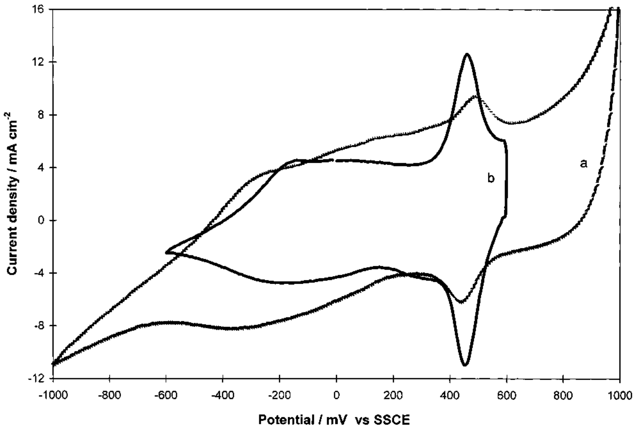

Figure 3. Cyclic voltammetry at 20 mV s^{-1} of 30 μm thick (Nafion coated) PEDOT/PSS layers in 1 M H_2SO_4(aq): (A) M4, (B) Q1.

−0.3 V are likely associated with the uptake of protons by the polymer.[20,21] Since the polymer blends contain an immobilized polyanion which compensates the charge on the PEDOT, electroneutrality during the charging and discharging of PEDOT is maintained by the movement of protons in to and out of the polymer layer (eq 1).

The scan rate dependences of currents in all voltammograms were linear for scan rates up to ca. 100 mV s^{-1}, indicating the electroactivity of the whole polymer layer in each case. Since the polymer layers were typically ca. 30 μm thick, this indicates that ion and electron transport in the polymer layers is very facile. Polymers with a larger fraction of PSS (and therefore lower PEDOT content) exhibited smaller voltammetric currents and charges per gram, as expected.

The sharp reversible peaks at ca. 0.45 V are due to the Fe^{3+} incorporated into the polymers during their synthesis. The polymer blends having a greater proportion of PSS contained a commensurately larger proportion of iron, and this was reflected in the relative currents for the $Fe^{3+/2+}$ waves (e.g. compare the two voltammograms in Figure 3). The $Fe^{3+/2+}$ peaks decay very slowly when the polymer layer is covered with a Nafion membrane, as in Figure 3. However, in the absence of the Nafion membrane, the $Fe^{2+/3+}$ is rapidly leached from the polymer by 1.0 M H_2SO_4(aq) and the $Fe^{3+/2+}$ waves disappear rapidly. As described above, the iron could be ion-exchanged out of the polymer blends (with K^+ or H^+), and the $Fe^{2+/3+}$ peaks in voltammograms of these exchanged polymers were either greatly diminished or absent.

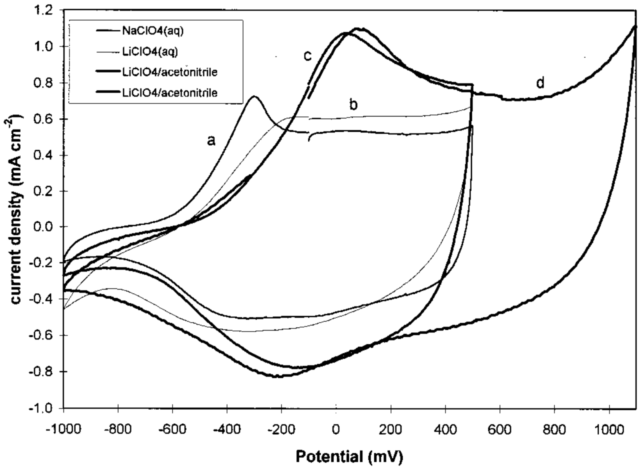

Figure 4. Steady-state cyclic voltammograms at 5 mV s^{-1} of 30 μm thick PEDOT/PSS (Q1) layers in 0.5 M $NaClO_4$(aq), 0.5 M $LiClO_4$(aq), and AN + 0.5 M $LiClO_4$.

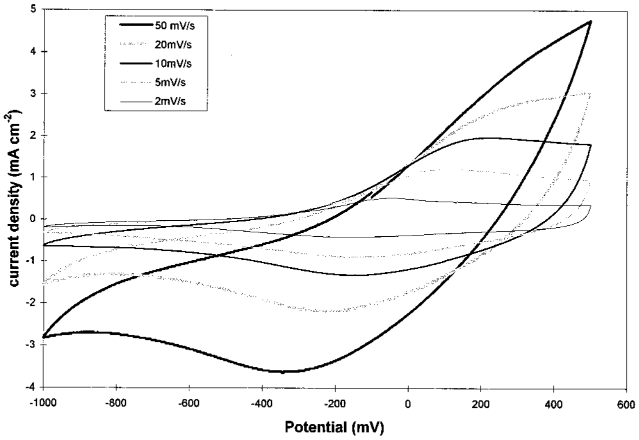

Figure 5. Cyclic voltammetry at various scan rates of a 30 μm thick PEDOT/PSS (Q1) layer in AN + 0.5 M $LiClO_4$.

Because of the strong interest in the use of conducting polymers in lithium and lithium ion batteries[19] and supercapacitors,[22] we have also made a preliminary investigation of the cyclic voltammetry of one of the PEDOT/PSS samples (Q1) in aqueous and nonaqueous $LiClO_4$ solutions. Aqueous $NaClO_4$ was also used, to provide evidence for the involvement of cations in the electrochemistry of the polymer. These experiments were performed on electrodes *without* a bonded Nafion layer (i.e., the electrolyte solution was in direct contact with the polymer layer). Typical voltammograms are shown in Figures 4 and 5.

The voltammograms in Figure 4 show some, but not large, differences when the cation or the solvent are varied. The differences observed between voltammograms in $NaClO_4$(aq) and $LiClO_4$(aq) suggest that cations are involved in the electrochemistry of the polymer, as predicted by eq 1. The electrochemistry of the polymer is facile and stable in all three electrolyte solutions employed. The stability of the polymer is illustrated by the fact that voltammograms a−c in Figure 4 were unchanged for at least 12 cycles at 5 mV s^{-1}.

In AN + $LiClO_4$, the polymer is stable over a wide potential range, and at 5 mV s^{-1} it has a reversible charge capacity of ca. 80 C g^{-1}. This compares favorably with results reported for electrochemically prepared PEDOT films.[18] However, in a Li battery this charge capacity would give an energy density of only ca. 70 W h kg^{-1} (based on the mass of the cathode material alone, and assuming an average cell voltage of 3 V). PEDOT/PSS is therefore more likely to be of use in a supercapacitor, where its facile electrochemistry can produce large power densities.[18] Our preliminary voltammetric investigation of the kinetics of the charging and dis-

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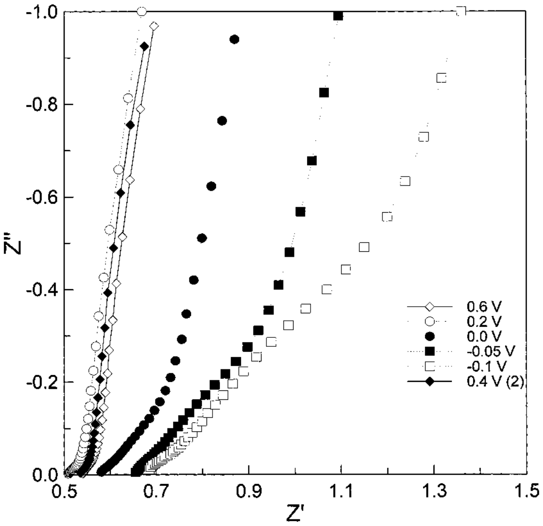

Figure 6. Complex plane impedance (Nyquist) p1ots for a 30 μm thick PEDOT/PSS layer (sample MS1a) in 1 M H_2SO_4(aq).

charging of PEDOT/PSS in AN + $LiClO_4$ (Figure 5) was hampered by the large uncompensated solution resistance in our cell. However, the voltammogram at 50 mV s^{-1} shown in Figure 5 shows that current densities greater than 3 mA cm^{-2} can be obtained during the discharge of a ca. 30 μm thick PEDOT/PSS layer. This would correspond to a power density of over 1000 W kg^{-1} in a 1 V supercapacitor, which is in the range reported in ref 18. It can be expected that significantly higher power densities will be achieved under optimal conditions.

Ac Impedance. The impedance response of conducting polymers has been modeled by either single or dual rail finite transmission line equivalent circuits.[23-25] The dual rail circuit (see Figure 1 in ref 23) is simply two parallel distributed resistances associated with electron and ion transport (R_E and R_I, respectively) through the polymer (where one is assumed to be negligible in the single rail model) connected by an “infinite” number of capacitors, which represent the solution−polymer interfacial differential capacitance throughout the bulk of the film. Ideal behavior gives a 45° slope Warburg-like region in Nyquist plots at high frequencies which at lower frequencies curves up to become vertical (constant real impedance), corresponding to the pure capacitance response of the entire polymer film.

All samples of PEDOT/PSS examined in this work gave Nyquist plots approximating the ideal behavior described above (e.g. Figure 6), although significant and sometimes considerable deviations from ideality were observed. For instance, Z' always increased with decreasing ω (ω is angular frequency in rad^{-1}) in the low-frequency region, where it should be constant, and the slope of the Warburg-like region usually deviated from 45°. Such deviations are generally attributed to surface roughness and film inhomogeneity, which can introduce a frequency dependence to both the low-frequency and Warburg-like resistances.[26,27] However, despite these nonidealities, the Nyquist plots show well-defined regions from which values of R_I for the PEDOT/PSS layers were derived.

We have examined in some detail the potential dependence of the electronic and ionic conductivities of the near ideal impedance behavior of PPY/PSS[28-31] and, by using the transmission line model, ac impedance proves to be a simple means of extracting ionic conductivities for conducting polymers. Values of R_I are derived from the recorded impedance data of the polymer blends by two methods, outlined briefly here. We have described these methods more fully elsewhere.[23]

Extrapolating the low-frequency (near) vertical capacitive portion of the Nyquist plot back to the real impedance axis gives Z'_{LF}, which is composed of

$$Z'_{LF} = R_s + R_\Sigma/3 \tag{3}$$

where R_s is the uncompensated solution resistance. If R_E is negligible, which will often be the case for an oxidized conducting polymer, R_Σ will be equivalent to R_I. Note that the 1/3 comes from the low-frequency behavior of the coth function that describes the transmission line circuit.[32] Alternatively, R_I (from R_Σ) can be determined from a plot of the square of the total impedance, $|Z|^2$ (corrected for solution resistance), vs ω^{-1} in the Warburg-like region. The slope is R_Σ/C, with C available from a plot of the imaginary impedance, Z'', vs ω^{-1} in the low-frequency, capacitive region (slope $1/C$). By comparing values obtained from these two analyses, we can assess the magnitude of the errors caused by the nonideality of the data.

Figure 6 shows Nyquist plots of impedance data for a PEDOT/PSS polymer blend examined in 1 M H_2SO_4(aq) solution at applied bias potentials between 0.6 and −0.1 V (vs SSCE). Between 0.6 and 0.2 V there is little variation of the impedance response with potential, with all plots showing a relatively narrow Warburg-type region and then a near vertical capacitance region. At these potentials the PEDOT is highly oxidized (p-doped), so its electronic resistance (R_E) is expected to be low. The high-frequency real axis intercept, Z'_{HF}, therefore corresponds almost entirely to the solution (plus Nafion membrane) resistance of the cell. It is clear from the relatively narrow Warburg-like regions that the ionic resistance is also quite small, indicating that the proton conductivity of the PEDOT/PSS polymer blend is very high. This is consistent with previous results for PPY/PPS blends[10] and is assumed to be due to the presence of the PSS and its accompanying mobile protons.

At bias potentials of 0 V (vs SSCE) and lower, the oxidation level of the PEDOT decreases to a level where its electronic resistance becomes significant. Simultaneously, more protons move into the film to compensate

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Table 4. Ionic Conductivities and Capacitances from Ac Impedance at 400 mV

		ionic conductivity (mS cm^{-1})		
sample	x^a	from Z'_{LF}	from Warburg region	capacitance (C g^{-1})
MS1	0.5	3.4	3.9	38
		2.4	2.3	37
		4.2	4.4	55
Q1[b]	0.4	13	16	30
MB	1.5	0.7	0.7	60
MS1a	1.0	7.3	23	69
		30	23	51
M3[b]	1.4	5.0	3.7	43
M4	2.1	2.2	1.6	35

[a] PEDOT:PSS ratio. [b] Nafion bonded.

the charge on the immobile PSS and therefore decrease the ionic resistance for the polymer layer. The effect that this has on the appearance of the Nyquist plots is that Z'_{HF} shifts to higher real impedance and the length of the Warburg region increases (hence shifting the extrapolated Z'_{LF} value). Because of these complications, and the reasonably constant ionic conductivity observed over the 0.2−0.6 V potential range, we have restricted our quantitative comparison of the different polymer blends to only the impedance response at 0.4 V.

The Z'' vs ω^{-1} plots for all of the PEDOT/PSS blends were linear, while the $|Z|^2$ vs ω^{-1} plots were generally somewhat curved over the Warburg(-like) region (as we have reported elsewhere for polypyrrole[20]), but treated as linear. Conductivities were derived from the measured resistances by assuming that the polymer layers were 30 μm thick. This thickness value was estimated from a scanning electron micrograph of the cross section of an electrode prepared with 2.5 mg cm^{-2} of polymer MB. Ionic conductivities at 0.4 V calculated from the impedance data by the two methods and respective capacitance values (determined from the Z'' vs ω^{-1} plots) for some representative samples are given in Table 4. These ionic conductivities are similar to those we have obtained for proton conduction in PPY/PSS blends.[10]

In most cases, conductivities determined by the two data analysis methods agree reasonably well, although there are a few large discrepancies. Similar discrepancies are seen in some cases between results for individual electrodes of the same polymer. There is therefore considerable uncertainty (ca. ±25% based on the relative standard deviation of the six values for MS1) in the conductivity values reported in Table 4. Within this uncertainty, conductivities were found to not be significantly dependent on the polymer composition. This is surprising, since the concentration of protons in the films, which increases with increasing PSS fraction, varies considerably between the extremes of composition examined in this work. The reason for the lack of $[H^+]$ dependence is unclear, but it may indicate that the low-frequency resistances measured for PEDOT/PSS layers contain an additional component in addition to the layer's ionic resistance. The ionic conductivities reported in Table 4 may therefore be underestimated. The PPY/PSS blends previously investigated did show the expected dependence of the ionic conductivity on $[H^+]$.[10]

The capacitance values reported in Table 4, which should be proportional to the active mass of the conducting polymer (PEDOT), show a dependence on PEDOT mass fraction. Although there is considerable uncertainty in both the composition and capacitance values, the data are consistent with a linear relationship through the origin. The intercept at a mass fraction equal to 1 of a linear regression forced through the origin is 110 F g^{-1}, which is similar to the value of ca. 100 F cm^{-3} reported for electrochemically prepared PEDOT perchlorate.[18]

Another feature of the impedance data that shows a significant difference between polymers of different composition is the potential dependence in the potential region where R_E becomes significant as the polymer is reduced (e.g. 0 V and lower in Figure 6). The effects of R_E are more marked (i.e., begin at a higher potential and correspond to larger values of R_E) for the polymers containing more PSS. This is consistent with the fact that in these blends the PEDOT concentration is lower and hence changes in its electronic conductivity would more severely affect the electronic conductivity of the blend as a whole.

Conclusions

PEDOT/PSS blends can be conveniently prepared from aqueous or aqueous acetonitrile solutions of EDOT and NaPSS by oxidation using Fe(III) salts. The use of acetonitrile in the synthesis solution reduces the amount of solvent that is required and generally leads to polymers with a higher PEDOT to PSS ratio.

Under the conditions employed in this work PSS is the main counterion incorporated into the oxidized PEDOT during its formation, and its presence modifies the properties of the PEDOT. Of particular interest is the fact that PEDOT/PSS is a cation exchanger under most conditions. Reduction or partial reduction of the oxidized PEDOT leaves an excess of immobile sulfonate groups whose charge is balanced by mobile cations.

The PEDOT/PSS blends exhibit high electronic and ionic (cation) conductivities and facile eletrochemistry in both aqueous and acetonitrile electrolytes. These properties make them attractive materials for use as catalyst supports in fuel cells[14,15] and cathode materials in supercapacitors or high-power Li batteries.

Preliminary results show that the PEDOT/PSS blends have comparable energy and power densities to the electrochemically prepared PEDOT reported in ref 18; however, their facile chemical synthesis would be a major advantage for mass production. Furthermore, the incorporation of PSS should enhance cation transport in the polymer and lead to higher power densities than are possible with PEDOT alone.

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