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ULTRACAPACITORS USING P- AND N- DOPABLE POLY(3-ARYLTHIOPHENE)S

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The unique p- and n- dopability of polythiophenes was utilized to prepare ultracapacitors that promise high energy density and power density. To understand the charge transport mechanisms that occur during the electrochemical switching between the neutral and doped states, we prepared a series of Poly(3-(p-X-phenyl)thiophene) (X=-CMe3, -Me, -OMe, -H,-F,-Cl,-Br,-CF3,-SO2Me). Their electrochemical polymerization, electronic and ionic conductivity, solvent and electrolyte transport were studied using various techniques. Ultracapacitors prepared with these polymers as the active materials were examined for their cell impedance and effective capacitance during continuous charge/discharge cycles.

INTRODUCTION

Many current and potential applications of conducting polymers, such as in rechargeable batteries,14 electrochemical capacitors,4,5 electrochromic devices,6-9 molecular electronic devices,10-13 and electrochemical sensors14-17 utilize the rapid electrochemical switching capabilities between the oxidized (p-doped) and neutral or reduced (n-doped) forms. During the switching, not only electrons move in the polymer and cross the electrode/polymer interface, but also electrolyte ions move in the polymer pore solution and cross the polymer/bulk electrolyte solution interface to maintain the film electroneutrality. Measurements of the charge transport are important to evaluate these polymers for their intended applications, to provide the basis for improving their performance, and to design new polymers with better quality. It has been the focus of intensive current research using a variety of electrochemical techniques, such as cyclic voltammetry,18-23 chronoamperometry,24-27 chronopotentiometry,28-32 techniques using dual working electrodes,10, 33-35 rotating disc voltammetry,36-38 ionic conductivity measurements on polymer membranes,25,39 impedance spectroscopy,40-51 and electrochemical quartz crystal microbalance.52-64 Most of these studies focused on polypyrroles and polythiophenes. For these polymers the slow ion movement in a conductive polymer film often limits their switching rate.19,20,65,66 It was demonstrated that by covalently attaching anion-exchange centers to the polymer backbone the ion transport rate in the polymer was enhanced.67-70 It was also shown by Naoi and coworkers71-73 that the polymer formed on a nitrile butadiene rubber pre-coated electrode has regulated morphology, which improves ion transport. Polymers exhibiting so called “self-doping mechanism”, achieved either by containing polyelectrolyte anions entrapped during the electrochemical polymerization74-82 or by
polymerizing their monomers containing covalently bonded anionic groups,\textsuperscript{7,83-88} have also shown enhanced ion transport rate.

Our research involves searching for suitable conducting polymers that will be useful as the active electrode materials for electrochemical capacitors. Polyheterocycles are promising candidates due to their facile electrochemical polymerization, with especially polythiophenes exhibiting promising properties in their doped and neutral states.\textsuperscript{7,8} We are particularly interested in those materials exhibiting both p- and n- doping capabilities for constructing the so called Type III capacitors.\textsuperscript{9} When this capacitor is charged, one electrode is p-doped and the other is n-doped. Discharging returns both electrodes to their neutral states. Since most studies on conducting polymers reported in the literature focus on the p-doped forms, reports on the n-doped polymers are relatively few\textsuperscript{91-97} and their properties are less well understood. Several factors that attribute to this situation are the poor stability of the n-doped polymers at very negative potentials and the slow electrolyte counterion movement in a dense film that can prevent the n-doping process from being observed if the experimental time scale is too short.

As we reported earlier,\textsuperscript{50} the type III capacitor has advantages over the other two types of configurations for the ultracapacitors using conducting polymer, namely, the high energy density (E=CV\textsuperscript{2}) due to the high cell voltage (~3V), and the high power density resulting from the fast release of stored charge from the doped and conductive electrodes. Our previous study\textsuperscript{50} has identified poly[3-(p-fluorophenyl)thiophene] (PFPT) as a promising candidate for such a device, and this study reveals further those factors that influence charge storage and release, and the preliminary characterization of this polymer in the capacitor configuration.

**EXPERIMENTAL**

**Chemicals**

Tetraethylammonium tetrafluoroborate (Et\textsubscript{4}NBF\textsubscript{4}) (Aldrich Chemical Co., >99%), Tetraethylammonium hexafluorophosphate (Et\textsubscript{4}NPF\textsubscript{6}), tetrabutylammonium hexafluorophosphate (But\textsubscript{4}NPF\textsubscript{6}) were recrystallized three times and dried in vacuum at 100 °C for 24 hours before use. A small amount of activated alumina (500 °C for 24 hours) was placed in the bottom of the electrochemical cell to remove residual amounts of water in acetonitrile (Aldrich Sure-Seal, 50 ppm H\textsubscript{2}O). In the later stage of studies, the water levels in the electrolyte and solvent were further lowered by drying the electrolyte in vacuum at 250 °C and by passing the solvent through an activated alumina column in a glove box. Water contents in the electrolyte solutions were determined using Fisher titration methods to be less than 8 ppm.

3-(p-fluorophenyl)-thiophene (FPT) was prepared through a nickel (II) catalyzed coupling reaction described in the literature.\textsuperscript{98} After being purified by sublimation, the white compound yields a m.p. 85.1 - 85.6 °C (lit.\textsuperscript{99} 86-87 °C). A complete descriptions on the synthesis of the monomers were given previously.\textsuperscript{100}
Cyclic voltammetry and impedance experiments were carried out in a three compartment cell consisting of a Pt working electrode (area 0.0045 cm²), a glassy carbon rod counter electrode, and a non-aqueous Ag/Ag⁺ (1.0 mM in 0.2 M Et₄NBF₄) reference electrode. The potential of the reference electrode was evaluated in a 0.2 M Et₄NBF₄ acetonitrile solution containing 2 mM ferrocene (Aldrich, 98%, sublimed). The measured formal potential of the ferrocene/ferrocenium couple was 0.075 V vs the above reference electrode. All potentials reported here were measured against this reference electrode.

The cyclic voltammetry was performed using a PARC Model 273A Potentiostat controlled with a GPIB data bus installed on an IBM compatible computer using Model 270/250 Research Electrochemistry Software (version 4.0, EG & G Instruments Inc.).

For impedance measurements, the 273A Potentiostat was coupled to an Solertron Instruments 1260 ImpedancdGain-Phase Analyzer. Zplot for Windows (Version 1.1, Scribner Associates, Inc.) software was used to control the experiments and acquire data.

Electrochemical quartz crystal microbalance (EQCM) experiments were performed using an Electrochemical Nanobalance Model EQCN-601 coupled to a Potentiostat Model PS-205 (Elchema, Inc). Voltscan (version 3.0) software (Elchema, Inc) was used for the data acquisition with a GPIB data bus installed on an IBM compatible computer. An AT-cut quartz crystal wafer having a fundamental vibration frequency of 5 MHz was used. To prepare the quartz crystal electrode similar to those of Bruckenstein and Shay, a circular gold film flag electrode was deposited on each face of the quartz crystal in vacuum. The two centrally positioned circular electrodes sandwiching the quartz crystal form the piezoelectric active area, and the two opposite leads provide the electrical connection. The piezoelectrical and electrochemical active area for these quartz crystal electrodes were 0.307 and 0.432 cm² respectively. In EQCM experiments, the quartz crystal electrode was clamped to the open end of a custom-made cylindrical electrochemical cell, so that one face of the quartz crystal contacts with the electrolyte solution in the cell and the other face is exposed to the air. The cell was filled with the electrolyte solution and sealed air-tight in a glove box, which was then placed in a N₂ filled Faraday Cage (Model EQCM-602, Elchema) to minimize the interference from the air components and the surrounding electromagnetic field. The EQCM was calibrated by electrochemical deposition of silver from a solution containing 10 mM AgNO₃ and 0.2 M HClO₄(aq). Deposition and subsequent stripping of silver at the electrode at a constant current density of 0.5 mA cm⁻² gave a symmetric triangular mass vs. time curve, and the sensitivity of the EQCM was found to be 6.10 ng Hz⁻¹. Drifting was within 20 Hz range for a period of 3 hours when the cell was filled with the air or an electrolyte solution.

In our previous studies on the electrochemical polymerization of FPT from a 1.0 M Et₄NBF₄ acetonitrile solution containing 0.1 M FPT, a current density of 3.56 mA cm⁻² was found to give good polymer films. This current density was used to prepare PFPT films on various substrate electrodes throughout this work. The optimal current density was a compromise between a low current density, where severe loss of soluble oligomers and prolonged exposure of the deposited polymer film to the polymerization potential occur, and a high current density, where overoxidization of the deposited polymer could rapidly occur as the electrode potential was increased.

The film thickness and morphologies were observed on gold sputtered films using a Phillips XL-30 Scanning Electron Microscope operated at an accelerating voltage of 15 kV. The polymer films were electrochemically deposited on the indium doped tin oxide (ITO)
After the potential of a newly polymerized film was scanned to -0.6 V, the film coated electrode was rinsed with acetonitrile, dried in the air, and then broken at a right angle along the polymer film coated electrode surface to create a cross section of the polymer film. A plot of the deposition charge density vs. the measured dry film thickness gives a straight line from 0.5 to 8 μm film thickness range and a polymerization charge density of 96 mC cm² to one micrometer dry film thickness. This charge density to the film thickness ratio can be used to estimate the dry film thickness from the deposition charge.

All electrochemical experiments except EQCM’s were carried out in dry glove box. The low background currents from 1.0 to -2.4 V in the cyclic voltammograms of a bare Pt electrode in a 0.2 M Et₄NBF₄ acetonitrile solution indicated that the glove box was in good condition in terms of the water and O₂ level. The oxygen level was monitored using an oxygen analyzer (Thermox CG 1000, Ametek) to be less than 0.8 ppm.

RESULTS AND DISCUSSION

Effect of Substitution on Redox Potentials of Monomers and Polymers.

The effects of substitution on the redox properties of the monomers and polymers were observed, and Table 1 lists the oxidation potentials of the monomers, and the formal oxidation and reduction potentials for the polymers. Figure 1 and 2 show the trends in the redox properties for the monomers and polymers. As expected the potentials shift cathodically for electron-donating substituents and anodically for electron-withdrawing groups. Both inductive and resonance effects influence the oxidation potential of monomers. For example, -CF₃, which has similar steric requirements and resonance values (sr) as -CH₃, shifts the oxidation peak to higher potential due to its higher electron-withdrawing ability. When the substituents have similar inductive strength (e.g., -F and -Cl) the one with higher electron donating ability (in this case -F) shifts the oxidation potential to a lower value. The effect is more pronounced for the monomers than for the polymers (the shifts are in the order of 200-300 mV in the monomers and 50-100 mV in the polymers relative to thiophene and polythiophene respectively), and the size of the substituent does not have a significant effect. The overall diminished substituent effect in the polymers suggests a decreased conjugation between the substituted phenyl rings and the polythiophene backbone. Figure 2 also shows that the difference between the p- and n-doping formal potentials of the polymers is essentially unchanged upon substitution. This is not unexpected since the symmetries of the frontier orbitals of 3-arylthiophenes are such that the substituents can interact with both levels, shifting them downwards (or upwards) to comparable extents, thus the $E_{\text{gap}}$ remains essentially the same. In our attempt to increase the stability of n-doped polymer by adding a strong electron withdrawing group to shift the redox potential of the polymer anodically, the polymerization potential of the monomer is also increased anodically, which can lead to the overoxidation of the polymer film during polymerization. Of this poly(3-arylthiophene) series studied, PFPT gives an over-all better film quality and morphology, and was thus used for more complete characterizations as reported in the following sections.
EQCM Studies on Electrochemical Polymerization.

There are several recent reviews for the applications of EQCM technique, which measures \textit{in situ} mass change of the working electrode during electrochemical experiments. This technique is extremely powerful to study the ions and solvent transport accompanying the electrochemical switching of conducting polymers. A change of the mass firmly (Δm) attached to the working electrode induces a change in the quartz crystal oscillation frequency (Δf), as shown by the Sauerbrey equation:

\[ Δf = \frac{-2Δmf_0^2}{A\sqrt{m_qr_q}} \]  

where $f_0$ is the resonant frequency of the unloaded crystal (= 5 MHz), $r_q$ the density of quartz (=2.648 g cm$^{-3}$), and $m_q$ the shear modulus of quartz (=2.94x10$^{11}$ g cm$^{-1}$ s$^{-2}$). Thus frequency change, which can be accurately measured, is proportional to the mass change on the working electrode. To satisfy the Sauerbrey equation in EQCM experiments, the mass of the film must be less than 1% of the mass of the uncovered quartz resonator, and the film must behave as a rigid layer. For polypyrrole, it has been shown that the rigid-layer approximation holds up to 5 mm. A polymer excessively swollen by the electrolyte solution can fail the rigid layer requirement. In this case, the calculated mass change from Δf according to the Sauerbrey equation is less than the true mass change due to the attenuation of the shear wave strength through the elastic structure of the swollen polymer film.

The electrochemical polymerization of FPT from 0.1 M monomer acetonitrile solutions containing 0.2 M, 1.0 M and 2.0 M Et$_4$PF$_6$ was studied using EQCM. In these experiments, a constant anodic current was applied for 35 seconds to form the polymer, which was immediately reduced with a constant cathodic current. The electrode potential and polymer mass on the electrode were recorded for both the polymerization and discharge processes as shown in Figure 3. The very high electrode potential at the beginning of the polymerization indicates the difficulty in oxidizing the monomer at the bare Au electrode. The electrode potential decreased rapidly within 2 to 5 seconds and then remained relatively constant during the rest of polymerization. During the discharge process, the electrode potential decreased as the oxidized polymer was reduced. The end of discharge was indicated by the rapid decrease of the electrode potential.

The onset point of the mass increase curve signals the attachment of the polymer onto the electrode and thus the beginning of polymer film formation. It is important to notice that these onset points lag behind the instant of passing the polymerization current. This observation indicates that the anodic reaction of FPT forms soluble oligomers initially through the oxidative coupling reaction. As the polymerization proceeds, the high molecular weight oligomers become insoluble in the monomer solution and precipitate to the electrode to form the polymer film. This is due to the accumulation of the oligomers in the vicinity of the electrode and the decreased solubility of oligomers as their molecular mass increased.

Figure 3 also shows that the induction period (the time interval between the instant of passing polymerization current and the onset point of mass curve) decreases as the
Electrolyte concentration is increased. Since the induction time is approximately the time needed for the oligomers to accumulate and pass the saturation concentration prior to their precipitation to the electrode, the electrolyte concentration dependence of induction time indicates that the oligomers are formed in a region thinner and closer to the electrode as the electrolyte concentration is increased. Such a picture is consistent with the concept of electrochemical double layer structure. The thickness of the double layer of the positively charged oligomers and electrode (which can be viewed as a giant ion) decreases as the electrolyte concentration increases.

Formation of oligomers in the solution during the polymerization and their precipitation to form the polymer film on electrode were once more indicated after the termination of the polymerization with a constant cathodic current, which reduced the polymer film (and oligomers in the vicinity of electrode). An unexpected mass increase peak was shown to superimpose on the mass decrease curve, which is now due to the expulsion of electrolyte anions and a decrease in film solvation (see below) when the film is reduced. However, the mass increase peak can only be explained by the continuous precipitation of the oligomers from the solution after turning off the polymerization current. The time difference between the end of polymerization and the mass increase peak again bears the same dependence on electrolyte concentration as does the induction time, indicating that the region of oligomer formation extended further away from the electrode in a less concentrated electrolyte solution.

The mass increase curve for the polymerization in 2.0 M electrolyte solution is more close to the ideal curve as shown by the nearly linear mass increase with the deposition charge. This behavior demonstrates that the deposited polymer film, at least in 2.0 M electrolyte solution, meets the rigid layer requirement for using the Sauerbrey equation. Polymerization in a less concentrated electrolyte solution showed a longer induction period at the beginning of polymerization and a more rapid film formation rate after the induction period. Also, the final mass of the neutral polymer as shown by the mass at the end of the discharging curve was higher. Although the rigid layer behavior was not certain for the polymers formed in 0.2 M and 1.0 M electrolyte solution due to the curvature of their mass curves, the higher mass observed in a less concentrated electrolyte solution is not caused by the deviation of Sauerbrey equation. As discussed before, the mass calculated for an elastic layer from the frequency change using Sauerbrey equation is lower than the true film mass due to the attenuation of the shear wave through the swollen film, and hence the reduced sensitivity ($\Delta m/\Delta f$) of EQCM.

From the length of discharging time (Figure 3), the cyclic voltammetric charge (Figure 4) and the dry mass of the polymer, the polymerization efficiency calculated decreases as the electrolyte concentration is decreased. The excess mass observed in Figure 3 for PFPT in a dilute electrolyte solution must be due to the solution mass in the film pores. This result indicates that the film formed in a less concentrated electrolyte solution has a more extended porous structure, and supports the previous conclusion about the formation of a polymer film through the oligomer precipitation. Since in a more concentrated electrolyte solution the oligomers are formed in a region closer to the electrode surface, the amount of oligomers lost to the bulk solution decreases, resulting in a higher polymerization efficiency and a denser polymer structure.

Electrolyte and Solvent Transport during Potential Cycling

Fig 4. shows the cyclic voltammograms and mass changes of PFPT films recorded
with EQCM. The mass of the neutral polymer film after several redox cycles was higher than that of the newly formed film at the end of discharge in Figure 3. When oxidized, the film mass increased, indicating the insertion of solvated electrolyte anions from the bulk electrolyte solution to the film to compensate the positive charges on the oxidized polymer chains. On the return scan, the film mass decreases and the electrolyte anions were expelled from the film when the positive charges on the polymer chains were removed. Mass changes were similar for the reduction of polymer except that electrolyte cation movement was involved to maintain polymer film electroneutrality.

Not only is the neutral mass of the film polymerized in a dilute electrolyte solution higher than the one polymerized in a more concentrated electrolyte solution, but the mass changes during the n- and p- doping processes for the former are also higher than in the latter. Film mass increase after being doped can be attributed to three sources: the mass of doping ions, the mass of electrolyte salt possibly accumulated after the redox cycling, and the mass of solvent due to the solvation of the charged film and doping ions. As the electrolyte concentration increases, the film polymerization efficiency increases, and thus more doping ions are in the doped film. Also, the accumulation of electrolyte in the polymer film is expected to occur more readily in a concentrated electrolyte solution. Thus the first two factors tend to increase the mass of the doped film as the concentration of electrolyte solution is increased. The observation that the biggest mass change occurred for a film polymerized and cycled in the least concentrated electrolyte solution clearly indicates that polymer film solvation is the determining factor for the observed mass difference in the three electrolyte solutions.

Table 2 lists the mass content of the PFPT films polymerized in the three electrolyte solutions. For PFPT films the electrolyte solution content (including solvent surrounding the charges in the doped polymer) increases as the concentration of the electrolyte solution is decreased. The fact that the electrolyte solution content for the n-doped film is less than that of a p-doped film also indicates that the negatively charged carriers on the polymer chains and the doping electrolyte cations in the n-doped polymer were less solvated than the positively charged carriers and the doping anions in the p-doped polymer. This important conclusion is affirmed by the dynamic mass change during the potential cycling. The mass of a neutral film (at -0.6 V vs Ag/Ag⁺) increases after p-doping, but decreases after n-doping.

Two-Probe Measurement of Electronic Conductivity

An electrode that consisted of two Pt band (2500x120 mm²) electrodes separated with a gap of 20 µm was prepared according to Shiavon and co-workers to measure in situ the polymer's electronic conductivity at various electrode potentials based on the two-probe principle. In this experiment, polymer film was electrochemically polymerized with a charge density of 0.939 C/cm² to cover the two band electrodes and the gap. The film electronic conductivity was then measured by the dc current that flows between the two electrodes at a 60 mV DC voltage. As compared to the use of microelectrode reported in literature, the band electrode offers certain advantages. Firstly, the electrodes were reusable by gently polishing to renew the surface. Secondly, band electrodes have very low lead resistance (0.1Ω), which allows us to measure high film electronic conductivity. Thirdly, the polymerization process is more reproducible on the band electrodes than on the microelectrodes. The high diffusion rate of oligomers
formed in the vicinity of a microelectrode is sufficiently high, and subsequently, the polymerization rate is low according to the polymerization process discussed in previous section.

Figure 5 shows the equipment and cell configuration used to measure the film electronic conductivity. A DTDP mercury relay switch switched at 1 Hz between the potential control and the conductivity measurement of the polymer film. Both steady current for the cyclic voltammogram and DC current were obtained as shown in Figure 6. The geometry of the polymer in the gap was estimated from the polymerization charge and the electrode geometry, yielding a factor of 0.15 S cm⁻¹ per mA DC current to convert the DC current to the film electronic conductivity. As expected, the polymer film was non-conductive in its neutral state (-1.75 V to 0.65 V). When the film is doped (> 0.60 V for p-doping, and < -1.75 V for n-doping), film electronic conductivity increases rapidly.

Table 3 lists the measured DC currents of p- and n-doped PFPT in six electrolyte solutions. The electronic conductivity of p-doped film is shown here to be electrolyte anion sensitive while that of n-doped film to be electrolyte cation sensitive. From this table the effects of electrolyte on the film electronic conductivity can be arranged in the following series:

For the p-doped film: film conductivity doped with BF₄⁻ > CF₃SO₃⁻ > PF₆⁻ > AsF₆⁻

For the n-doped film: film conductivity doped with Me₄N⁺ > Et₄N⁺ > Bu₄N⁺

Impedance Spectroscopy

The complex phenomena involved in the electrochemistry of conducting polymers have rendered it difficult to extract unambiguous information from impedance data, and even to select an appropriate kinetic model. Some authors have used the model proposed for redox polymers, and metal oxide electrodes to explain their impedance data. In such treatment, the movement of charge balancing ions is assumed to be a diffusion process driven by concentration gradients. Others treat the polymer film as a porous electrode, where ion movement within the polymer matrix is due to migration and is driven by a potential gradient. Discrepancies often arise when comparing results from the two different models.

Current theories of charge transport in electroactive polymer film coated electrodes can be divided into three groups, the redox layer model, the porous electrode model, and the metal oxide electrode model. The metal oxide electrode model was derived by Ho and coworkers in studying lithium (a neutral electroactive species) insertion in tungsten trioxide (conducting and electroactive) thin film electrode. They treated the insertion of lithium in the electrode as driven by diffusion, not by migration.

Mathias and Hass have proposed an impedance model for redox polymer coated electrodes using the modified diffusion/migration equation for electron hopping and the standard Nernst-Planck equations for counterion movement. They have assumed that the redox reaction of the polymer layer starts at the electrode/polymer interface.

Albery and coworkers have also proposed an impedance model for modified electrodes and thin layer cells. From the fundamental transport equations Albery and
coworkers\textsuperscript{146} related electron and counterion charge transport to the transmission line circuit similar to that shown in Figure 7, where $R_{E}$ and $R_{\text{ion}}$ are the distributed polymer electronic and ionic resistances respectively across the polymer thickness. The polymer's capacitance ($C_{P}$), which is also distributed uniformly across the film, has been described by Feldberg\textsuperscript{147} as an indistinguishable combination of a faradaic pseudo capacitance and a double layer capacitance. The current flows across the electrode/polymer interface through the metallic contact, and across the polymer/solution interface through the ionic contact. Albery's model differs from previous work in that the potentials that drive the current through the polymer rail and solution rail of the transmission line are the modified Nernst potential and modified Donnan potential.\textsuperscript{146}

The impedance response of a porous carbon electrode in a sulfuric acid solution, for example\textsuperscript{141}, can be described using the simple model of a single uniform pore. The mathematic form of the impedance response is:\textsuperscript{142}

$$Z = \frac{R_{\text{ion}}}{j\omega C} \cosh \sqrt{j\omega R_{\text{ion}} C}$$

where $R_{\text{ion}}$ is the total ionic resistance in the pore and $C$ the total distributed interfacial capacitance of the pore. The equivalent circuit for this impedance is the simple transmission line shown in Figure 8. The resistive path here represents the slow migration of ions in the pore solution and the zero resistance rail represents the fast electron transport in the electronically conducting electrode material.

Further extensions of the porous electrode model includes the electrode rail resistance ($R_{E}$). The equivalent circuit is then the same as shown in Figure 7\textsuperscript{136, 137, 142}. It can be thought at this point that Albery's redox model derived from a microscopic point of view serves the theoretical explanation for the porous electrode model derived from a macroscopic point of view. The values of $R_{E}$, $R_{\text{ion}}$ and $C_{P}$ can be derived from the experimental impedance data using the following two equations:

$$\frac{1}{R_{\omega}} = \frac{1}{R_{E}} + \frac{1}{R_{\text{ion}}}$$

$$R_{E} = R_{E} + R_{\text{ion}}$$

where $R_{\omega}$ is the high frequency intercept of the 45° Warburg-type region in the complex plane impedance plot minus the uncompensated solution resistance ($R_{s}$), and $R_{s}/3$ is the theoretically constant real impedance at low frequency minus $R_{s}$. However, in almost all reported impedance experiments on conducting polymers, instead of the ideal vertical line for an ideal capacitance response at low frequency, a slightly sloped line has been obtained. The value of ($R_{s} + R_{s}/3$) is thus obtained by extrapolating the experimental data at low frequency to the real axis. Since the impedance data form a characteristic shape in complex impedance plane, most of the data has been analysed using this method.

Figure 9 shows the complex plane impedance plots for PFPT film coated Pt
electrode immersed in 0.2 M \( \text{Et}_4\text{NBF}_4 \) electrolyte solution at electrode potentials ranging from the p-doped state to the n-doped state. From the characteristics of these plots, it was found that when the polymer films are either nearly fully oxidized (at potential > 0.6 V) or nearly fully reduced (at potential < -1.8 V) the rate of charging the polymer is limited by the slow ion transport rate. But in the potential range between -1.5 to 0.2 V, the polymer film shows no electrochemical activity and has a very low electronic conductivity as compared to its ionic conductivity. At the low doping level, a semicircle was observed at high frequency range due to the electron transfer process at the electrode/polymer interface. Albery and Mount have recently included the charge transfer process at the interface.\(^{148, 149}\) A detail impedance study on the charge transfer and transport for a polypyrrole film has also been reported.\(^{150}\)

For the p-doping process (Figure 9 a), increasing the electrode potential increases the polymer’s ionic conductivity. Clearly, the major mobile ionic species in the film at this potential range is the electrolyte anions (\( \text{BF}_4^- \)), whose concentration, and thus the polymer film ionic conductivity, increases as the number of positive charges on the oxidized polymer chains increases.

The ionic resistance of a nearly neutral polymer film (-1.5 V < at potential < 0.2 V, Figure 9c) was found to be in the range of 2.05 to 3.48 \( \Omega \text{cm}^2 \). Even though the polymer film has no electrochemical activity in this potential range, the ionic resistance increases about 70% from 0 V to -1.5 V. This result indicates that the polymer film becomes less solvated after the de-doping process. This conclusion was further supported by the EQCM data during the potential cycles, where a gradual decrease in film mass was observed after the de-doping process (Figure 4).

As the electrode potential is decreased below -1.6 V (Figure 9d), the polymer’s electronic conductivity increases considerably. This is shown by the shift of the high frequency intercept on the real impedance axis of the polymer film coated electrode towards that of the bare Pt electrode. However, at a potential below -1.8 V, the length of the Warburg-type line increases as the electrode potential is decreased, indicating that the resistance of the more resistive line, which is now the ion transport path in the polymer film, increases. Such an increase in the ionic resistance is contrary to the increased number of mobile cations as the polymer film is reduced. This is only possible when the incorporated electrolyte cations (\( \text{Et}_4\text{N}^+ \)) in the polymer film used to compensate the negative charges on the reduced polymer chains are largely immobilized due to forming ion-pairs with the negatively charged polymer chains, and thus contribute little to the polymer film’s ionic conductivity. The solvent and electrolyte transport data from EQCM (Table 2) indeed shows that the p-doped state is more solvated than the n-doped state. In addition, the film after p-dedoping is more solvated than after n-dedoping, as shown by the mass curve in Figure 4, due to the higher solvation state of the p-doped polymer.

Figure 10 shows the variation of the polymer film capacitance with the frequency of potential perturbation. For the p-doped polymer, the frequency at which the charging/discharge process is considered nearly complete is about 1 Hz, while for the n-doped polymer this frequency is about 0.1 Hz. The derived film electronic and ionic conductivities from the impedance data for PFPP film are listed in Table 4. The p- and n-doped polymer film ionic conductivities in various electrolyte solutions are listed in Table 5.

From this table, the effects of electrolytes on the film ionic conductivity can be arranged in the following series:
For the p-doped film: film conductivity doped with $\text{BF}_4^-$ > $\text{CF}_3\text{SO}_3^-$

For the n-doped film: film conductivity doped with $\text{Me}_4\text{N}^+$ > $\text{Et}_4\text{N}^+$ > $\text{Bu}_4\text{N}^+$

These are in good accordance with the two series generated from Table 3, showing the effect of electrolyte on the film electronic conductivity. The observed effects of electrolyte on the electronic and ionic conductivity clearly demonstrate that the mobility of charge carriers in the polymer phase and in the solution phase are related and mutually affected through their formation of ion pairs. The fact that both electronic and ionic conductivities of the p-doped polymer are about one order of magnitude higher than those of the n-doped form also indicates tighter ion-pair formation between the charge carriers in the n-doped polymer.

**Stability during Potential Cycling**

The purpose of this set of experiments was to evaluate the stability of PFPT in various electrolyte solutions. The stability of this and other similar p- and n-dopable conducting polymers has been our concern in making practical type III electrochemical capacitors. For reliable and rapid comparison studies, the polymer films were deposited on the Pt electrode (area=0.0045 cm$^2$) under identical conditions by anodic oxidation of their monomer solution containing 1.0 M Et$_4$NBF$_4$ and 0.1 M PFPT for a deposition charge of 240 mC/cm$^2$. Repeated tests showed that the cyclic voltammograms of these PFPT film covered electrodes were satisfactorily reproducible. Five types of electrolytes (Me$_4$NCF$_3$SO$_3$, Et$_4$NBF$_4$, Et$_4$NPF$_6$, and Bu$_4$NPF$_6$), which cover three types of cations and three types of anions, were used for the continuous potential cycling tests. In each electrolyte solution, the PFPT film-covered electrodes were cycled in three different potential regions, i.e., p-doping only, n-doping only and both p and n-doping regions.

Figure 11 shows the cyclic voltammograms of PFPT in 0.2 M Et$_4$NBF$_4$ solution under continuous cycling in the region covering both p and n doping. The dedoping charges for both p- and n-doped films decreases with increased number of cycles, as shown in Figure 12a. The best film stability was observed when the film was cycled in the p-doping region, and the worst stability when cycled in the n-doping region. The film exhibited varying stability in the five electrolyte solutions chosen here. It seems that the stability of p-doped film is affected by the anions in the solution only, and the n-doped film by the cations. The p-doped films with PF$_6^-$ anions have similar stabilities in Et$_4$NPF$_6$ and But$_4$NPF$_6$, and the n-doped films with Et$_4$N$^+$ cations have similar stabilities in Et$_4$NBF$_4$ and Et$_4$NPF$_6$. The film has the best stability in the p-doped form and worst stability in the n-doped form in Me$_4$NCF$_3$SO$_3$. From these results the effects of electrolyte on film stability can be arranged in following series:

stability of p-doped film with $\text{CF}_3\text{SO}_3^-$ > $\text{BF}_4^-$ > $\text{PF}_6^-$

stability of n-doped film with $\text{Bu}_4\text{N}^+$ > $\text{Et}_4\text{N}^+$ > $\text{Me}_4\text{N}^+$

It may be possible to use electrolytes such as Bu$_4$NCF$_3$SO$_3$ to increase the film stability. However, the use of such an electrolyte can decrease both the film's electronic and ionic conductivities. The above trends of electrolyte effects may result from the various hygroscopic nature of the doping ions, since the polymer film exhibited rapid degradation with added trace amount of water.
Characterization of Type III Ultracapacitors

PFPT type III ultracapacitors were assembled with two identical PFPT coated 1 cm² Torey carbon paper (Spectraorp, 15 mil; 0.28 g cm⁻³) electrodes sandwiching a 20 mil porous separator (Lydall Manning Nonwovens, glass micro fiber). The PFPT on each of the electrode was deposited at a charge density of 10 C/cm² electrode area from 0.1 M FPT monomer solution containing 1.0 M Et₄NBF₄. The capacitor assembly was immersed in a 0.2 M Et₄NBF₄ acetonitrile solution for the impedance measurement and cell charging/discharging test.

Figure 13 shows the cell impedance spectra in the complex impedance plane at selected cell voltages. The cell impedance can be explained based on the equivalent circuit shown in Figure 7 for each electrode with Rₘ representing the ionic resistance of the solution in the separator. At a low cell voltage (<2.0V), both electrodes were in the neutral form, and the intercept of high frequency data on the real axis gives the sum of the ionic resistance of the two polymer films plus the solution in the separator. At 2.2 V cell voltage, both electrodes were doped at a low level and the film exhibited high electronic resistance (Rₖ>>Rₖ). This was shown by the high frequency intercept coinciding with that of the neutral film electrode in the discharged cell. At this voltage, the cell current flows through the less resistive ionic conduction path to charge/dischARGE the first polymer layer at the carbon electrode/polymer interface. As the cell voltage increased above 2.2 V, the film electrode electronic conductivity increased rapidly due to the increased doping level at both electrodes. This is shown in Figure 13 by the shift of the intercept of high frequency data on the real axis to a low value. At a cell voltage >2.6 V, the real axis intercept eventually reaches the minimum value, exhibiting the characteristic feature for the case of Rₖ<<Rₖ. In this case the cell current flows in the polymer film electrode through the less resistive electronic conduction path to charge/dischARGE the first polymer layer at the polymer/electrolyte solution interface. The high frequency intercept on the real axis gives the solution ionic resistance in the separator(Rₖ). As the cell voltage further increases beyond 2.6 V, we observe that the length of Warburg line increases, indicating the increase in cell ionic resistance. Since the Rₖ of p-doped film decreases and Rₖ of n-doped film increases with doping level in the single electrode impedance study, the increase in cell ionic resistance with cell voltage is due to the overwhelming effects of the slow ionic transport in the n-doped film electrode. Table 5 lists the values of Rₖ and Rₖ of the polymer electrode in the capacitor cell extracted from the impedance data.

Table 5 lists the values of Rₖ and Rₖ of the polymer electrode in the capacitor cell extracted from the impedance data.

In Figure 14 the impedance data were plotted for the cell capacitance as a function of charging/discharging frequency. The cell capacitance begins to increase at 2.2 V (as determined Eₚ-Eₙ), and reaches the maximum at about 2.6 V (as determined Eₚ'-Eₙ'). At all cell voltage, a charging/discharging frequency > 0.1 Hz is not sufficiently low to reach the total cell capacitance.

The PFPT cell was also tested for the charging/discharging capacitance on a Maccor battery tester. Figure 15 shows the cell capacitance as a function of the charging/discharging current density. The cell capacitance decreased rapidly as the charging/discharging current increases. The total cell capacitance, estimated from the deposition charge of the polymer film and the polymerization efficiency, was 0.84 F cm⁻². Figure 16 shows the cell power density as a function of cell energy density from the data shown in Figure 15. For comparison, data for a Type 1 polyaniline cell charged to 0.75 V in 2.0 M HBF₄ (aq) were also plotted. The PFPT cell performance confirms our
expectation for the high energy density and power density of the type III capacitor. Further improvements in cell performance can be achieved by decreasing $R_e$ using more concentrated electrolyte solution. A decrease in $R_e$ can also be achieved using high surface area carbon paper to decrease the polymer film thickness. Above all, for practical applications, increasing the cell stability beyond 10,000 cycles remains a crucial issue to be solved.

**CONCLUSIONS**

The EQCM studies on the electrochemical polymerization of FPT show the formation of soluble oligomers prior to their precipitation to form the polymer film on a substrate electrode. By increasing electrolyte concentration in the monomer solution, the polymerization efficiency increases and the porosity of the polymer decreases.

The mass changes during a cyclic voltammetric study using EQCM show that the oxidation of PFPT is accompanied with the insertion of electrolyte anions and the reduction is accompanied with the insertion of electrolyte cations. Also, the p-doped film is more extensively solvated than the n-doped film, indicating formation of tighter ion-pairs between the negative charges on the polymer chains and the doping electrolyte cations in the n-doped film.

Ionic conductivity of PFPT measurements with impedance spectroscopy show that the ionic conductivity of p-doped film increases with the doping level, and that of n-doped film decreases with the doping level. This again indicates that the slow mobility of counterions in the n-doped film is due to strong ion-pair formation. From the film ionic conductivities measured in various electrolyte solutions, the following series were obtained: ionic conductivity of p-doped film with $\text{BF}_4^-$ > $\text{CF}_3\text{SO}_3^-$; ionic conductivity of n-doped film with $\text{Me}_4\text{N}^+$ > $\text{Et}_4\text{N}^+$ > $\text{Bu}_4\text{N}^+$.

Electronic conductivities of PFPT measured with dual band electrodes show very low conductivity in the neutral form. Doping the film causes rapid increase in film electronic conductivity. Both electronic and ionic conductivities of p-doped film are about one order of magnitude higher than those of n-doped film. This is a strong indication that in the n-doped polymer, the mobilities of the charge carriers in the polymer (polarons or bipolarons) and in the pore solution (doping electrolyte cations) are mutually hindered due to their formation of tighter ion-pairs. From the film electronic conductivities measured in various electrolyte solutions, the following series were obtained: electronic conductivity of p-doped film with $\text{BF}_4^-$ > $\text{CF}_3\text{SO}_3^-$ > $\text{PF}_6^-$ > $\text{AsF}_6^-$; electronic conductivity of n-doped film with $\text{Me}_4\text{N}^+$ > $\text{Et}_4\text{N}^+$ > $\text{Bu}_4\text{N}^+$.

The fact that the doping electrolyte ions have the same effects on the film’s electronic and ionic conductivities, again, manifests the nature of ion pairs formed between the charge carriers in the polymer phase and those in the pore solution phase.

The film stability during continuous potential cycling in various electrolyte solutions shows that the film had higher stability in p-doping/dedoping cycles than in n-doping/de-doping cycles. Film stability is only sensitive to the electrolyte anions in the p-doping/dedoping cycles, and to the electrolyte cations in the n-doping/dedoping cycles. The following two series were found:
film stability of p-doped film with CF$_3$SO$_3^-$$>$BF$_4^-$$>$PF$_6^-$$>$
cum

This suggests that enhanced film stability could be observed in electrolyte containing both
large cations and anions, such as Bu$_4$NCF$_3$SO$_3$. However, the film doped in such
electrolyte would exhibit decreased electronic and ionic conductivities for both p- and n-
doped forms.

Preliminary characterization of the type III ultracapacitor based on PFPT coated
carbon paper electrode confirmed the high performance expected for such a device. A high
power density of 10 kw/kg and a energy density of 47 whr/kg were obtained with 1 cm$^2$
test cell. However, for practical application, further improvements in film stability and
conductivity, especially for the n-doped form, are required.

ACKNOWLEDGMENTS

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Table 1. Monomer oxidation potentials and the polymer’s formal potentials for the n-doping (E‘n) and p-doping (E‘p) processes in a 0.2 M Et4NBF4 acetonitrile solution.

<table>
<thead>
<tr>
<th>-X</th>
<th>Eox, m</th>
<th>E‘n</th>
<th>E‘p</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V vs. Ag+/Ag</td>
<td>V vs. Ag+/Ag</td>
<td>V vs. Ag+/Ag</td>
</tr>
<tr>
<td>OCH3</td>
<td>0.804</td>
<td>-2.088</td>
<td>0.626</td>
</tr>
<tr>
<td>CH3</td>
<td>0.928</td>
<td>-2.044</td>
<td>0.640</td>
</tr>
<tr>
<td>t-Bu</td>
<td>0.943</td>
<td>-2.047</td>
<td>0.676</td>
</tr>
<tr>
<td>H</td>
<td>0.991</td>
<td>-1.954</td>
<td>0.706</td>
</tr>
<tr>
<td>CF3</td>
<td>1.016</td>
<td>-1.937</td>
<td>0.792</td>
</tr>
<tr>
<td>F</td>
<td>1.024</td>
<td>-1.968</td>
<td>0.697</td>
</tr>
<tr>
<td>Cl</td>
<td>1.042</td>
<td>-1.919</td>
<td>0.770</td>
</tr>
<tr>
<td>Br</td>
<td>1.076</td>
<td>-2.033</td>
<td>0.694</td>
</tr>
<tr>
<td>SO2CH3</td>
<td>1.117</td>
<td>-1.894</td>
<td>0.740</td>
</tr>
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</table>

Table 2. Mass transport of counterion and electrolyte solution in PFPT films at selected electrode potentials determined with EQCM.

<table>
<thead>
<tr>
<th>Electrolyte conc. / mol dm⁻³</th>
<th>0.2</th>
<th>1.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry film mass/ mg Poly. efficiency</td>
<td>26.04</td>
<td>27.56</td>
<td>28.88</td>
</tr>
<tr>
<td>Poly. efficiency</td>
<td>65.8%</td>
<td>68.6± 2.0%</td>
<td>72.9%</td>
</tr>
</tbody>
</table>
(Table 2 continued)

<table>
<thead>
<tr>
<th>Electrode potential / V</th>
<th>Film mass during potential cycling at 10 mV s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total mass / mg</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>39.5</td>
</tr>
<tr>
<td>b</td>
<td>49.1</td>
</tr>
<tr>
<td>c</td>
<td>51.6</td>
</tr>
<tr>
<td>d</td>
<td>64.3</td>
</tr>
<tr>
<td>Dopant-ion / mg</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>2.66</td>
</tr>
<tr>
<td>b</td>
<td>-</td>
</tr>
<tr>
<td>c</td>
<td>-</td>
</tr>
<tr>
<td>d</td>
<td>2.3</td>
</tr>
<tr>
<td>Electrolyte + Solvent / mg</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>30.8</td>
</tr>
<tr>
<td>b</td>
<td>23.0</td>
</tr>
<tr>
<td>c</td>
<td>25.5</td>
</tr>
<tr>
<td>d</td>
<td>35.9</td>
</tr>
</tbody>
</table>

- Neutral film mass after n-doping.
- Neutral film mass after p-doping.

Table 3. Electronic and ionic conductivities of PFPT film in a 0.2 M Et₄NBF₄ solution measured from impedance and two-probe measurements.

<table>
<thead>
<tr>
<th>Potential V vs Ag⁺/Ag</th>
<th>R∞ Ω cm⁻²</th>
<th>RΣ/3 Ω cm⁻²</th>
<th>R离子 Ω cm⁻²</th>
<th>Rₑ Ω cm⁻²</th>
<th>σ_ionic μS cm⁻¹</th>
<th>σₑ μS cm⁻¹</th>
<th>two-probe σₑ μS cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.0</td>
<td>6.35</td>
<td>19.0 a</td>
<td>. a</td>
<td>10.5</td>
<td>high</td>
<td>9.6x10⁴</td>
<td></td>
</tr>
<tr>
<td>-1.9</td>
<td>1.55</td>
<td>4.64 a</td>
<td>. a</td>
<td>43.0</td>
<td></td>
<td>1.6x10⁴</td>
<td></td>
</tr>
<tr>
<td>-1.8</td>
<td>0.38</td>
<td>0.99</td>
<td>0.45 b</td>
<td>99.5</td>
<td>563</td>
<td>960</td>
<td></td>
</tr>
<tr>
<td>-1.6</td>
<td>3.67 c</td>
<td>2.51 b</td>
<td>180 c</td>
<td>68.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1.5</td>
<td>3.45</td>
<td>3.45 d</td>
<td>. d</td>
<td>72.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1.0</td>
<td>3.39</td>
<td>3.39 d</td>
<td>. d</td>
<td>73.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.8</td>
<td>2.94</td>
<td>2.94 d</td>
<td>. d</td>
<td>85.0</td>
<td>low</td>
<td>&lt;8x10⁻²</td>
<td></td>
</tr>
<tr>
<td>-0.5</td>
<td>2.12</td>
<td>2.12 d</td>
<td>. d</td>
<td>118</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>2.05</td>
<td>2.05 d</td>
<td>. d</td>
<td>122</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>1.57 c</td>
<td>66.3 c</td>
<td>159</td>
<td>3.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.16</td>
<td>0.470</td>
<td>0.18 b</td>
<td>203</td>
<td>1.39x10³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>0.319</td>
<td>0.957 a</td>
<td>. a</td>
<td>260</td>
<td></td>
<td>3.4x10³</td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>0.250</td>
<td>0.762 a</td>
<td>. a</td>
<td>328</td>
<td></td>
<td>3.6x10⁴</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>0.210</td>
<td>0.642 a</td>
<td>. a</td>
<td>390</td>
<td></td>
<td>6.1x10⁵</td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>0.190</td>
<td>0.564 a</td>
<td>. a</td>
<td>443</td>
<td>high</td>
<td>1.6x10⁶</td>
<td></td>
</tr>
</tbody>
</table>

a Film exhibits high electronic conductivity. The film ionic conductivity was calculated using the porous metal electrode model.
b Conductivities were calculated according to the dual transmission line model.
c Conductivities were obtained by fitting the impedance data to the dual transmission line model with charge transfer process at the Pt/polymer film interface.
d Film exhibits low electronic conductivity and is electrochemically inactive.
Table 3. Maximum dc current for p- and n- doped PFPT in 0.2 M electrolyte acetonitrile solution at a 60 mV dc voltage across the two band electrodes connected by the film.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>p-doped film / mA</th>
<th>n-doped film / mA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₄NCF₃SO₃</td>
<td>8.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Et₄NCF₃SO₃</td>
<td>7.6</td>
<td>0.65</td>
</tr>
<tr>
<td>Et₄NBF₄</td>
<td>10.5</td>
<td>0.64</td>
</tr>
<tr>
<td>Bu₄NBF₄</td>
<td>10.5</td>
<td>0.29</td>
</tr>
<tr>
<td>KPF₆</td>
<td>7.0</td>
<td>-</td>
</tr>
<tr>
<td>KAsF₆</td>
<td>6.6</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4. Ionic conductivity of PFPT film in various electrolyte solutions.

<table>
<thead>
<tr>
<th>Electrode Potential V</th>
<th>Bu₄NBF₄ Ionic Conductivity / μS cm⁻¹</th>
<th>Et₄NBF₄ Ionic Conductivity / μS cm⁻¹</th>
<th>Me₄NCF₃SO₃ Ionic Conductivity / μS cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.0</td>
<td>3.1</td>
<td>10.5</td>
<td>61.4</td>
</tr>
<tr>
<td>-1.9</td>
<td>8.0</td>
<td>43.0</td>
<td>102</td>
</tr>
<tr>
<td>-1.8</td>
<td>16.8</td>
<td>99.5</td>
<td>116</td>
</tr>
<tr>
<td>0.6</td>
<td>224</td>
<td>260</td>
<td>182</td>
</tr>
<tr>
<td>0.7</td>
<td>272</td>
<td>328</td>
<td>211</td>
</tr>
<tr>
<td>0.8</td>
<td>329</td>
<td>390</td>
<td>227</td>
</tr>
<tr>
<td>0.9</td>
<td>392</td>
<td>443</td>
<td>260</td>
</tr>
</tbody>
</table>

Table 5. Derived electronic resistance and ionic resistance of polymer electrode from the impedance spectra of a PFPT capacitor submerged in a 0.2 M Et₄NBF₄ acetonitrile solutions.

<table>
<thead>
<tr>
<th>Cell volt V</th>
<th>R_e</th>
<th>R_{low}</th>
<th>R_{ion}</th>
<th>R_{ion}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ω cm²</td>
<td>Ω cm²</td>
<td>Ω cm²</td>
<td>Ω cm²</td>
</tr>
<tr>
<td>0.0</td>
<td>3.5</td>
<td>-</td>
<td>1.07</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>3.5</td>
<td>-</td>
<td>1.07</td>
<td>-</td>
</tr>
<tr>
<td>2.0</td>
<td>3.5</td>
<td>-</td>
<td>1.07</td>
<td>&gt;&gt; R_{ion}</td>
</tr>
<tr>
<td>2.2</td>
<td>2.25</td>
<td>3.75</td>
<td>358</td>
<td>0.52</td>
</tr>
<tr>
<td>2.4</td>
<td>1.63</td>
<td>3.50</td>
<td>3.20</td>
<td>0.13</td>
</tr>
<tr>
<td>2.6</td>
<td>1.37</td>
<td>4.0</td>
<td>3.95</td>
<td>&lt;&lt; R_{ion}</td>
</tr>
<tr>
<td>2.8</td>
<td>1.37</td>
<td>4.8</td>
<td>5.15</td>
<td>&lt;&lt; R_{ion}</td>
</tr>
<tr>
<td>3.0</td>
<td>1.37</td>
<td>5.0</td>
<td>5.45</td>
<td>&lt;&lt; R_{ion}</td>
</tr>
</tbody>
</table>

R_e = 1.37 Ω cm², R_{low} was estimated from the R_{total} at 0.1 Hz
Figure 1. Plot of the oxidation potential $s$ of the monomers against Hammett constants for the para position ($\sigma_p$).

Figure 2. Plots of the formal potentials of the polymer oxidation (square points) and reduction (circle points) against Hammett constants for the para position ($\sigma_p$).
Figure 3. Electrode potential and mass changes (part B) during the polymerization and the immediate discharge processes at constant currents (part A) in 2.0 M (a), 1.0 M(b) and 0.2 M(c) Et₄NBF₄ acetonitrile solutions.

Figure 4. Cyclic voltammograms and mass changes for PFPT films polymerized and cycled in 2.0 M (a), 1.0 M(b) and 0.2 M(c) Et₄NBF₄ acetonitrile solutions at a scan rate of 10 mV s⁻¹.

Figure 5. Equipment and cell configuration for measuring in situ film electronic resistance using two probe principle.
Figure 6. Cyclic voltammogram and DC current across the dual band electrodes at 60 mV voltage for a PFPT film coated dual band electrode in 0.2 M Et$_4$NCF$_3$SO$_3$ acetonitrile solution at a scan rate of 10 mV s$^{-1}$.

Figure 7. Albery's dual rail transmission line circuit. $R_s$ is uncompensated bulk electrolyte solution resistance.

Figure 8. Equivalent circuit for polymer film coated electrode according to the porous metal electrode model. $R_s$ is uncompensated bulk electrolyte solution resistance.
Figure 9. Complex plane impedance spectra of the bare Pt electrode (at the open circuit potential) and the PFP film coated Pt electrode at selected electrode potentials in a 0.2 M Et$_4$NBF$_4$ electrolyte solution.
Figure 10. PFPT film capacitance as a function of charging/discharging frequency for the impedance data shown in Figure 9.

Figure 11. Cyclic voltammograms of a PFPT film coated electrode in 0.2 M Et₄NBF₄ acetonitrile solutions at the 1st, 10th, 30th, 50th, 100th cycles.
Figure 12. Plots of the de-doping charges against the number of continuous cycles in 0.2 M Et₄NBF₄ (a), 0.2 M Et₄NPF₆ (b), 0.2 M Bu₄NPF₆ and 0.2 M Me₄NCF₃SO₃ acetonitrile solutions. Symbols on the curves are x-- cathodic charge of p-doped polymer cycled in p-doping/de-doping region; Δ--- and --- the cathodic charge of p-doped polymer and the anodic charge of n-doped polymer when cycled in p- and n-doping/de-doping region; and ⧫--- anodic charge of n-doped polymer cycled in n-doping/de-doping region.
Figure 13. Complex plane impedance spectra of 1 cm² PFPT capacitor test cell at selected cell voltages in a 0.2 M Et₄NBF₄ acetonitrile solution.

Figure 14. Plots of PFPT cell capacitance as a function of charging/discharging frequency for the impedance data shown in Figure 13.

Figure 15. Capacitance of 1 cm² PFPT capacitor as a function of discharge current density.

Figure 16. Plot of cell power density against cell energy density for PFPT capacitor from the discharge data in Figure 13. Data for polyaniline Type I were shown for comparison.
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