Charge- and Ion-Transport Properties of Polypyrrole/Poly(styrenesulfonate):Poly(3-octylthiophene) Bilayers

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The electrochemical, electronic, charge-transport, and ion-transport properties of a conducting polymer bilayer, prepared using polypyrrole/poly(styrenesulfonate) (PP/PSS) and poly(3–octylthiophene) (POT) have been investigated by cyclic voltammetry, optoelectrochemistry, and a combination of electrochemical and gravimetric techniques using the electrochemical quartz crystal microbalance (EQCM). This PP/PSS:POT bilayer presents separate redox switching potentials demonstrating that charge is efficiently transferred through the inner PP/PSS layer to the POT outer layer. While the bilayer exhibits reversible redox processes for both components during rapidly repeated cyclic voltammetric scans, poising the potential at a highly reducing value (−1.2 V vs Ag/Ag$^+$) for a sufficient time prior to starting a potential scan severely limited the redox processes of the PP/PSS inner layer. This is most likely due to inhibited counterion transport through the neutral POT outer layer.

Introduction

One of the unique aspects of conducting polymers is their ability to be redox switched between the doped (conducting) and undoped (insulating) states. The electrochemical switching of a conducting polymer involves transport of both electrons and ions (often along with solvent) in and out of the film. The dominant ionic species responsible for the ion-transport mechanism can be either anions or cations depending on polymer–ion interactions. These interactions can be controlled by judicious choice of the charge balancing dopant anion used during electrosynthesis or by changing the electrolyte solutions used during redox cycling.[1–3] For example, in contrast to polypyrrole doped with small anions, where the anions tend to dominate transport during switching, cation-dominated transport occurs in polypyrrole films when large, immobile, multianions and polyelectrolytes (such as poly(styrenesulfonate)) are used as the electrolyte during electrochemical synthesis.[4,5] Many of the present and potential applications of conducting polymers, such as electrochemically controllable ion-transport membranes or drug-delivery devices, will perform in an optimal manner with specific ion transport. As such, it is important to develop a detailed understanding of the ion flux properties of these materials during redox switching and to utilize these properties in creating new electrode structures with engineered ion-transport properties.

In developing conducting polymer modified electrodes for redox switching and ion-transport applications, it would be useful to have separate redox processes at which different ions are the dominant mobile species. This would be accomplished with conducting polymer bilayers where the components have well-separated oxidation potentials and opposite ion-transport characteristics. The concept of polymeric bilayer electrodes, a sequence of two electroactive polymer films on a conducting electrode, was first introduced by Murray et al.,[6–8] using redox polymers. These systems have been of interest since the polymer/polymer heterojunction may serve as a charge-trapping interface when the inner film's redox chemistry occurs at a potential lower than that of the outer film.[7,8] The charge-trapping concept was extended to bilayer and multilayer electrodes with junctions between a redox polymer and an electronically conducting polymer and between two conducting polymers.[9–14]

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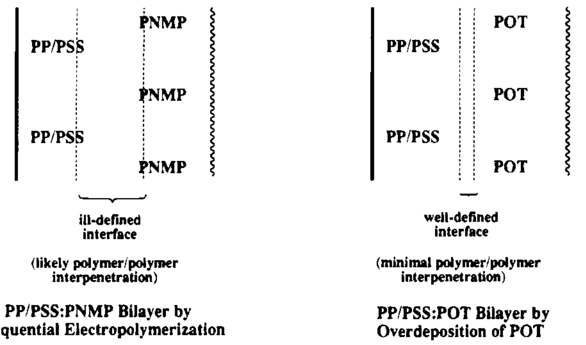
Scheme 1



We have shown that a conducting bilayer, where the inner-film redox chemistry occurs at a lower potential than the outer film, prepared by sequential electropolymerization methods using polypyrrole/poly(styrenesulfonate) and poly(*N*-methylpyrrole chloride) (PNMP-Cl), has separate redox switching potentials and electrode-potential-dependent dual-ion-transport behavior.[15a] This bilayer exhibits cation-dominated transport at low potential and anion-dominated transport at high potential. A drawback to the sequential electropolymerization method is that, after initial formation of a swollen inner conducting polymer layer, the second monomer can penetrate the film and be partially electropolymerized within the first layer. This leads to an ill-defined and difficult to characterize interface between the polymers as illustrated in Scheme 1. The utilization of soluble, high molecular weight, conducting or electroactive polymer, solution cast over the inner layer will provide a more definitive interface. As an example of a nonelectronically conducting electroactive polymer overlayer, we have recently utilized poly(vinylferrocene) (PVFc) in a PP/PSS:PVFc bilayer which shows distinct dual-ion-transport properties.[15b]

The development of poly(3-alkylthiophenes) as a broad class of soluble conducting polymers that can be electrochemically switched suggests they may be useful in bilayer structures. As with PVFc, the ability to solution coat the high molecular weight polymer as an outer film provides the opportunity for bilayers with distinct interfaces. In this paper, we describe the electrochemical and electronic characteristics, as well as the charge- and ion-transport properties, of a conducting polymer bilayer which consists of a PP/PSS inner film and a poly(3-octylthiophene) (POT) outer film. In the course of this work, the cyclic voltammetric behavior of a poly(pyrrole tetrafluoroborate):poly(3-octylthiophene tetrafluoroborate) bilayer, prepared using sequential electropolymerization of the two monomers, has been reported[14a] and its properties are compared to the bilayer properties for the system investigated here.

Experimental Section

Reagents. Pyrrole (Aldrich Chemical) was purified immediately before use by passing it through a microcolumn constructed from a Pasteur pipet, glass wool, and activated alumina. This procedure was repeated until a colorless liquid was obtained. Poly(sodium 4-styrenesulfonate) (Aldrich Chemical, NaPSS) was dialyzed for 48 h using Spectra/POR membranes, MWCO:3500, prior to use. Lithium perchlorate (Aldrich Chemical) was used as received. The water used in the experiments was double distilled. Acetonitrile (CH_3CN) and chloroform ($CHCl_3$) were purchased from Fisher Scientific, and the CH_3CN was distilled over P_2O_5 under nitrogen prior to use.

Preparation of Polymer and Bilayer Films. The electrosyntheses of polypyrrole/poly(styrenesulfonate) films were carried out in aqueous solutions of 0.1 M pyrrole and 0.1 M NaPSS. The electrolyte/monomer solutions were purged with argon prior to use and experiments carried out under an argon blanket. Polymer films were synthesized potentiostatically at +0.8 V vs Ag/AgCl reference electrode. The thickness of the PP/PSS films was controlled by the amount of charge consumed for the electropolymerization. A linear relationship between the thickness of the PP/PSS films and the deposition charge has been reported with 240 mC cm^{-2} charge density yielding a 1 μm film of PP/PSS.[16] Typical thicknesses were between 300 and 500 nm. The films were washed thoroughly with double distilled water to remove excess monomer. Poly(3-octylthiophene) was chemically prepared using anhydrous $FeCl_3$ in $CHCl_3$ described previously.[17] POT films (density = 1.07 g cm^{-3}) of thickness varying between 200 and 500 nm, were obtained by casting from chloroform solutions. The thickness of the POT films was determined using the mass of POT deposited over a specific area of working electrode. The bilayers with PP/PSS as inner film and POT as outer film were prepared by first electropolymerizing 0.1 M pyrrole in 0.1 M NaPSS(aq) at +0.8V vs Ag/AgCl. The PP/PSS film was washed with double distilled water and allowed to dry at ambient temperature. Subsequently, a POT film was cast from a chloroform solution on the top of the PP/PSS film.

Characterization of Polymer and Bilayer Films. Cyclic voltammetry was carried out using an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat, employing a 0.5 cm^2 Pt or a 5 cm × 0.7 cm indium tin oxide (ITO) conducting glass (40 Ω/square, Delta Technologies) working electrode, a Pt-plate counter electrode, and a Ag/Ag^+ reference electrode. The electrolyte was $LiClO_4$ (0.1 M) in CH_3CN. All electrochemical experiments were carried out at room temperature under an argon atmosphere. PP/PSS was electrochemically synthesized onto indium tin oxide (ITO) glass using the constant-potential conditions described above. POT films were cast either directly onto ITO conducting glass or on the top of a PP/PSS film to construct a bilayer. The ITO supported films were placed in a cuvette with a Pt counter electrode and silver wire quasi-reference. The silver wire was used as a quasi-reference in in situ applications due to size limitations. In our experimental conditions, the potential of the Ag wire was calibrated to be −0.2 V vs Ag/Ag^+. The supporting electrolyte was $LiClO_4$ (0.1 M) in CH_3CN. The electronic properties were examined using a Varian Cary 5E UV−vis−NIR spectrophotometer. Electrode potentials were controlled using the EG&G potentiostat/glavanostat. The electrochemical quartz crystal microbalance (EQCM) system was used to monitor mass changes associated with the redox processes of the conductive polymers under investigation by monitoring the change in the resonant frequency of an oscillating quartz crystal. An AT-cut quartz crystal, with gold "keyhole" electrodes, was used as an oscillator and working electrode. A Pt counter electrode and Ag/Ag^+ reference electrode were employed in the electrochemical cell. Details of the EQCM system and its application to charge- and ion-transport properties of

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conducting polymers have been described elsewhere.[1,2,4,18,19] A JEOL JSM-6400 scanning electron microscope was used to examine PP/PSS film surfaces under an applied voltage of 5 keV. PP/PSS films were electrochemically synthesized onto indium tin oxide (ITO) glass and analyzed without conducting overcoating since the specimens were sufficiently conducting to avoid charging effects caused by electron irradiation.

Results and Discussion

Bilayer Structure. To elucidate the redox switching induced charge and ion transport of a conducting polymer bilayer, it is first necessary to understand the contributions of the separate components. When the bilayer is constructed with the most easily oxidized polymer as the inner layer, and the oxidized inner layer serves only as an electron-transfer layer to access the outer layer, the electrochemical response of the bilayer should be the sum of the single-layer contributions. When the bilayer is constructed with the most easily oxidized polymer as the outer layer, charge trapping is possible as noted earlier. Since the charge-trapping phenomenon isolates the electrochemistry of the outer film and it is our desire to have both films easily accessible in ion supply devices, we have focused our study on the former example.

To confirm that PP/PSS overcoated with POT form true bilayer structures, PP/PSS film surfaces were examined by scanning electron microscopy (SEM). PP/PSS films, 300 and 500 nm in thickness, were electrosynthesized on ITO-coated glass. The analysis by SEM reveals that the PP/PSS films form a continuous electrode coating for both thicknesses and prevent direct contact of POT outer film with the underlying electrode. It was also observed that the morphology of PP/PSS film surface changes from a smooth compact structure to a slightly more disordered morphology as the film thickness increases.

Cyclic Voltammetry. The electrochemical properties of PP/PSS, POT, and PP/PSS:POT bilayer films were characterized by cyclic voltammetry. All potentials are reported relative to the Ag/Ag$^+$ reference electrode and were carried out in 0.1 M LiClO$_4$/CH$_3$CN solutions. PP/PSS film was repeatedly scanned between -1.3 and -0.1 V at a scan rate of 50 mV/s until the current response was stable. This "break-in period" is typically used to equilibrate the ion-transport properties and morphology of the films. The film was then scanned progressively to more anodic potentials (up to $+0.7$ V) as shown in Figure 1. PP/PSS is electroactive with an anodic peak E_{pa} at -0.25 V. The anodic response of PP/PSS is stable up to $+0.3$ V while the cathodic current response increases with increased switching potential. This is as expected since scanning to higher oxidative potentials creates a more highly doped polymer and yields more undoping current. Scanning beyond $+0.3$ V leads to the development of a second anodic response as evident by the upswing of the current. The increase of the cathodic peak current stops (no further dopant sites are created) and the peak current of the initial anodic response decreases with increased switching potential. This instability of the redox switching is important as the overlayer polymer of the bilayer will have a higher redox potential than the inner film and overoxidative degradation must be avoided. A scan rate dependence study with switching potentials of -1.3 and -0.1 V showed that both the anodic and cathodic current peaks scale linearly with scan rate, as expected for an electrode with surface-bound electroactive sites.

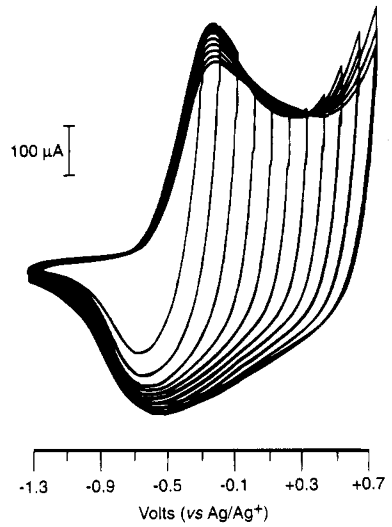

Figure 1. Cyclic voltammograms of PP/PSS film (~500 nm thick) recorded in 0.1 M LiClO$_4$/CH$_3$CN at a scan rate of 50 mV/s.

A similar study of the electroactivity of POT alone was accomplished by scanning the potential between -0.5 and $+0.9$ V. Within this range of potentials, the POT is quite stable and can be repeatedly redox switched without any loss of electroactivity. The anodic and cathodic peaks appear respectively at $+0.7$ and $+0.5$ V at a scan rate of 50 mV/s. As shown in Figure 2, the current peaks scale linearly with the scan rate.

After investigating the redox properties of each polymer film alone, the bilayer structure was probed by scanning PP/PSS:POT between -1.3 and $+0.9$ V. After stabilization of the current signal with 10 scans, the scan rate dependence of the CV was investigated as shown in Figure 3. Two redox waves clearly appear on the CV, corresponding respectively to PP/PSS and POT oxidation and reduction. Comparing Figure 3 to Figures 1 and 2, the bilayer exhibits the expected summation of the two components with peaks found at the same potentials. The outer layer does not attenuate the current response from the inner layer as evidenced by a range of anodic peak currents ($i_{p,a}$) of 370–440 µA for PP/PSS (500 nm, 50 mV/S) alone during multiple scanning relative to an $i_{p,a}$ of 425 µA for the PP/PSS in the bilayer as seen in Figure 3a. Again the peak currents all scale with the scan rate as expected. This demonstrates that the charge transfer to the outer layer is well mediated by the inner layer. Scheme 2 illustrates the successive redox processes occurring in a PP/PSS:POT bilayer during a potential scan. It is evident that there are three distinct redox states for the bilayer: fully neutral, inner layer oxidized with outer layer neutral, and fully oxidized. The ion-transport characteristics noted will be detailed later. The PP/PSS:POT bilayer can be cycled repeatedly between oxidized and neutral states with only a slight loss of the material electroactivity. To determine the extent of this stability, the PP/PSS:POT bilayer CV was recorded just after

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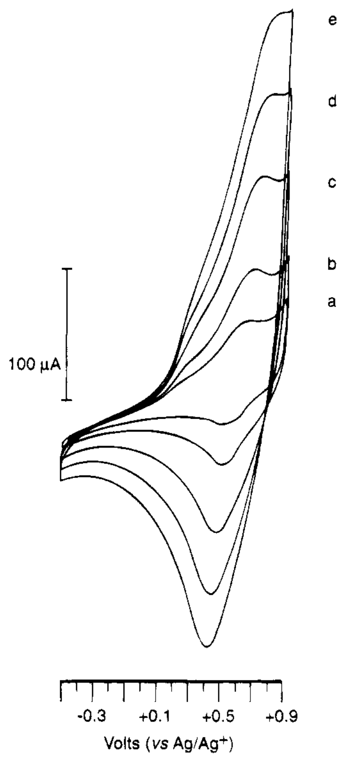


Figure 2. Cyclic voltammograms of POT film (~200 nm thick) recorded in 0.1 M $LiClO_4/CH_3CN$ as a function of scan rate: (a), 25, (b) 50, (c) 100, (d) 150, and (e) 200 mV/s.

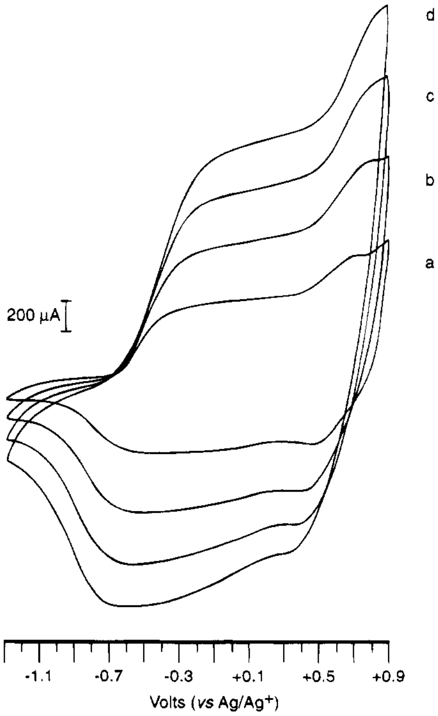
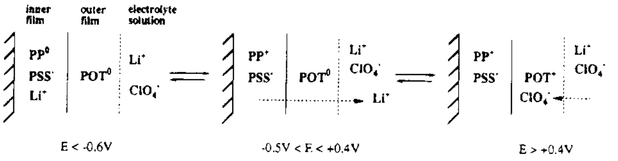


Figure 3. Cyclic voltammograms of PP/PSS:POT bilayer (~500 nm PP/PSS, 400 nm POT) recorded in 0.1 M $LiClO_4/CH_3CN$ as a function of scan rate: (a) 50, (b) 100, (c) 150, and (d) 200 mV/s.

Scheme 2



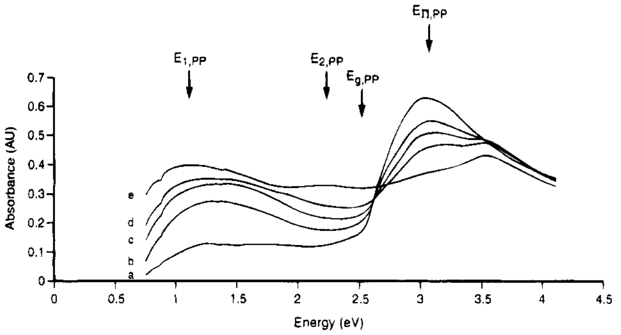


Figure 4. Optoelectrochemical spectra of PP/PSS (~400 nm thick) as a function of applied potential: (a) −1.3, (b) −0.9, (c) −0.5, (d) −0.3, and (e) −0.1 V.

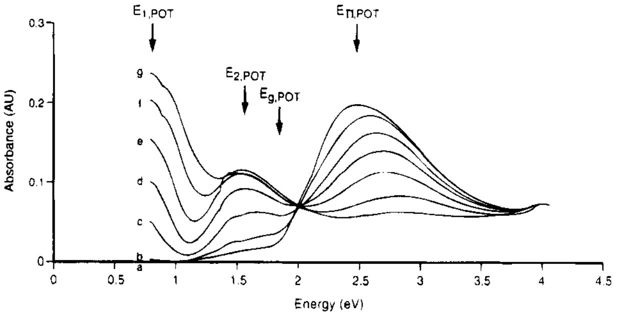


Figure 5. Optoelectrochemical spectra of POT (~250 nm thick) as a function of applied potential: (a) 0.0, (b) +0.5, (c) +0.6, (d) +0.7, (e) +0.8, (f) +0.9, and (g) +1.0 V.

stabilization of the current signal and the peak currents determined. After 60 more scans at a scan rate of 50 mV/s the peak currents decreased by only 15%, which shows that the bilayer is relatively stable. While these experiments demonstrate the coelectroactivity of the bilayer, they yield no information on either the electronic properties nor on the ion transport. Therefore, subsequent optoelectrochemistry and microgravimetric analyses were carried out.

Electronic Spectroscopy. Optoelectrochemical analysis of thin films of conjugated polymers allows their electronic states to be probed in situ during electrochemical oxidation and reduction.[20] The optoelectrochemical properties of PP/PSS, POT, and PP/PSS: POT bilayer films in the undoped and doped states have been studied as shown in Figures 4−6. Figure 4 shows a series of absorption spectra recorded during the oxidation of neutral PP/PSS film (~400 nm thick) on ITO conducting glass at different applied potentials. At −1.3 V, only a $\pi-\pi^*$ transition ($E_{\pi,\mathrm{PP}}$) is observed at 3.1 eV, as expected for neutral polypyrrole. Oxidation of the polymer results in the emergence of two new optical absorptions: first a broad band between 0.8 and 1.5 eV ($E_{1,\mathrm{PP}}$) and later a weak absorption evolving between 2 and 2.5 eV ($E_{2,\mathrm{PP}}$), due to the formation of two bipolaron bands. The decay and shift of the $\pi-\pi^*$ transition ($E_{\pi,\mathrm{PP}}$) to higher energies accompanies the emergence of these two new absorption bands. An electronic bandgap ($E_{\mathrm{g,pp}}$) for the polymer, as determined by the onset of the π,π^* transition, is observed at 2.5−2.6 eV, and a distinct isosbestic point is evident as doping is

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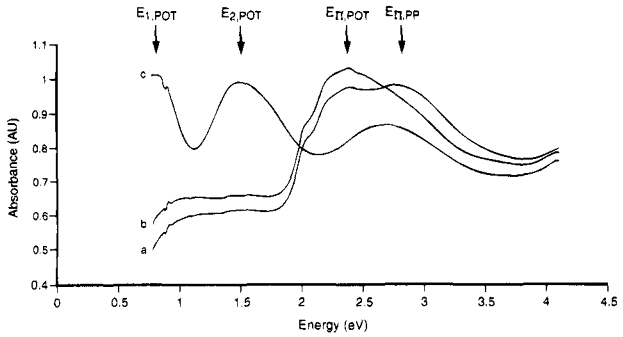

Figure 6. Optoelectrochemical spectra of PP/PSS:POT (~300 nm PP/PSS, 500 nm POT) as a function of applied potential: (a) −1.3, (b) 0.0, and (c) +0.7 V.

carried out. This isosbestic point indicates that dopant sites are created with loss of neutral sites and that the doping is reversible.

The in situ absorption spectra of POT (~250 nm thick) recorded at a series of increasing applied potentials are presented in Figure 5 and are similar in nature to those observed for PP/PSS. With an applied potential of 0.0 V, only the interband transition ($E_{\pi,\mathrm{POT}}$) peaking at 2.5 eV is observed. At intermediate stages of oxidation, additional peaks appeared below 0.7 eV ($E_{1,\mathrm{POT}}$) and at about 1.5 eV ($E_{2,\mathrm{POT}}$) within the gap region. These two absorption bands are again due to the existence of bipolaron levels.[21,22] As the doping proceeds, the intensity of the interband absorption decreases continuously and its absorption maximum shifts to higher energy due to the fact that the bipolaron states coming in the gap are taken from the valence band and conducting band edges. This evolution of the absorption spectrum for POT upon electrochemical doping is in full agreement with the optical data on poly(thiophene) derivatives reported by other groups.[23,24] Using the onset of the absorption, a bandgap ($E_{g,\mathrm{POT}}$) of 1.8−1.9 eV is determined.

Figure 6 shows the in situ absorption spectra of a PP/PSS:POT (~300 nm PP/PSS and 500 nm POT) bilayer recorded at three different applied potentials. In obtaining these results, a full set of potentials were measured which showed a continuous evolution of the spectra. For clarity, we show only the spectra for the potentials that best illustrate the three distinct redox states of the bilayer. At −1.3 V, a potential at which both polymers are in the neutral state, two absorption peaks are observed, which correspond respectively to $E_{\pi,\mathrm{POT}}$ at 2.4 eV and $E_{\pi,\mathrm{PP}}$ at 2.9 eV. The apparent bathochromic shift for $E_{\pi,\mathrm{PP}}$ from 3.1 to 2.9 eV is likely due to an effect of summing the absorbances of the PP/PSS and POT and not a true change in the PP electronic structure. At 0.0 V, a potential at which PP/PSS is converted to the oxidized state, but POT remains in the neutral state, the polypyrrole absorption at $E_{\pi,\mathrm{PP}}$ decreases slightly in intensity while the poly(3-octylthiophene) absorption at $E_{\pi,\mathrm{POT}}$ remains high. At the same time there is a slight increase in the absorption at lower energy. Finally, at +0.7 V, both polymers are in the oxidized state and two new absorptions appear below 0.7 and at 1.5 eV. As mentioned before, these absorptions have been attributed to electronic transitions between the valence band and the two bipolaron levels of POT. These experiments indicate that the electrons are easily transferred through the inner layer to the outer layer which allows the optoelectrochemical properties of the POT outer layer to be probed during the switching.

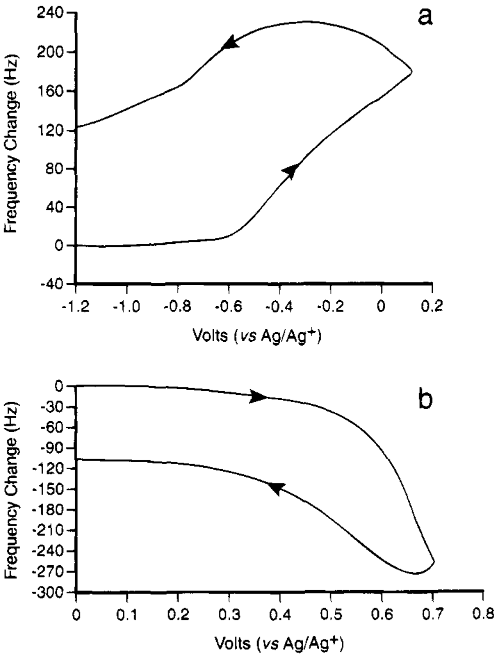

Figure 7. Frequency response during potential scanning of (a) PP/PSS film (~500 nm thick) and (b) POT film (~500 nm thick) redox cycled at 25 mV/s in 0.1 M $LiClO_4/CH_3CN$.

Comparison of the CV and spectroscopic results initially seem counterintuitive. While the CV behavior of the bilayer shows both redox processes to be easily accessible, the optoelectrochemistry suggests that oxidation of the inner film is inhibited at 0.0 V. Increasing the electrode potential to +0.7 V leads to complete bilayer oxidation. The fact that the electron-transfer reactions are accompanied by both ion and solvent movement during switching of conducting polymers and that the ion-transport process can limit the switching rates led us to investigate these phenomena in detail.

Microgravimetric Analysis. The direction of the dominant ion flux during the redox switching of PP/PSS, POT and PP/PSS:POT bilayer was investigated using the EQCM. Figure 7a shows the frequency response of a PP/PSS film (~500 nm thick) during a potential scan in 0.1 M $LiClO_4/CH_3CN$. Upon oxidation, the film loses mass as evidenced by an increase in frequency, attributable to expulsion of Li^+ from the film which is initiated at −0.6 V. This indicates the cation-dominant transport nature of the film, resulting from the immobility of incorporated polymeric anions which are intimately entangled with the polypyrrole chains. By comparing the frequency response for PP/PSS in CH_3CN and aqueous solutions, it appears that electrochemical cycling from the neutral to oxidized states and back results, in both cases, in an incomplete mass recovery. This hysteresis is likely attributable to the slow kinetics

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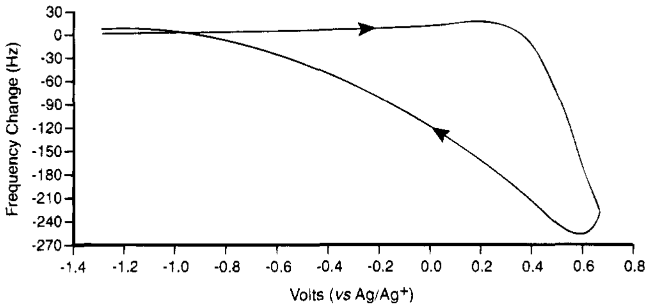

Figure 8. Frequency response during potential scanning of PP/PSS:POT bilayer (~500 nm PP/PSS, 500 nm POT). Redox cycled at 25 mV/s in 0.1 M $LiClO_4/CH_3CN$.

of ion transport as a close examination of the absolute frequency on consecutive scans shows that the microbalance equilibrates toward its original frequency between scans when held at −1.2 V.

The frequency response for a PP/PSS film in an aqueous electrolyte during a cyclic potential scan, as originally observed by Smyrl et al.[25] and also observed in our studies using aqueous $LiClO_4$, is significantly different than in CH_3CN-based electrolytes. In aqueous $LiClO_4$, the ion-transport processes can be divided into two regions. Scanning anodically from −1.2 to −0.3 V, cation-dominated transport is evident by a frequency increase (mass loss) resulting from the expulsion of hydrated cations (Li^+) from the film. Scanning to higher potentials results in a frequency decrease (net mass gain) most likely due to incorporation of anions (ClO_4^-) into the film. We find that while there is still evidenced hysteresis in the frequency response in an aqueous electrolyte, the magnitude of this hysteresis is significantly smaller.

To confirm the expected anion-dominant transport during the redox switching of POT, microgravimetric measurements were again carried out. Figure 7b shows the frequency change of a POT film (~500 nm thick) during a cyclic potential scan in 0.1 M $LiClO_4/CH_3CN$. Scanning anodically between 0.0 and +0.7 V, with the film initially in the neutral state, a frequency decrease (mass increase) starting at +0.4 V is observed as ClO_4^- ions move into the polymer film as it is oxidized. Upon subsequent reduction, there is a frequency increase associated with the diffusion of anions out of the film. This is a typical anion-dominant transport system, where the anions in the polymer film and electrolyte solution serve as mobile dopant ions moving into or out of the film as the polymer is electrochemically switched between oxidized and neutral states. Similar hysteresis in the frequency response is evident here as observed for PP/PSS.

Figure 8 shows the frequency response of a PP/PSS:POT bilayer (each layer ~500 nm thick) during a cyclic potential scan over the full potential range −1.3 to +0.65 V. A slight, and very slow, increase of frequency (~25 Hz) occurs starting at −0.8 V when scanning anodically from −1.3 to +0.2 V. At these low potentials, the inner PP/PSS film begins to dope, but the rate of doping seems to be quite slow. Note that the bare PP/PSS film exhibits a frequency change of 180 Hz at +0.2 V. Scanning to more anodic potentials results in a substantial frequency decrease (200−250 Hz) beginning at ca. +0.4 V as the POT outer layer is rapidly and efficiently doped. The initial frequency increase is attributable to expulsion of cation (Li^+) from the PP/PSS inner film upon oxidation, while the frequency decrease thereafter is due to incorporation of anions (ClO_4^-), possibly into both polymer films. These results suggest that the oxidation and reduction of the inner PP/PSS layer is limited by the diffusion of counterions through the POT. Referring back to the CV-determined reversible redox processes illustrated in Scheme 2, it can be seen that, under these conditions, the ion-transport processes are altered.

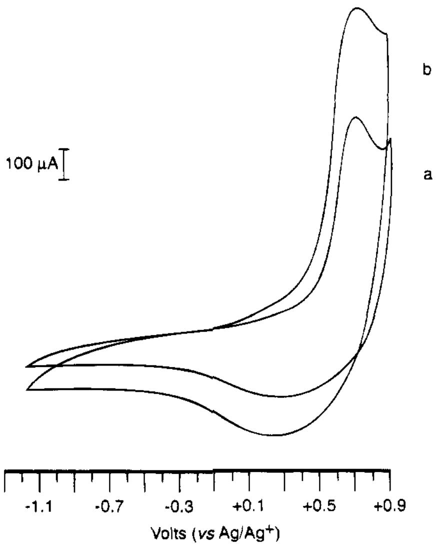

Figure 9. Cyclic voltammograms of PP/PSS:POT bilayer (~500 nm PP/PSS, 300 nm POT) recorded in 0.1 M $LiClO_4/CH_3CN$, after holding the potential at −1.2 V during 10 min. Scan rates: (a) 50 and (b) 100 mV/s.

The contrast of the response times of the bilayer during the different experiments can be explained by the electrochemical history of the system before starting the redox switching in cyclic voltammetry, optoelectrochemistry, and EQCM experiments. For the optoelectrochemical measurements, the PP/PSS:POT bilayer film was held at −1.3 V for a few minutes in order to stabilize the absorbance prior to recording the spectrum at this potential. The spectrum was recorded at 0.0 V after applying a step potential from −1.3 to 0 V. Prior to initiating the potential scan of the bilayer during the EQCM experiment, the potential was also held at −1.3 V in order to stabilize the frequency. On the other hand, no potential equilibration was utilized in the CV measurements. The bilayer was placed in the electrolyte solution and the redox switching was immediately started by repeatedly scanning between −1.3 and +0.9 V. As shown previously in Figure 3, the CV presents two well-separated oxidation waves corresponding to the PP/PSS inner layer and to the POT outer layer, indicating that the redox process of each layer is not inhibited by the other layer. It is likely that the ion content within the film is different with these two handling procedures and that the PP/PSS inner layer is depleted of necessary cations when held at −1.3 V. The POT out layer then inhibits movement of these ions from the electrolyte. During the rapid switching experiments, the slow ion-transport processes do not allow the ion concentrations to equilibrate and the necessary charge-balancing ions remain in the film. To confirm this

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(25) Lien, M.; Smyrl, W. H.; Morita, M. *J. Electroanal. Chem.* **1991**, *309*, 333.

hypothesis, a CV of a PP/PSS:POT bilayer was recorded by scanning between −1.2 and +0.9 V after holding the potential at −1.2 V for 10 min prior to initiation of the scan. These results are shown in Figure 9. The CV obtained under these conditions exhibits only one sharp anodic peak at about +0.7 V along with a broad reduction wave. This indicates that the POT outer layer shifts the oxidation of PP/PSS and that both polymers are oxidized simultaneously. These results clearly show that when the bilayer is equilibrated at a low potential, the oxidation of the inner PP/PSS layer is severely limited by the diffusion of counterions through the neutral POT outer layer and that the PP/PSS layer is oxidized simultaneously with the POT. Recently, similar CV behavior has been reported by Bobacka et al.[14a] for a poly(pyrrole tetrafluoroborate):poly(3-octylthiophene tetrafluoroborate) bilayer (PP/POT), prepared by sequential electrochemical polymerization methods and studied in 0.1 M $LiBF_4$−propylene carbonate solutions. The CV for the PP/POT bilayer, after equilibration at −1.0 V (vs Ag/AgCl) for 2 min, shows that the PP and POT are oxidized simultaneously, exhibiting a single anodic peak at 1.3 V. After continuous cycling, a broad anodic wave gradually appears between −0.2 and 0.9 V. This can be attributed to oxidation of the PP layer and is accompanied by a decrease in the peak current at 1.3 V. From these results, they conclude that the redox processes in PP/POT may be limited by the transport of the charge-compensating counterions through the neutral POT outer film. Initial oxidation of the POT increases its ionic conductivity, allowing the PP inner layer to oxidize rapidly. This interpretation is in good agreement with our experiments and demonstrates the importance of both the inner and outer layers on the ion-transport properties of these bilayer electrodes.

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