Rectifying Bilayer Electrodes: Layered Conducting Polymers on Platinum

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The preparation of sequential bilayer structures made from any pair of polybithiophene, I, polypyrrole, II, and poly(3-bromothiophene), III, by anodic electropolymerization on platinum electrodes is described, and the electrochemical properties of the junction between the two conducting polymer are discussed. Voltammetric evidence shows that the polymers in the outer layers of the electrodes Pt/I/II and Pt/III/II can be trapped in the oxidized state and that charge can be released via an appropriate redox couple in solution. Geometrical relaxation and/or overoxidation induced at high anodic potentials significantly alter the shapes of the resulting voltammograms.

Introduction

Polymeric bilayer electrodes—a sequence of electroactive polymeric films built up on a metallic or a semiconductive electrode—made from redox polymers have been of recent interest since the polymer/polymer heterojunction may serve as a charge-trapping interface, allowing for unidirectional charge transport.[1-6] Electric contact between the metal electrode and the outer film, which are physically separated, is reached only through the redox levels of the inner polymer film. The rectifying ability of the polymer/polymer interface depends on the polymerization sequence and on the potential difference between the redox levels in the inner film and those in the outer film.

Recently, electronically conducting organic polymers, materials that can be reversibly switched from an insulating to a conducting state,[7] have been used as components of bilayer and multilayer electrodes. Consequently, junctions between a redox polymer and a conducting polymer[8-12] and between two conducting polymers[12-16] have been reported. Thus, electrochemical[8,9] and spectroscopic[10,11] methods have been used to study the rectifying properties of heterojunctions between conducting polypyrrole derivatives and poly[Ru^{II}(4-vinyl-4′-methyl-2,2′-bipyridine)]$^{2+}$ redox complexes[8,10] and the doping–undoping of outer conducting polythiophene layers through the discrete redox levels of an inner poly[Ru^{II}(4-vinyl-2,2′-bipyridine)]$^{2+}$ complex.[9,11]

Multilayer structures based solely on conducting polymers are expected to exhibit new and interesting optical, electronic, and transport properties related to the presence of mobile defects such as polarons and bipolarons in the bandgap of these quasi-one-dimensional materials.[17] Consequently, the electropolymerization of polypyrrole on polycarbazole[13] and the use of conducting polymer/conducting polymer junctions (polypyrrole/polythiophene[14,15] and polypyrrole/polyaniline[16]) as Schottky barriers have been reported. The practical utility of a rectifying Pt/n-doped polypyrrole/p-doped polythiophene bilayer electrode prepared by Aizawa and co-workers[15] is limited by the known instability of p-doped polythiophene in common organic solvents at room temperature.[18] (Only recently, a preliminary study has described the electrochemistry of p-doped polythiophene in liquid NH_3 and in acetonitrile at low temperatures.[19]) A recent study described the electrochemistry of bilayer and trilayer structures made from polypyrroles substituted with redox couples (poly(pyrrole)$_2$–paraquat, PPyr$_2$–PQ^{2+}, polypyrrole–phenothiazine, PPyr–PTZ, and polypyrrole[Ru^{II}(2,2′-bipyridine)]$^{2+}$, PPyr[Ru^{II}]).[12] Conduction of charge across the polymer films and any properties associated with heterojunctions of such polymers were directly attributable to electron exchange between redox centers. However, charge transport across a conducting polymer/conducting polymer heterojunction may also reflect the delocalized band structure of these materials.

Here we present the cyclic voltammetric characteristics of anodically electrosynthesized bilayer electrodes in which discrete internal and outer layers consist of electronically conducting polymers. The conducting polymers used in our experiments were prepared by electrooxidation of poly(2,2′-bithiophene), I, polypyrrole, II, or poly(3-bromothiophene), III, and the bilayer electrodes were made by sequential layer formation between each pair of these polymers: Pt/I/II, Pt/II/I, Pt/I/III, Pt/III/I, Pt/II/III, and Pt/III/II. Our results show that the outer layers of the bilayer electrodes Pt/I/II and Pt/III/II can be trapped in the oxidized state by controlling the electrode potential and that charge can be released to a soluble redox species, hydroquinone, H_2Q, which undergoes oxidation at the outer layer–solution interface. The cyclic voltammetric response of the I-containing bilayer electrodes is greatly

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Table I. Conditions for Electropolymerization of Bilayer Electrodes

bilayer	deposition charge, mC ± 0.1		electrolysis potential, V ± 0.1 vs $Ag/AgNO_3$	
	inner layer	outer layer	inner	outer
Pt/I/II	2.3	1.9	1.0	0.9
Pt/II/I	3.0	1.6	0.9	1.0
Pt/I/III	3.9	1.8	1.0	1.4
Pt/III/I	1.5	1.6	1.4	1.0
Pt/II/III	1.1	1.5	0.9	1.4
Pt/III/II	1.5	1.0	1.4	0.9

influenced by geometrical relaxation of this polymer which has not been observed in other bilayer structures made from redox polymers.

Experimental Section

Reagents and Equipment. Acetonitrile (Baker) was doubly distilled from CaH_2 and stored over 3-Å molecular sieves. Tetrabutylammonium hexafluorophosphate, $TBAPF_6$ (Southwestern Analytical Chemicals, electrometric grade), was recrystallized from ethyl acetate (Baker). 2,2′-Bithiophene (Aldrich, 98 %), hydroquinone, H_2Q, and methyl-1,4-benzoquinone, MBQ, (Aldrich, 98 %) were used without any further purification. Pyrrole (Aldrich, 97%) was passed over neutral alumina before use. 3-Bromothiophene (Aldrich, 97%) was distilled. Electrochemical measurements were controlled with a PAR 175/173/179 system and a Houston 2000 x–y recorder. Profilometry measurements were performed with a Sloan-Dektak profilometer. Scanning electronic micrographs, SEM, were taken with a JEOL JSM-C 35 instrument. UV–vis absorbance spectra were taken with a Hewlett-Packard 8451-A diode array single-beam spectrophotometer.

Electrodes and Cells. Polymerizations and electrochemical experiments were made in a one-compartment cell containing 0.6 M $TBAPF_6$ in acetonitrile. A platinum disk (1.0 mm^2) and a Pt wire were used as working and auxiliary electrodes, respectively. The electrochemical potentials were recorded relative to a silver/0.1 M silver nitrate reference electrode, $Ag/AgNO_3$ (+0.310 V against a saturated calomel electrode, SCE). The Pt disk electrodes were polished with 1.0- and 0.3-μm alumina before each experiment. All solutions were bubbled with nitrogen for 15 min prior to the experiments, which were conducted under nitrogen. For profilometry and SEM measurements of dry single layer and bilayer films, samples were prepared on a 1-cm^2 Pt foil, washed with acetonitrile, and dried at 140 °C for 2 h.

Single-Layer Electrodes (Conducting Polymers on Pt). Pt/I electrodes were prepared from 2,2′-bithiophene-containing (0.05 M) electrolyte solutions at +1.0 V vs $Ag/AgNO_3$. Pt/II electrodes were prepared from pyrrole-containing (0.1 M) electrolyte solutions at +0.9 V. Typically, the total charge deposited for Pt/I and Pt/II electrodes was ca. 3 mC. Pt/III was made from a 3-bromothiophene-containing (0.1 M) electrolyte solution at +1.4 V. (A typical deposition charge was ca. 1.5 mC.)[20]

Bilayer Electrodes (Layered Conducting Polymers on Pt). The inner layers of Pt/I/II, Pt/II/I, Pt/I/III, Pt/III/I, Pt/II/III, and Pt/III/II bilayer assemblies were electrosynthesized as above. Typically, for electropolymerization of a second layer, the single-layer electrodes were dipped into 0.6 M $TBAPF_6$/acetonitrile solutions containing the corresponding monomer. Thus, I was electropolymerized onto either Pt/II or Pt/III anodes at +1.0 V from 2,2′-bithiophene-containing (0.05 M) electrolyte solutions, II was deposited on either Pt/I or Pt/III electrodes at +0.9 V from pyrrole-containing (0.1 M) electrolyte solutions, and III was formed on either Pt/I or Pt/II electrodes at +1.4 V from 3-bromothiophene-containing (0.1 M) electrolyte solutions. After the layers had been deposited, the resulting bilayer electrodes were removed, washed with acetonitrile, and transferred to monomer-free electrolyte solutions for cyclic voltammetric measurements. A summary of the conditions employed for the electrooxidative synthesis of bilayer electrodes is given in Table I.

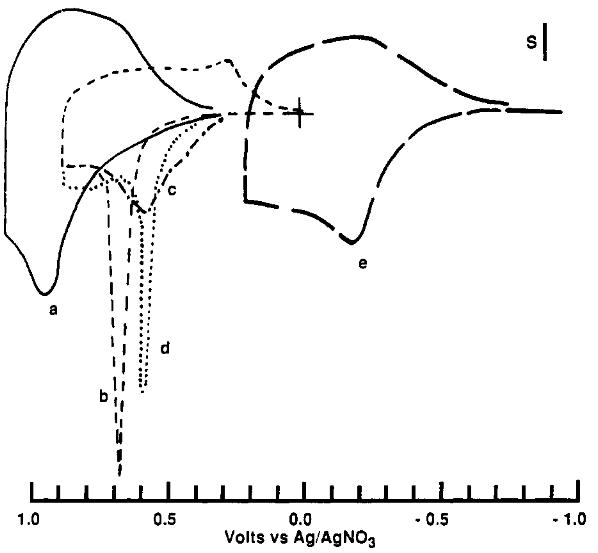

Figure 1. Cyclic voltammograms of Pt/polymer coated electrodes in monomer-free acetonitrile containing 0.6 M $TBAPF_6$: (a) Pt/poly(3-bromothiophene) (Pt/III) at 20 mV s^{-1} (S = 1.0 μA); (b) Pt/polybithiophene (Pt/I) first scan at 5 mV s^{-1} at room temperature (S = 2.5 μA); (c) Pt/I second consecutive scan at 5 mV s^{-1} at room temperature (S = 2.5 μA); (d) Pt/I first and second consecutive scans at 5 mV s^{-1} at 60 °C (S = 1.0 μA); (e) Pt/polypyrrole (Pt/II) at 20 mV s^{-1} (S = 5.0 μA). The Pt disk area is 1.0 mm^2.

Results and Discussion

Single-Layer Electrodes. A. Polythiophene, I. Cyclic voltammograms of a Pt/I electrode in 0.6 M $TBAPF_6$/acetonitrile at 5 mV/s in the potential region between −0.5 and +0.9 V at room temperature are shown in Figure 1, curves b and c. (A dry I film, deposited at the same charge density on a 1-cm^2 Pt foil, was 5 μm thick.) The first potential scan exhibits one sharp oxidation peak at +0.68 V and a broad reduction wave at ca. +0.53 V with a sharp shoulder at +0.30 V (curve b), in agreement with published data.[21] The charges passed in the oxidation and reduction of the polymer film are 0.60 and 0.56 mC, respectively. Charging rates of conducting polymers are known to be slightly faster than the corresponding discharging rates, i.e., the amount of charge passed during the oxidative sweep is greater than the charge recorded during the reverse reduction sweep of the film.[22,23] If the electrode potential is immediately recycled between −0.5 and +0.9 V, the voltammogram becomes more symmetrical: the initially observed oxidation peak is replaced by a wider wave at +0.58 V with a shoulder at a lower potential (curve c), the reduction waves remaining unchanged. Consecutive potential cycles do not produce any further alteration in the shape of the voltammogram. If the electrode is held at −0.5 V for ca. 15 min and the electrode potential is then scanned between the same limits, the original shape of the voltammogram is fully restored. The cycling-dependent changes in the shape of the oxidation peak are not observed when the potential of the same electrode is repeatedly swept at high temperatures (ca. 60 °C, curve d), indicating that the observed changes at room temperature are caused by geometrical

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(20) When deposition charges larger than 2 mC were attempted, the resulting polymers peeled from the electrode.

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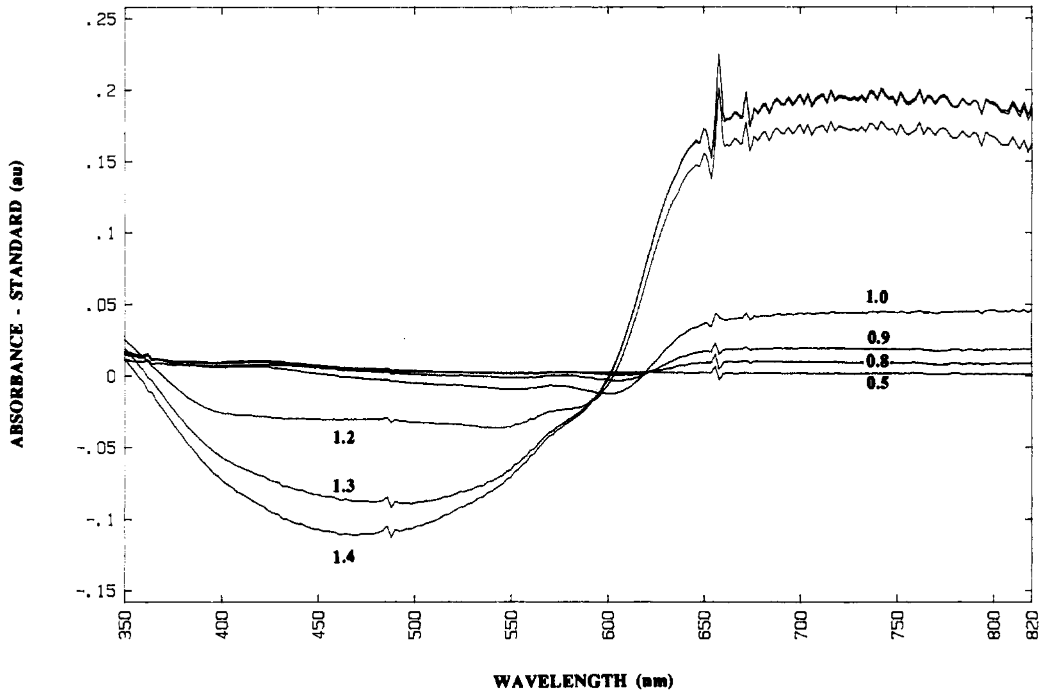

Figure 2. Difference UV-visible absorption spectra of an indium-tin oxide/poly(3-bromothiophene) electrode (ITO/III) as a function of potential in monomer-free acetonitrile containing 0.6 M $TBAPF_6$ at 2 mV/s at room temperature. Numbers indicate the applied potential in V vs a silver wire.

relaxation during charging and discharging and not to degradation of the polymer.[24,25] Similar relaxation processes have also been observed for polypyrrole films.[26]

However, degradation of polythiophene does occur if the potential is scanned to more positive values. Polythiophene exhibits an irreversible oxidation peak at ca. +1.4 V.[27] If the electrode potential of a polythiophene-coated electrode[28] was swept in the direction 0.0 → +1.6 → 0.0 V, held at 0.0 V for 5 min, and then swept in the range 0.0 → +0.9 → 0.0 V, an overoxidized material exhibiting two broad oxidation waves at +0.50 and +0.62 V, respectively, and two broadened but unshifted reduction waves was obtained. The sharp oxidation peak at +0.68 V could no longer be seen. After a few cycles in the range 0.0 → +1.6 → 0.0 V, the electroactivity of the polymer was lost completely. Although this problem can be avoided easily by restricting the potential range, partial degradation of an inner polythiophene film may occur when preparing bilayer electrodes (e.g., Pt/I/III) in which polymerization of the outer layer occurs at higher anodic potentials than required for the inner layer polymerization.

B. Polypyrrole, II. Figure 1, curve e, shows the voltammogram of a Pt/II electrode at 20 mV/s. The dry thickness of a II film deposited at the same charge density on a 1-cm^2 Pt foil was 2 μm. The oxidation and reduction of II occur at -0.19 and -0.20 V, respectively. The total anodic and cathodic charges are 0.21 and 0.22 mC. No splitting of the anodic wave is observed upon repeated scanning. Overoxidation of II occurs at ca. +1.3 V.[29] The redox waves of overoxidized II shift toward more positive potentials (ca. +0.1 V).[29]

C. Poly(3-bromothiophene), III. Figure 1, curve a, shows the voltammogram of a Pt/III electrode at 20 mV/s. The thickness of a III film deposited under similar charge density conditions on a 1-cm^2 Pt foil was 1 μM. The oxidation and reduction waves of III are at +0.95 and +0.85 V. Total anodic and cathodic charges were 0.1 and 0.09 mC. The shape of the voltammogram of III does not change upon continuous potential cycling within the potential bracket (0.0, +1.1 V).

Charging of Polymer Layers. The electrochemical response of an electroactive film on a metal electrode is determined by the kinetics of charge transfer at the metal-film interface and within the film, i.e., by electron transfer at the metal-film interface and by electrochemical charge (electron and counterion) transport through the film. In organic conducting polymers, the structural changes associated with the insulator/conducting transition make electrochemical analysis very complicated.[29] The kinetics of redox processes within an oxidized film is thought to be controlled by motion of ionic charge.[30-32] Changes in the shapes of the voltammograms of polypyrrole and polythiophene induced by potential cycling have been recently explained as geometric relaxation (interconversion between planar and twisted conformations in the polymeric chains) based on quantum mechanical descriptions of bipolarons.[25]

In our cyclic voltammetric experiments, similar relaxation processes are observed for I but not for II nor III. The presence of the 3-bromo substituent in III may slow relaxation of the polymeric chain. However, we clearly observe two isosbestic points at 620 (between 0.0 and ca. +1.0

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(24) As the temperature increases, the anodic peak becomes sharper and shifts cathodically. This temperature dependence of the peak has been used to calculate the entropy of oxidation in polythiophene; see: Waltman, R. J.; Diaz, A. F.; Bargon, J. *J. Electrochem. Soc.* **1984**, *131*, 1452-1456.

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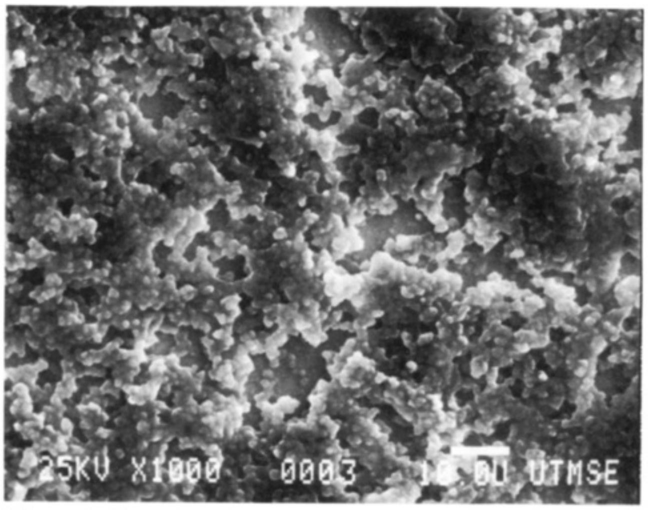

Figure 3. Scanning electron micrograph of a Pt/I/II electrode. The thickness of the bilayer film is 6 μm. The Pt foil area is 1 cm^2.

V) and 590 nm (between ca. +1.2 and +1.4 V) during the redox transitions of III by in situ spectroelectrochemical experiments, indicating several potential-dependent equilibria within the polymer. Figure 2 shows UV–visible difference absorption spectra recorded during the oxidation and reverse reduction of an indium–tin oxide/III electrode at 2 mV/s (between 0 and +1.4 V vs an Ag wire quasi-reference electrode) in 0.6 M TBAPF$_6$/CH$_3$CN with respect to the absorption at 0.0 V, which exhibits a maximum at ca. 510 nm, in agreement with published data.[33] The relaxation phenomena observed, together with the overoxidation in I and II, affect the shape of the voltammograms attainable on bilayers (see below).

Establishing Surface Coverage in Pt/I, Pt/II, and Pt/III. In an effective rectifying bilayer electrode, the metal electrode and the outer polymeric layer must not be in direct contact. To establish whether pinholes might persist in the internal layers, cyclic voltammograms of a 0.1 M solution of a reversible redox probe, methyl-1,4-benzoquinone, MBQ, were obtained at both Pt and Pt/polymer electrodes in 0.6 M TBAPF$_6$/acetonitrile. On Pt, MBQ exhibits a one-electron reversible reduction at ca. −1.0 V vs Ag/AgNO$_3$ and a second quasi-reversible one-electron reduction at ca. −2.0 V, in analogy with that observed for quinones in aprotic solvents.[34,35] In this potential region, (−1.0 to −2.0 V), polymer films I, II, and III are insulators. No reduction current could be observed when the Pt/I, Pt/II, or Pt/III, respectively, were held at a constant potential (−1.3 V), indicating that they were essentially pinhole free. However, since morphological changes occur when conducting polymers switch from the reduced to the oxidized state, the possibility that an electroactive species permeates the oxidized polymer film and reacts at the Pt electrode cannot be ruled out.

Bilayer Electrodes. A. Polypyrrole on Polythiophene on Pt (Pt/I/II). Evidence for the formation of a bilayer was attained by scanning electronic microscopy (SEM) and by profilometry measurements. SEM indicates that the surface of an oxidized Pt/I film deposited after passing ca. 170 mC (dry film thickness = 4 μm) on a 1-cm^2, 0.025-mm-thick Pt foil is smooth and featureless. Figure 3 shows the morphological changes induced in the film after being coated with II (deposition charge 160 mC). The thickness of the dry bilayer electrode was 6 μm. The irregular external coating indicates that the polymer grows preferentially outward from the inner layer.

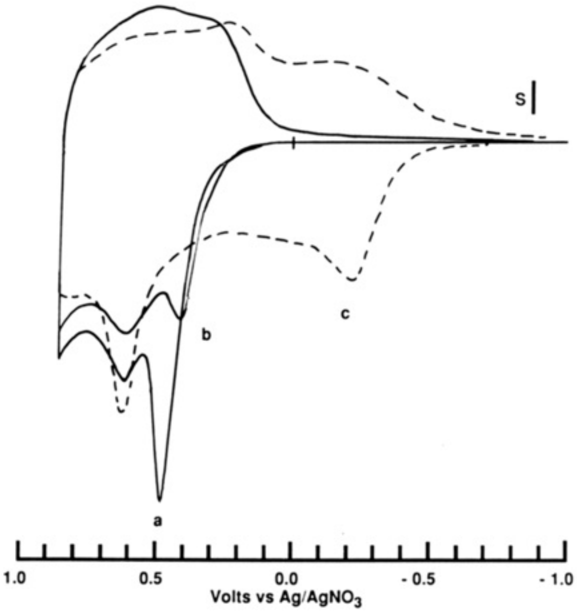

Figure 4. Cyclic voltammograms of Pt/polymer bilayer electrodes in 0.6 M TBAPF$_6$/acetonitrile at room temperature: (a) Pt/I/II first scan at 5 mV s^{-1} (S = 1.0 μA); (b) Pt/I/II second consecutive scan at 5 mV s^{-1} (S = 1.0 μA); (c) Pt/II/I at 20 mV s^{-1} (S = 5.0 μA). The Pt disk area is 1.0 mm^2.

Figure 4 (curves a and b) shows the cyclic voltammograms of a Pt/I/II bilayer electrode in 0.6 M TBAPF$_6$/acetonitrile at 5 mV/s at room temperature. The oxidation wave of II, which occurs at −0.2 V in Pt/II, is missing from the first positive potential scan (curve a), indicating that no II is polymerized directly on Pt. The two oxidation peaks at +0.49 and +0.64 V can be assigned to the oxidation of II mediated by the inner layer ("trapping" peak) and the oxidation of I, respectively. At 20 mV/s only one broad oxidation wave at +0.70 is observed.[36] The total anodic charge was 0.87 mC (compared to 0.53 mC in the Pt/I single-layer electrode), suggesting that electrooxidation of the outer layer (II) is effectively being mediated by the inner film I. Thus, upon reaching the potential at which I is oxidized, the insulating layer becomes conducting, allowing charge to flow to II. Upon reversal of the scan direction, layer I becomes insulating before charge can be drained from II. Thus, the first reverse cathodic scan shows no reduction wave for II and the cathodic charge passed is only 67% of the anodic charge (0.58 mC), indicating that the outer film has been trapped in the oxidized state.[37]

A subsequent positive scan (Figure 4, curve b) shows a considerable reduction in the observed anodic current. Instead, a broad anodic wave at +0.60 V and a peak at +0.42 V attributable to rearrangement in the inner layer are observed. The reverse reduction scan is unchanged. The anodic current does not increase further upon continuous scanning in this potential range, showing that the

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(36) For other Pt/I/II electrodes in which a smaller deposition charge was used for the outer layer II, the oxidation prepeak fused with the peak at +0.64 V.

(37) Typically, after a complete negative sweep, the electrode potential was held at the lower limit (−1.0 V) until the current decayed to zero. Then the total reduction charge was recorded. This rules out the possibility that the cathodic and anodic charges only represent different charging and discharging rates.

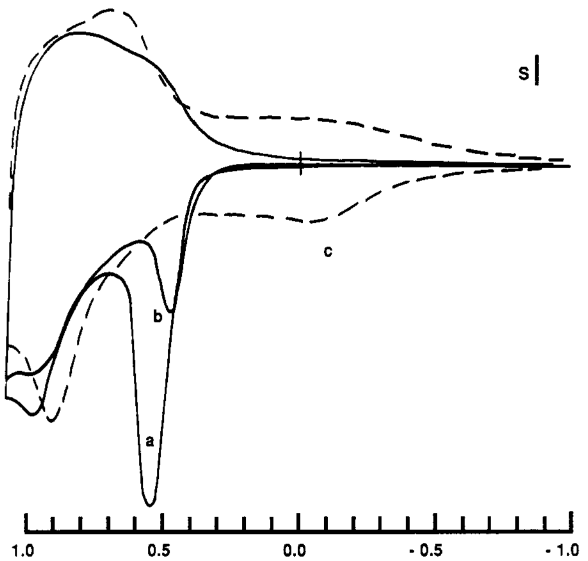

Figure 5. Cyclic voltammograms of Pt/polymer bilayer electrodes in 0.6 M TBAPF$_6$/acetonitrile at 20 mV s^{-1} at room temperature: (a) Pt/III/I ($S = 0.5\ \mu A$); (b) Pt/I/III ($S = 2.5\ \mu A$). The Pt disk area is 1.0 mm^2.

trapped charge is not released from the outer film.

Charge release does occur on a longer time scale. After the electrode is left at a resting potential for about 6 h, the anodic current increases and the voltammogram a in Figure 4 is obtained again, establishing that charge is released slowly to impurities in solution.[38] Charge can be more efficiently released when the solution is made 0.1 M in hydroquinone, H_2Q, after scanning the electrode potential several times between −1.0 and +1.0 V and disconnecting the electrodes. After ~30 min, more than 90% of the current density supplied via the initial oxidation can be recovered, indicating that the outer layer is reduced (untrapped) by H_2Q (whose oxidation potential is +0.6 V in acetonitrile).[39]

Some changes in the shapes of the oxidation peaks occur when the cyclic voltammogram of the bilayer is run at 60 °C. In the first scan, only one oxidation peak at +0.50 V is observed: the second wave at +0.64 V is absent. The reduction waves and the total anodic and reduction charges remain the same as in the experiment at room temperature. In the second scan, the oxidative wave appears at the same potential, i.e., there is no cathodic shift as was seen at room temperature, and the total anodic charge passed again decreases by ca. 30%. This behavior is identical with the temperature dependence of Pt/I (see above), which implies that the shape of the voltammogram of this bilayer is controlled by relaxation of the inner layer I.

B. Polythiophene on Polypyrrole on Pt (Pt/II/I). Figure 4, curve c, shows the voltammogram of a Pt/II/I electrode, which closely resembles a superimposition of the component films, Figure 1 (curves b and e), as expected. The oxidation of the inner and outer films of the electrode occur as distinct waves at −0.19 and +0.65 V, respectively, suggesting that the external layer is at equilibrium with the Pt electrode. Reduction waves for I and II are at +0.18 (sharp) and ca. −0.2 V (broad, not well-defined), respectively. The total anodic and cathodic charges are equal to within 10% (0.68 and 0.61 mC, respectively). On a second scan, the oxidation peak of layer I shifts to +0.60 V, as is consistent with the potential shift observed for Pt/I.

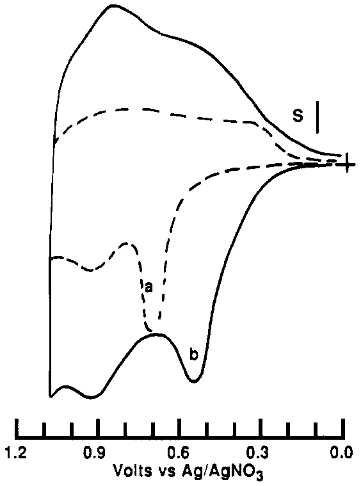

Figure 6. Cyclic voltammograms of Pt/polymer bilayer electrodes in 0.6 M TBAPF$_6$/acetonitrile at 20 mV/s at room temperature: (a) Pt/III/II first scan; (b) Pt/III/II second consecutive scan; (c) Pt/II/III ($S = 1.0\ \mu A$). The Pt disk area is 1.0 mm^2.

C. Polythiophene on Poly(3-bromothiophene) on Pt (Pt/III/I). A cyclic voltammogram of a Pt/III/I bilayer electrode is shown in Figure 5a. Although, by analogy with Pt/I/II, charge trapping was expected from this system, the observed voltammogram shows oxidation waves for I and III at +0.67 and +0.91 V, respectively. The amount of charge passed during oxidation is 0.024 mC. Although the charge passed during reduction of the film is only 0.013 mC, the remaining charge is released if the system is held at 0.0 V for ~5 min, reflecting a charge leakage between the electrode and the outer layer. This leakage may occur via partial overlap of the redox waves of the two polymers, which implies that effective charge-trapping properties are expected only from polymer/polymer systems that are electroactive in potential regions separated by more than 200 mV. Alternatively, although a control experiment had demonstrated the absence of pinholes in Pt/III (reduced form), the leakage may be partly a consequence of the deposition of strands of the outer polymer directly on the Pt surface, which would make a conducting path across the inner layer.

D. Poly(3-bromothiophene) on Polythiophene on Pt (Pt/I/III). A Pt/I/III bilayer electrode exhibits the cyclic voltammogram (between 0 and +1.1 V) shown in Figure 5, curve b. Oxidation waves for I and III are at +0.55 (sharp) and ca. +0.9 V (broad, not well-defined). Thus, the oxidation of I occurs at a less positive potential from that seen in Pt/I and Pt/III/I. Corresponding reduction waves for I and III are at ca. +0.5 V (broad) and +0.85 V, respectively. The reduction peak for I at ca. +0.3 V (in Figures 1a and 5a) is not present in Figure 5b. The data in Figure 5b suggest then that III is at equilibrium with the Pt electrode and that I may have been partly overoxidized as a consequence of the material's exposure to high anodic potentials (+1.4 V) during the electrosynthesis of the outer III film.

E. Polypyrrole on Poly(3-bromothiophene) on Pt-(Pt/III/II). Cyclic voltammograms for Pt/III/II, shown in Figure 6 (curves a and b), suggest that some charge trapping occurs in the outer layer (in contrast to what it is observed for the Pt/II/III electrode, see below). At the first anodic sweep (curve a), the absence of a peak at the normal oxidation potential of II indicates that the outer

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[38] Water in solution contributes to the charge release from the bilayer electrode. When the system was made 0.01 M in water, the trapped charge was released in about 2 h.

[39] Parker, V. D. *Electrochim. Acta* **1973**, *18*, 519–522.

layer is not in electrical contact with the Pt electrode. The two peaks at +0.55 and +1.0 V can be assigned to the oxidation of II mediated by the inner layer (trapping peak) and the oxidation of III, respectively. The integrated anodic charge for the first sweep was 0.25 mC (compared to 0.11 mC for the single-layer electrode), and the corresponding cathodic charge was 0.13 mC. A second scan (curve b) shows a 65% reduction of the prepeak at 0.58 V. On the fourth consecutive scan, the prepeak current has been reduced to 28%. Thereafter, the voltammogram stabilizes. After seven potential cycles in the potential range −1.0 → +1.0 → −1.0 V and after holding the electrode potential at −1.0 V for 3 h before recycling between these same limits, 65% of the prepeak current is restored.

Restoration of ca. 95% of the initial prepeak current could also be obtained by cycling the electrode potential (about five times) until equilibrium had been established, opening the circuit, making the electrolyte solution 0.1 M in H_2Q, waiting for about 30 min, transferring the electrode to a new electrolyte solution, and rerecording the voltammogram. This experiment indicates that discharge of the electrode outer III layer occurs by reaction with H_2Q in analogy with the results obtained on Pt/I/III.

F. Poly(3-bromothiophene) on Polypyrrole on Pt (Pt/II/III. A cyclic voltammogram of Pt/II/III at 20 mV s^{-1} is shown in Figure 6, curve c. Integrated charges for the first forward anodic and reverse cathodic sweeps were 0.24 and 0.24 mC, respectively. The oxidation wave of II occurs at a slightly less negative potential, −0.1 V, from that seen in Pt/II, and its reduction wave is not well-defined, indicating that the material is overoxidized during the electrosynthesis of the outer III film. The oxidation peak of III is at +0.92 V and the reduction peak occurs at +0.67 V. Notice that although the oxidation peak of III appears at the same potential independently of the polymerization surface (Pt, Pt/I, and Pt/II), the reduction peak of III clearly exhibits a polymerization surface effect.[40]

Kinetics in Conducting Bilayers. Two kinetic processes influence the electrochemical response of bilayer film electrodes, i.e., the charge transport across the film/film interface and the charge transport within the inner film.[3-5] On the cyclic voltammetric time scale, the charge transport across the junction between two conducting polymers is fast, as shown by Figures 4c (Pt/II/I) and 5b (Pt/I/III), whose outer layers exhibit redox waves at their normal potentials. Figures 4a and 6b (Pt/I/II and Pt–III/II, respectively) represent the voltammetric evidence for the (outer film) charge-trapping reactions

$$\mathrm{I^+ + II \rightarrow I + II^+} \tag{1}$$

$$\mathrm{III^+ + II \rightarrow III + II^+} \tag{2}$$

The untrapping reaction of II^+ is effected by the treatment with hydroquinone:

$$\mathrm{H_2Q + II^+ \rightleftharpoons H_2Q^{+\bullet} + II} \tag{3a}$$

$$\mathrm{H_2Q^{+\bullet} \rightleftharpoons Q + H_2Q} \tag{3b}$$

In Pt/III/II the cyclic voltammetric prepeak at +0.54 V in Figure 6a represents the trapping reaction (2) predicted for a bilayer electrode in which kinetics is controlled by charge transport through the inner polymeric layer.[3,4] The fact that this system does not trap charge indefinitely indicates that some mixing between the redox states of the layered films occurs. We predict that a longer lasting trapping lifetime would be obtained if III were synthesized from 3,3′-dibromo-2,2′-bithiophene rather than from the monomer 3-bromothiophene, since the anodic wave of a conducting polymer made from oligomeric units is narrower than the wave of the same polymer made from the single monomer.[21]

The prepeak at +0.49 V in Pt/I/II at room temperature (Figure 4a) is caused by the trapping reaction shown as (1). The Pt/I/II electrode represents the best charge-trapping system we have obtained to date.

Conclusions

Selected pairs of conducting polymers can be formulated as bilayers on metal electrodes to achieve unidirectional charge transport. Cyclic voltammetry showed that the outer layer of the electrodes Pt/I/II and Pt/III/II can be trapped in the oxidized state for several hours. Charge is easily released from the outer layers via an appropriate redox couple present in solution. Although the cyclic voltammetric data for charge trapping at the polymer/polymer interface in Pt/III/II can be interpreted by conventional schemes used to describe a similar phenomena in redox polymeric bilayer films, kinetic analysis of the data for Pt/I/II is complicated by simultaneous conformational changes occurring in the internal polymeric layer. The polymers used as inner films in these experiments were on the order of a few micrometers thick in order to guarantee an effective physical separation between the metal and the outer layer. Recently, by optimizing electropolymerization conditions, we have obtained thinner Pt/I/II electrodes (ca. 100 nm thick) with charge-trapping characteristics similar to those shown above. However, the question of how thin can a film allow for charge trapping without endangering the performance of the resulting bilayer structure still remains.

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Registry No. I, 80029-99-8; II, 30604-81-0; III, 84928-93-8; H_2Q, 123-31-9; MBQ, 553-97-9; $TBAPF_6$, 3109-63-5; Pt, 7440-06-4; indium–tin oxide, 50926-11-9; acetonitrile, 75-05-8; pyrrole, 109-97-7; 2,2′-bithiophene, 492-97-7; 3-bromothiophene, 872-31-1.

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[40] Voltammograms recorded during the electrooxidative synthesis of III on Pt by cycling the electrode potential between 0.0 and +1.4 V vs $Ag/AgNO_3$ reveal two reduction peaks at early stages of the polymerization at +1.0 and +0.7 V, respectively. These peaks collapse into one broad reduction peak as the polymeric film thickness increases. Thus the specific polymerization surface may influence the observed potential of the reduction peak of the resulting polymer.