vesicle solutions (10 mg/mL) and then mixing the resulting solutions and measuring the turbidity at 450 nm. A total amount of 100 μL of ethanol was added. The following equation was used to correct for turbidity change due to dilution: corrected turbidity = observed turbidity × (volume of aqueous vesicle solution + volume of ethanol added)/(volume of aqueous vesicle solution).

Acknowledgment. We thank Prof. W. Drenth for many stimulating discussions.

Registry No. 1, 85850-53-9; **1** homopolymer, 85850-54-0; L-dimethylhexadecyl[11-((1-*N*-formylaminoethyl)carbonyloxy)undecyl]ammonium bromide, 85850-57-3; *N*-formyl-L-alanine *p*-nitrophenyl ester, 61167-49-5; dimethylhexadecyl(11-hydroxyundecyl)ammonium bromide, 85850-56-2; 11-bromoundecanol, 1611-56-9; nickel capronate, 16034-23-4; dimethylhexadecylamine, 112-69-6.

Redox Conduction in Mixed-Valent Polymers

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Abstract: The redox conduction of thin films of Os and Fe polypyridine polymers was measured by steady-state voltammetry in the electrochemical cell Pt electrode (electron acceptor)/polymer film/porous Au electrode (electron donor)/electrolyte solution/SCE. The redox conduction becomes turned on at potentials near E° of the polymer M(III/II) couple and is dependent on generating the mixed-valent state of the polymer, and the current achieves a limiting value at an overall 1:1 M(III)/M(II) polymer film composition. The limiting current occurs because the 1:1 composition gives maximal M(III) and M(II) concentration gradients in the film, not because the 1:1 composition has an intrinsically greater conductivity. The sandwich electrode assembly is also used to explore certain characteristics of bilayer electrodes.

Organic and organometallic polymers that have significant electrical conductivity are of interest both for their potential technological utility and as models for gaining a more cathodic understanding of the electronic conductivity of materials.[1-5] Polymers incorporating discrete electron donor/acceptor (i.e., electron transfer) sites are an important class of conducting materials, and have recently been intensively investigated as electroactive films on electrodes.[6-32] In many such polymers, electron transport is thought[31] to occur by a hopping mechanism, and this mechanism has been dubbed "redox conduction".

In previous investigations[10,11,21,24,26,31,33-50] of redox conduction

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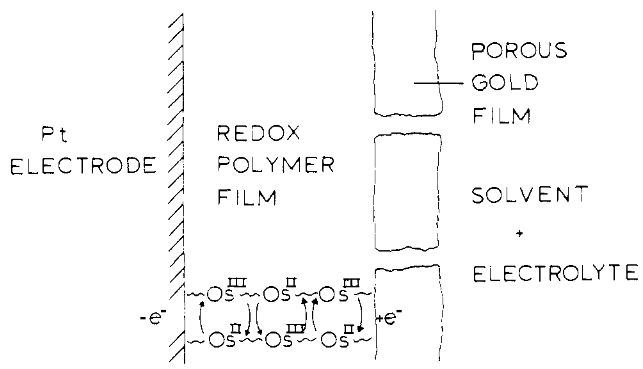

Figure 1. Schematic diagram of the sandwich electrode used in this work, showing the proposed mechanism of redox conduction.

(i.e., the rate of electron transport) in redox polymers, using chronoamperometry, chronocoulometry, and voltammetry, the redox polymer film is contacted on one side with an electrode whose potential is controlled and is wetted on the other side by the solvent of the electrochemical cell and supporting electrolyte. The mechanism[17,22,31,48] for redox conduction involves electron self-exchange reactions between adjacent oxidized (acceptor) and reduced (donor) polymer sites, e.g.,

By the self-exchange reaction, the electron moves (hops) from physical site a to site b and is thereby translocated toward or away from the electrode. The self-exchange reaction is formally analogous to intramolecular electron transfers in mixed-valent dimers and oligomers dissolved in solutions,[51,52] but the molecular details of intersite electron transfer in the polymer are much less well understood[18,31,44] and may sometimes be dominated by the polymer dynamics. It should be emphasized that self-exchange reactions (and consequent motion of electrons) in the polymer can be driven by concentration gradients of fixed oxidized and reduced redox sites and do not require the presence of an electrical potential gradient.[53a] The "redox mobility" of the electron migrating in this manner is expressed as a diffusion coefficient, D_{ct}. Redox conduction thus has differences from other forms of electron conduction which depend on spatially delocalized electron occupancy states.

In a further study of redox conduction,[53b] we have determined and report here how redox conduction of a mixed-valent polymer film varies with its mixed-valent composition, using a sandwich cell arrangement, a *wetted* polymer film, and electrochemical techniques. Sandwich cells are commonly employed to measure electrical conductivity of materials, including mixed-valent mixtures,[54-56] but in the *dry* state. In the present case, not only must both electrodes of the sandwich make good electrical contact to the polymer film but one electrode must also be porous to the flow of solvent and electrolyte into/out of the redox polymer film. Electrochemical oxidation or reduction of the polymer requires a free flow of electrolyte counterions (to maintain electroneutrality) and solvent (to swell the polymer).

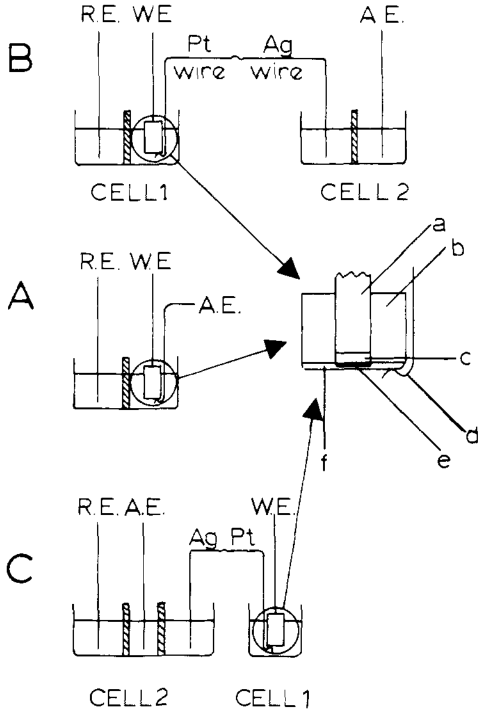

Figure 2. Schematic diagrams of the cell arrangements used in this work. R.E. = reference electrode; W.E. = working electrode; A.E. = auxiliary electrode; a = brass shaft; b = Teflon shroud; c = Pt electrode; d = Pt wire (pressure contact); e = redox polymer; f = gold film.

In our experiment, a thin (1000–5000 Å) polymer film was deposited onto a platinum electrode and a *porous* gold contact then vapor deposited onto the polymer (Figure 1). The polymer films are prepared by electrochemical polymerization of the electroactive monomers[23,44,57] $[Os(bpy)_2(4\text{-py-NHCOCH}{=}CHPh)_2]^{2+}$ or $[Fe(4\text{-vinyl-}4'\text{-methyl-}2,2'\text{-bipyridine})_3]^{2+}$ in acetonitrile and are abbreviated $Pt|poly[Os(bpy)_2(p\text{-cinn})_2]^{2+}$ and $Pt|poly[Fe(vbpy)_3]^{2+}$, respectively, where *bpy* is 2,2′-bipyridine. The potential of the Pt electrode is controlled relative to that of a reference electrode elsewhere in the cell, so that the Pt contact serves as electron acceptor, oxidizing one side of the film. The porous Au electrode serves as electron donor to re-reduce oxidized sites that migrate across the film by electron hopping (Figures 1 and 2A). Steady state concentration gradients of oxidized and reduced polymer film sites, and a steady state current, are estalished, from which the electron-diffusion coefficient D_{ct} can be calculated.[58]

Another aim of this work was to develop interfacial structuring techniques facilitating use of the rectifying properties of bilayer electrodes[57,60,61] as electronic devices. To this end, some novel cell arrangements (Figure 2, parts B and C) have been used to relate the present results to those of our previous reports.

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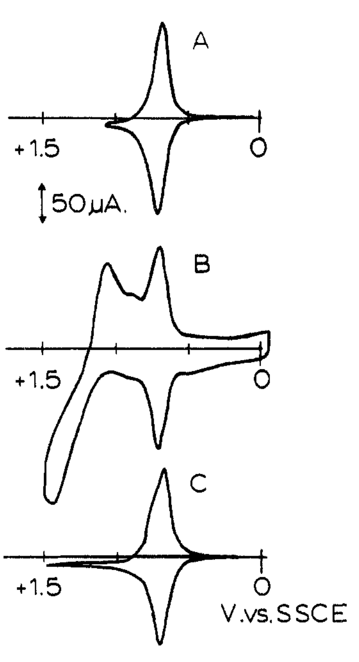

Figure 3. Cyclic voltammograms at 0.1 V/s in 0.1 M Et_4NClO_4/CH_3CN: curve A, a Pt|poly$[Os(bpy)_2(p\text{-cinn})_2]^{2+}$ electrode; curve B, with a shorting gold contact; curve C, with a gold contact after conditioning. $\Gamma_T = 2.0 \times 10^{-8}$ mol/cm^2.

Experimental Section

Synthesis of the electroactive monomers $[Os(bpy)_2(p\text{-cinn})_2]^{2+}$ and $[Fe(vbpy)_3]^{2+}$ and their electropolymerization to form films on electrodes are described elsewhere.[23,57] Briefly, to prepare a film of the osmium polymer, the potential applied to a Teflon-shrouded Pt-disk electrode is swept repeatedly between −1.0 and −1.6 V vs. Ag|AgCl in a ca. 0.5 mM, thoroughly degassed acetonitrile solution of monomer. The polymer film thickness increases linearly with the number of reductive potential sweeps as assessed by the increasing reduction-peak currents. The final surface coverage of redox sites (Γ_T) is accurately determined by measuring the electrochemical charge under a slow potential scan cyclic voltammetric curve for the $Os^{III/II}$ or $Fe^{III/II}$ wave in the polymer film, in monomer-free acetonitrile.

Electrochemical experiments were performed in 0.1 M Et_4NClO_4/acetonitrile with cells arranged as in Figure 2 and a conventional potentiostat and triangular wave generator. Electrochemical potentials are referenced to the NaCl-saturated SCE (SSCE). Gold vapor deposition was performed by using locally built equipment, employing resistive electrical heating of the gold to yield deposition rates of 0.2–0.5 Å s^{-1} at pressures of 1×10^{-5} to 2×10^{-5} torr. Gold films of ca. 200–1000 Å were used.

Electrode Conditioning. Following Au evaporation, it was found initially, on all samples, that there was a direct, shorting contact between the Pt electrode and the deposited Au film. The cyclic voltammetry of a Pt|poly$[Os(bpy)_2(p\text{-cinn})_2]^{2+}$ electrode before and after the electrode is covered with an Au deposit is shown in Figure 3, parts A and B, respectively. The short is evidenced in Figure 3B by the large charging current (due to the combined Pt and Au electrode areas) and by an Au oxidation wave at ca. 1.3 V. Since Os(III) sites in the polymer ($E° =$ 0.69 V) cannot mediate the oxidation of Au, the 1.3 V wave must be due to a short. Fortunately, for some electrodes (ca. 10%), continuous scanning of the Pt-electrode potential between 0 and +1.5 V or holding the potential at +1.5 V allowed enough Au to be dissolved to eliminate the short. The results presented here are all for electrodes that have been "conditioned" in this way. Where control of the Au-electrode potential is desired, a fine Pt wire gently pressure-contacts the part of the Au deposit overlapping onto the Teflon collar.

The shorting problem is possibly caused by penetration of Au vapor through the polymer membrane[62] during deposition. It was not eliminated by low deposition rates, because at low rates, powdery non-conducting Au films were produced. Alternatively the short could be caused by threads of Au filling pinhole defects in the polymer which may be especially likely at the edge of the Pt disk. One 1000-Å thread of diameter 100 Å (R = 30 ohms) would probably be sufficient to cause the observed shorting effects.

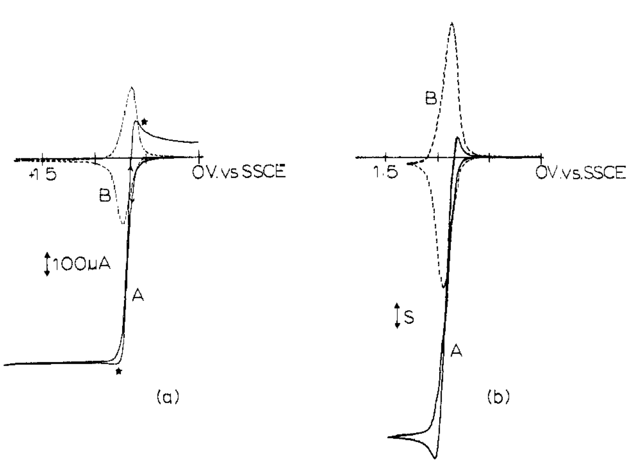

Figure 4. (a) Cyclic voltammograms at 0.1 V/s in 0.1 M Et_4NClO_4/CH_3CN of a Pt|poly$[Os(bpy)_2(p\text{-cinn})_2]^{2+}$|Au electrode (curve A) in the cell arrangement shown in Figure 2A and (curve B) in a normal cell arrangement with the Au electrode not connected. $\Gamma_T = 4.7 \times 10^{-8}$ mol cm^2. (b) Cyclic voltammograms at 0.1 V/s in 0.1 M Et_4NClO_4/CH_3CN of a Pt|poly$[Fe(vbpy)_3]^{2+}$|Au electrode (curve A) in the cell arrangement shown in Figure 2A and (curve B) with a normal cell arrangement with the Au electrode not connected. $\Gamma_T = 4.0 \times 10^{-8}$ mol/cm^2. S = 100 μA for A and 50 μA for B.

Results and Discussion

Poly$[Os(bpy)_2(p\text{-cinn})_2]^{2+}$. Figure 3C shows the cyclic voltammogram of a Pt electrode, coated with a poly$[Os(bpy)_2(p\text{-cinn})_2]^{2+}$ film, with the evaporated, conditioned gold contact not connected to the circuit. The electrochemistry of the polymer is unaffected by the conditioned gold film; the charge under the waves and the separations between the anodic and cathodic peak potentials in the voltammograms in curves A (before coating) and C are the same. This confirms that the gold film is porous and allows free transport of solvent and supporting electrolyte between the bulk solution and the polymer.

In order to create a steady-state mixed-valent osmium polymer film, the electrochemical cell of Figure 2A was used, in which the Pt working electrode acts as electron acceptor and the Au electrode acts as both electron donor and auxilary electrode. Slowly sweeping the potential of the Pt electrode (relative to reference) gives Figure 4a, curve A. Between 0 and +0.4 V vs. SSCE, a negligible current (<5 μA) flows. The Os(II) state of the polymer film has no states for electron transport at these energies and can be regarded as non-conducting. As the Pt-electrode potential approaches the Os(III/II) formal potential, an anodic current flows corresponding to Os(II) → Os(III) turnover at the Pt electrode. This current increases to a plateau of i_{lim} = 0.78 mA with a half-wave (half-maximum) potential, 0.69 V, that is equal to the formal potential of the polymer. The negative-going potential scan is similar. The small peaks (marked with asterisks) observed in the two potential sweeps correspond to the net oxidation and reduction of osmium sites in the film to form the mixed-valent state, as seen by reference to the cyclic voltammetry of the polymer (Figure 4a, curve B). The peaks with asterisks diminish at lowered scan rate, but the S-shaped current–potential curve with plateau current i_{lim} is a true steady-state response and is unaffected by change in potential sweep rate.

Poly$[Fe(vbpy)_3]^{2+}$. A similar experiment was performed by using the electrode arrangement of Figure 2A and poly$[Fe(vbpy)_3]^{2+}$ in place of the osmium polymer. Although the problem of shorting was less severe with this polymer, gold films evaporated on it were often non-conducting after conditioning. Figure 4b shows that the result for the iron polymer is similar to that for the osmium polymer (Figure 4a), and the interpretation is the same. The only notable difference is that the Figure 4b half-wave potential is more positive, 0.90 V, which is equal to the formal potential of the iron polymer. This shows that the potential at which redox conduction occurs is indeed controlled by the potential at which the polymer becomes mixed valent, which is near the formal potential of the polymer.

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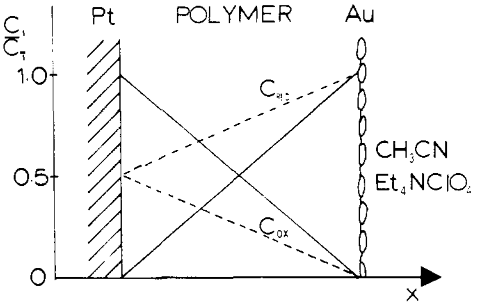

Figure 5. Steady-state concentrations of oxidized and reduced species through the polymer under conditions of maximum (—) and half-maximum (---) current.

Theory

It is now generally accepted that, during oxidation and reduction of redox polymers such as those in ref 11, 18, 22, 26, 31, 32, and 49, electrochemical charge is transported through the polymer by an electron-hopping mechanism.[31] It has been demonstrated experimentally[17,22,48] and theoretically modeled[37,49] that the charge transport can be treated as a diffusion of electrons which follows Fick's diffusion laws. To explain the results in Figure 4, the current driven through the polymer film at each potential is equated to the flux of Os(III) polymer sites at the Pt electrode, which is determined by the concentration gradient of these oxidized sites:

$$\frac{i}{nFA} = \text{CT flux} = \frac{D_{ct}[C_{ox(x=0)} - C_{ox(x=d)}]}{d} \tag{1}$$

where d is the polymer film thickness, x is the distance from the Pt electrode, and D_{ct} is the electron-diffusion coefficient. The steady-state concentrations of Os(III) and Os(II) species in the polymer film under conditions of maximum and half-maximum current are shown in Figure 5. In the experiments in this work, the concentration of Os(III) sites $C_{ox(x=d)}$ is 0 at the Au electrode, since a current flows at this electrode which is equal and opposite to that at the Pt electrode. At the Pt|polymer interface, the concentration of Os(III) sites, $C_{ox(x=0)}$, is given by the Nernst equation (we ignore activity effects[45,63] which cause a minor perturbation of the results)

$$C_{ox(x=0)} = \frac{C_T}{[1 + \exp((nF/RT)(E^\circ - E))]} \tag{2}$$

where $C_T = C_{ox} + C_{red}$ = the total concentration of osmium polymer sites, 1.2×10^{-3} mol/cm^3, based on dry weight film density.[44] Therefore the steady-state redox conduction current is given by

$$i = \frac{nFAD_{ct}C_T}{d[1 + \exp((nF/RT)(E^\circ - E))]} \tag{3}$$

and the limiting current driven through the polymer at sufficiently positive Pt potentials is given by

$$i_{lim} = \frac{nFAD_{ct}C_T}{d} \tag{4}$$

Hence, a value for the electron-diffusion coefficient (D_{ct}) can be obtained from i_{lim} if the polymer film thickness is known. The film thickness can be obtained by electrochemically measuring the surface coverage and using the relation $d = \Gamma_T/C_T$, so

$$i_{lim} = \frac{nFAD_{ct}C_T^2}{\Gamma_T} \tag{5}$$

Values of D_{ct}, for the osmium polymer, obtained from eq 5 are shown in Table I. With some scatter, they agree reasonably with the chronoamperometrically determined[44] value (1.3×10^{-9} cm^2 s^{-1}).

Table I. Electron-Diffusion Coefficient for Poly[Os(bpy)$_2$(*p*-cinn)$_2$]$^{2+}$ from Conductance Measurements

surface coverage Γ_T, mol/cm^2	electrode area A, cm^2	limiting current i_{lim}, µA	diff coeff D_{ct}, cm^2/s
1.6×10^{-8}	0.12	2000	1.8×10^{-9}
2.0×10^{-8}	0.11	560	8.0×10^{-10}
2.1×10^{-8}	0.11	465	7.0×10^{-10}
2.7×10^{-8}	0.12	500	8.1×10^{-10}
4.7×10^{-8}	0.11	1160	3.6×10^{-9}
		av	$1.5 \pm 0.9 \times 10^{-9}$

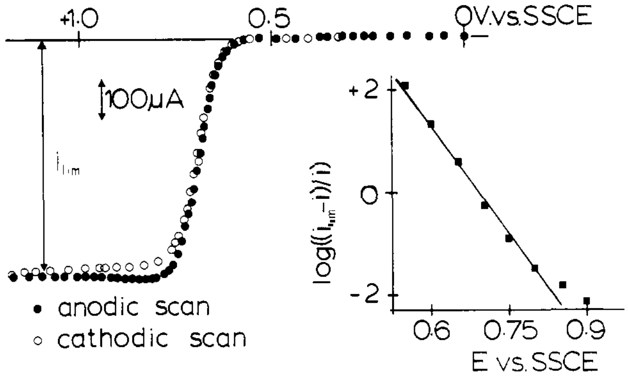

Figure 6. Steady-state current (i) as a function of potential for a Pt|poly[Os(bpy)$_2$(p-cinn)$_2$]$^{2+}$|Au electrode in the cell arrangement shown in Figure 2A, and a plot of log $[(i_{lim} - i)/i]$ vs. E. $\Gamma_T = 4.7 \times 10^{-8}$ mol/cm^2.

The high and low deviations of individual data may come from two sources. The need to "condition" the electrodes before use suggests that the gold contact or filaments thereof can penetrate deep into the polymer. The lower film thickness under residues of such filaments can lead to a smaller average film thickness, enhancing the value of D_{ct}. Second, "conditioning" of the electrodes involves dissolution of some of the gold, which if too extensive can yield a smaller cross-sectional gold contacting area and a small value of D_{ct}. Attention is being given in current experiments therefore to improving the quality of the Au contact used in the wetted sandwich cells.

An expression for the potential dependence of the steady-state redox conduction current can be obtained by combining eq 3 and 4

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{i_{lim} - i}{i} \right) \tag{6}$$

A plot of E vs. log $((i_{lim} - i)/i)$ should be linear with a slope of −59 mV. In order to obtain the experimental data to test this equation it was necessary to eliminate the current peaks due to oxidation/reduction of the polymer film, which was done by incrementing the Pt-electrode potential by small values and waiting for a short time (ca. 15 s) before taking the steady-state current measurement. The point by point result, using the osmium polymer, gave a linear plot of E vs. log $((i_{lim} - i)/i)$, Figure 6 with an experimental slope of −71 mV, which is in reasonable agreement with eq 6 given our neglect of activity effects.[45,63,64]

These results show that the steady-state redox conduction of these polymers can be quantitatively accounted for with simple relations.[53] Importantly, we see that the redox conduction is maximal when the film contains equal quantities of Os(III) and Os(II) states, on the average, but this is a result of achieving a *maximal concentration gradient of Os(III) and Os(II) sites* (recall Figure 5), *not because an average 1:1 Os(II)/Os(III) mixture has an intrinsically maximum conductivity.* In this respect, the interpretation of the present results is distinct from that given[54-56] the conductivity of (dry films) 50/50 mixed-valent redox polymer mixtures.

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(64) Rocklin, R. D.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 2104.

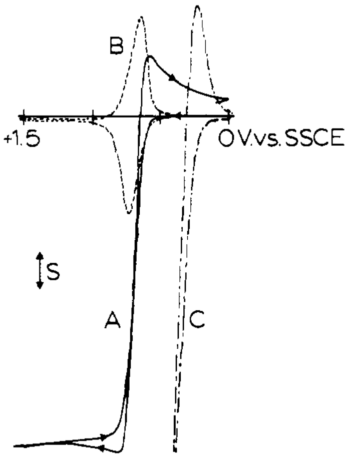

Figure 7. Cyclic voltammograms at 0.1 V/s in 0.1 M Et_4NClO_4/CH_3CN of a Pt|poly[Os(bpy)$_2$(*p*-cinn)$_2$]$^{2+}$|Au electrode (curve A) in the cell arrangement shown in Figure 2B and (curve B) in a normal cell arrangement. $\Gamma_T = 4.7 \times 10^{-8}$ mol/cm^2. Curve C is the voltammogram of a silver wire under the same conditions, $S = 100$ μA for A and B and 50 μA A for C.

A Pseudo-Bilayer-Electrode Experiment. We have shown in other work[57,60] that when a film of one redox polymer is separated from the electrode by another, different redox polymer, oxidation and reduction of the outer polymer film by the electrode becomes constrained to occur via the redox conduction current of the inner polymer film. If the potential(s) at which mixed-valent composition and redox conduction of the inner film is turned on by the electrode is appropriately placed with respect to oxidation or reduction potentials of the outer film, this causes the polymer film/film junction to be a rectifying junction.

In principle, the outer oxidizable or reducible film of a bilayer electrode does not have to be a redox polymer; it can alternatively for instance be a reversibly oxidizable metal or a reversibly reducible metal oxide. Also, the outer film actually does not have to be physically layered on the inner film; it can be located remotely if it is connected to the inner polymer film by a good conductor contact. We have used electrodes prepared in this work to demonstrate these two principles.

Ag oxidation normally occurs at a potential of ca. 0.1 V in acetonitrile as shown in Figure 7, curve C. If in a conventional three-electrode cell the Au contact on a Pt|poly[Os(bpy)$_2$(*p*-cinn)$_2$]$^{2+}$ electrode is connected directly to a silver wire which serves as the oxidizable outer bilayer film,[65] Ag dissolution now does not commence until a more positive potential (ca. 0.5 V) is reached. At the more positive potential, the osmium polymer has become mixed valent and electron transport occurs between the Pt and Au electrodes just as in Figure 4. This particular experimental arrangement suffers from the problem that Ag^+ ions produced by the Ag dissolution can gradually diffuse into the polymer film, be reduced, and cause a short. The problem is avoided by placing the Ag wire and Pt auxilary electrode in a separate cell as in Figure 2B. The resulting voltammogram, Figure 7, curve A, is the same as that obtained with all electrodes in the same cell. Oxidation of the Ag wire becomes in these experiments constrained to occur only when the osmium polymer becomes conducting. The plateau current in Figure 7, curve A, is reached for the same reasons as explained with eq 4, and the limiting current is the same as that observed for the same electrode when used in the cell configuration of Figure 2A.

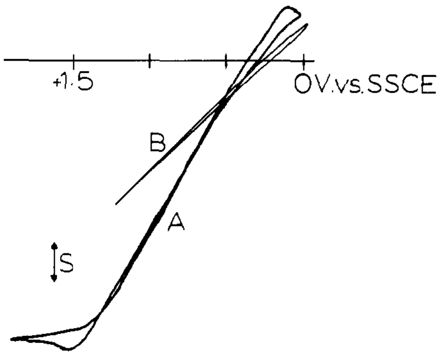

Figure 8. Cyclic voltammograms at 0.1 V/s in 0.1 M Et_4NClO_4/CH_3CN of a Pt|poly[Os(bpy)$_2$(*p*-cinn)$_2$]$^{2+}$|Au electrode (curve A) in the cell arrangement shown in Figure 2C and (curve B) of a silver wire in series with a 4.7K-ohm resistor and used in a normal cell arrangement. $\Gamma_T = 4.7 \times 10^{-8}$ mol/cm^2. $S = 100$ μA for A and 50 μA for B.

The result of Figure 7 shows that a remotely placed, oxidizable metal can be used for the outer film of a bilayer electrode without loss of bilayer rectifying character. The result also illustrates a steady state, as opposed to a transient[57,60] bilayer response, and the control of bilayer current by the rate of inner film (the osmium) electron transport, as opposed to limitation by electron transfer at a film/film interface.

Finally, we have examined a new cell configuration as in Figure 2C, in which the potentiostat now controls the potential of the *outer* bilayer electrode film, which is the Ag wire as described above. The polymer film was electrochemically converted to the 1:1 Os(II)/Os(III) state immediately prior to this experiment. The result of sweeping the Ag wire potential, shown in Figure 8, is a linear ohmic-like trace which achieves a limiting plateau current. Prior to attainment of the limiting current, the osmium polymer film acts as an uncompensated resistance element in series with the Ag "electrode". By reference to the effect of a 4.7K-ohm resistor (curve B), the uncompensated resistance is about 1.4K ohm. The limiting current is the same as observed with the cell of Figure 2A, and so the limiting current reflects the limiting redox conduction current of the osmium film.[66]

It should be repeated that all of the above experiments were conducted with the polymer film wetted with a solvent–electrolyte medium. The electrical conductivity of the dry state of the films has not yet been investigated.

Conclusions

The studies of conduction described here are formally analogous to those conventionally employed for dry pellets and films, namely a sandwich of the specimen between two metal contacts which serve to inject and remove electrons when a voltage is applied. However, in the present case, the film's ability to transport electrons is very dependent upon the applied voltage, relative to the reference electrode voltage. Electron conduction is definitely relatable to the $E°$ of the redox polymer, is dependent on electrochemically generating its mixed-valent state, and is driven by concentration gradients of the polymer oxidation states. This result verifies our characterization[66] of electron transport in redox polymers as occurring in a narrow (potential) band of conductivity. It is this special property of electron conduction by neighbor electron self-exchange reactions that gives bilayer electrode assemblies their unique rectifying properties.

The present measurements of the electron "redox mobility" as D_{ct} agree with the earlier chronoamperometric data. The chronoamperometric measurement[44] depends on the application of Fick's diffusion laws to a condition of transient electron transport control. The steady-state data here reinforce the accuracy of the "diffusing electron" picture.

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Registry No. Poly[Os(bpy)$_2$(*p*-cinn)$_2$](ClO$_4$)$_2$, 85883-07-4; poly[Fe(vbpy)$_3$]SO$_4$, 75931-34-9.

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[65] The Ag wire and Pt auxilary electrode (not connected to the Au film) are in the same cell as the working and reference electrodes.

[66] During these experiments i_{lim} gradually, irreversibly decreased due perhaps to excessive dissolution of the Au contact.