JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 103, NUMBER 1 JANUARY 14, 1981

Rectifying Interfaces Using Two-Layer Films of Electrochemically Polymerized Vinylpyridine and Vinylbipyridine Complexes of Ruthenium and Iron on Electrodes

H. D. Abruña, P. Denisevich, M. Umaña, Thomas J. Meyer, and Royce W. Murray*

Contribution from the Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received May 14, 1980*

Abstract: Polymerization of the complexes $[Ru(bpy)_2(vinyl\text{-}py)_2]^{2+}$ (I), $[Ru(vinyl\text{-}bpy)_3]^{2+}$ (II), $[Ru(bpy)_2(vinyl\text{-}bpy)]^{2+}$ (III), $[Ru(bpy)_2(vinyl\text{-}py)Cl]^{+}$ (IV), and $[Fe(vinyl\text{-}bpy)_3]^{2+}$ (V) can be initiated by electrochemical reduction in CH_3CN solvent to produce stable, adherent, electrochemically active films on Pt, vitreous carbon, SnO_2, and TiO_2 electrodes. Randomly site-mixed copolymer (one-layer) and *spatially segregated* two-layer films of the pairs I and IV and II and V can be prepared by simultaneous and sequential polymerization of the appropriate monomers, respectively. The spatial features were confirmed by variable-angle X-ray photoelectron spectroscopy. Cyclic voltammetry of the copolymers is the additive response of the two redox components. In the two-layer films, however, oxidation state changes of the outer polymer films are constrained to occur via electron-transfer mediation by the inner polymer film. The result is a rectifying property of the polymer two-layer interface which should be useful in mimicking electronic device behaviors such as Zener diodes.

Photosensitization and/or anticorrosive protection of semiconductor/solution interfaces, by coatings of electroactive substances, has experienced much research scrutiny, due to potential use in solar energy conversion schemes.[1] The alternate possibility that electrodes coated with electroactive substances might be made to exhibit rectifying properties even through neither the electrode nor the electroactive substance is individually a semiconductor has on the other hand received no attention. We present here the principle and experimental demonstration of a scheme for unidirectional current flow based on a conductor electrode (e.g., Pt) coated with *two (or more) physically discrete layers of electroactive materials of different redox potentials.* The essence of this two-layer or bilayer scheme[2] is that *electron transfer between the Pt electrode and the outer electroactive layer is forced to occur catalytically, by electron-transfer mediation through redox states of the inner electroactive layer.*

Demonstration of the bilayer scheme is based on the polymeric and copolymeric films of fully metalated vinylpyridine and vinylbipyridine complexes of ruthenium and iron, the chemistry of which is introduced here. A more complete report will be presented elsewhere. These films are the first examples of redox-polymer/modified electrodes[3] where electrode coatings are made by electrochemically initiating polymerization of metal complex monomers bearing vinyl-substituted ligands, e.g., $[Ru^{II}(bpy)_2(vinyl\text{-}py)_2]^{2+}$ (I) (bpy = 2,2′-bipyridine, vinyl-py = 4-vinylpyridine). Given that (i) in complexes like I there exist π-back-bonding interactions which put some electron density in the ligand π^* orbitals[4] and that reduction of the complex is ligand rather than metal localized[5] and that (ii) polymerization of vinylpyridine can be anionically initiated,[6] we reasoned that electrochemical reduction of I might initiate its polymerization. Not only does polymerization in fact occur but also the electrode used for the reductive initiation rapidly becomes coated with a stable, adherent, nonpassifying, electrochemically active, polymeric film of the complex.

---

[1] (a) Wrighton, M. S. *Acc. Chem. Res.* **1979**, *12*, 303. (b) Creutz, C.; Sutin, N. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2858. (c) Finklea, H. O.; Abruña, H.; Murray, R. W. *Adv. Chem. Ser.* **1979**, *No. 184*, 253. (d) Fujihira, M.; Ohishi, N.; Osa, T. *Nature (London)* **1977**, *268*, 226. (e) Miyasaka, T.; Watanabe, T.; Fujishima, A.; Honda, K. *J. Am. Chem. Soc.* **1978**, *100*, 6657. (f) Albery, W. J.; Bowen, W. R.; Fisher, F. S.; Foulds, A. W.; Hall, K. J.; Hillman, A. R.; Egdell, R. G.; Orchard, A. F. *J. Electroanal. Chem.* **1980**, *107*, 37. (g) Hamnett, A.; Dare-Edwards, M. P.; Wright, R. D.; Seddon, K. R.; Goodenough, J. B. *J. Phys. Chem.* **1979**, *83*, 3280.

[2] Although we shall discuss only bilayer electrodes here, the principles presented are readily extended to larger numbers of spatially segregated layers. Our use of the descriptor "bilayer" is not to be taken to mean a double monomolecular layer; here, films are much thicker.

[3] (a) Oyama, N.; Anson, F. C. *J. Electrochem. Soc.* **1980**, *127*, 640. Oyama, N.; Anson, F. C. *J. Am. Chem. Soc.* **1979**, *101*, 739, 3450. (b) Kaufman, F. B.; Engler, E. M. *Ibid.* **1979**, *101*, 547. Kaufman, F. B.; Schroeder, A. H.; Engler, E. M.; Kramer, S. R.; Chambers, J. Q. *Ibid.* **1980**, *102*, 483. (c) Kerr, J. B.; Miller, L. L. *J. Electroanal. Chem.* **1979**, *101*, 263. Kerr, J. B.; Miller, L. L.; Van de Mark, M. R. *J. Am. Chem. Soc.* **1980**, *102*, 3383. (d) Merz, A.; Bard, A. J. *Ibid.* **1978**, *100*, 3222. Itaya, K.; Bard, A. J. *Anal. Chem.* **1978**, *50*, 1487. (e) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135. Daum, P.; Lenhard, J. R.; Rolison, D. R.; Murray, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 4649.

[4] Taube, H. "Survey of Progress in Chemistry", Academic Press: New York, 1973; Vol. 6, p 1.

[5] Salmon, D. J. Ph.D. Thesis, University of North Carolina, Chapel Hill, NC, 1977.

[6] Kalir, R.; Zilkha, A. *Eur. Polym. J.* **1978**, *14*, 557.

0002-7863/81/1503-1$01.00/0

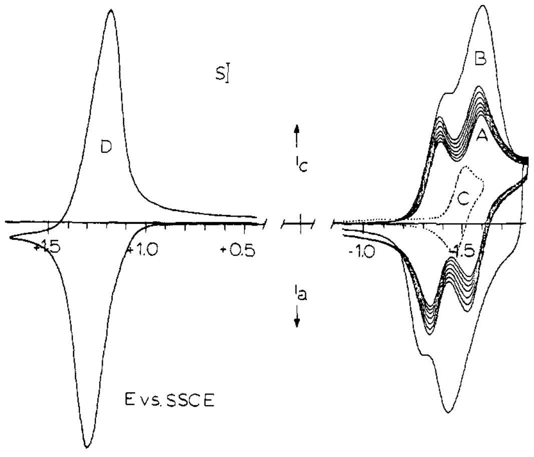

Figure 1. Cyclic voltammograms in 0.1 M Et_4NClO_4/CH_3CN: Curve A, first seven cyclical potential scans between 0 and −1.8 V vs. SSCE of a Pt electrode in an 0.5 mM solution of I, S = 5 μA; curve B, same electrode as curve A, after continuous scanning for 0.5 h and transfer to solution containing no dissolved I, at 1/10 the current sensitivity, S = 50 μA; curve C, a solution of dissolved IV, S = 2.5 μA; curve D, same electrode as curve B, in absence of dissolved I, scanning in the anodic region, S = 25 μA.

This polymerization chemistry seems rather general; related complexes which have been polymerized as films include $[Ru^{II}(vinyl\text{-}bpy)_3]^{2+}$ (II) (vinyl-bpy = 4-vinyl-4′-methyl-2,2′-bipyridine), $[Ru^{II}(bpy)_2(vinyl\text{-}bpy)]^{2+}$ (III), $[Ru^{II}(bpy)_2(vinyl\text{-}py)Cl]^{+}$ (IV), and $[Fe^{II}(vinyl\text{-}bpy)_3]^{2+}$ (V). Electrode materials employed include platinum, vitreous carbon, and the semiconductors SnO_2 and TiO_2.

Films prepared by reduction of one of the monomer complexes I–V are homopolymers (one-layer). If an appropriately chosen pair of complexes such as I and IV or II and V is simultaneously reduced, a one-layer copolymer film can be formed. On the other hand, if an electrode coated with a polymer of one complex is used to reduce a different monomer complex in another solution, a polymer of the second monomer forms at the solution boundary of the first polymer layer; i.e., a bilayer film is made. This procedure has been used to prepare bilayer films of the pairs I and IV and of II and V, where I and II are the inner and IV and V the outer polymer layers. These bilayer electrodes will be compared with the corresponding one-layer copolymer electrodes to demonstrate the rectifying characteristic of the bilayer scheme.

Experimental Section

Chemicals. The ligand 4-vinyl-4′-methyl-2,2′-bipyridine (vinyl-bpy) was prepared according to Spiro and Ghosh.[7] Treatment of 4,4′-dimethyl-2,2′-bipyridine with lithium diisopropylamide generated the α-lithio derivative which was then treated with an excess of dry, gaseous formaldehyde. The resulting 4-(hydroxyethyl)-4′-methyl-2,2′-bipyridine was dehydrated with P_2O_5 to yield the vinyl-bpy species.

A sample of vinyl-bpy employed in early stages of this work was contaminated with ca. 20% (NMR) of the starting material, dimethylbipyridine. The tris(bipyridine) complexes prepared from this sample were thus mixtures of complexes bearing three or fewer vinyl groups. A statistical distribution would be expected to comprise 51% "trivinyl", 38% "divinyl", 10% "monovinyl", and less than 1% unsubstituted (and nonpolymerizing) complex. A sample of II subsequently prepared from pure 4-vinyl-4′-methyl-2,2′-bipyridine gave electrode coatings identical with those prepared from the mixture in all discernible aspects.

Ruthenium and iron complexes I–V were prepared following standard procedures[8-10] (II from $RuCl_3$, III from $Ru(bpy)_2Cl_2{\cdot}2H_2O$, and V from $FeSO_4$). Under the conditions of preparation, no polymerization of the ligand or complexes has been observed.

Electrochemical solvents were 0.1 M Et_4NClO_4/acetonitrile (both for polymerization and electrochemical measurements) and 1 M H_2SO_4.

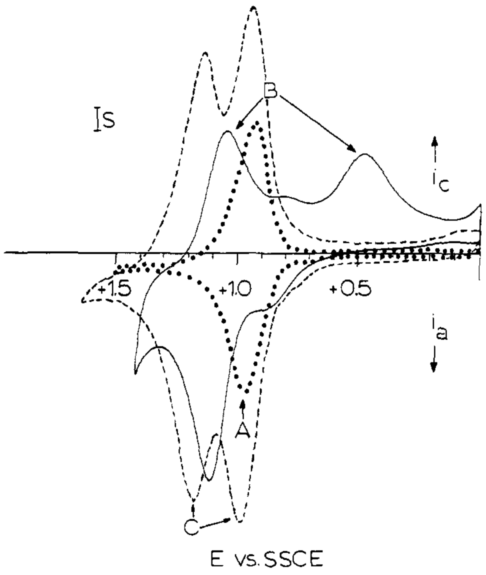

Figure 2. Cyclic voltammograms of polymer films on Pt electrodes: curve A, poly-V in 0.1 M Et_4NClO_4/CH_3CN at 50 mV/s, S = 10 μA; curve B, poly-I in 1 M H_2SO_4 at 200 mV/s, S = 25 μA; curve C, copolymer of poly-II and poly-V in 0.1 M Et_4NClO_4/CH_3CN at 50 mV/s, S = 2.5 μA.

Equipment. Electrochemical potentiostats, triangular wave generators,[11] and electrochemical cells were of local and conventional design. Electrochemical potentials are referenced to the NaCl-saturated SCE (SSCE). X-ray photoelectron spectroscopy (XPS) was conducted on a Physical Electronics Industry Model 548 AR spectrometer equipped with a movable slit for electron emission angular distribution measurements.

Results and Discussion

Electrochemically Initiated Polymerization of Vinylpyridine and Vinylbipyridine Complexes. Figure 1A shows the result of cycling the potential applied to a Pt electrode in a 0.5 mM solution of I in 0.1 M Et_4NClO_4/acetonitrile between 0 and −1.8 V vs. SSCE. From the first cycle, the voltammetric waves grow steadily; an insoluble, presumably polymeric form of I accumulates on the Pt surface. Continuous cycling (0.2 V/s) for 30 min followed by transfer of the thoroughly washed electrode to fresh 0.1 M Et_4NClO_4/CH_3CN containing *no* dissolved I yields well-defined reduction (Figure 1B) and oxidation (Figure 1D) waves for the accumulated polymeric I, designated Pt/poly-I. The formal potential for the poly-I, $Ru^{III/II}$ step, $E^{\circ\prime}_{surf}$ = 1.22 V vs. SSCE, is close to that of monomer I, 1.24 V, and the charge under this surface wave indicates that the film contains 1.45×10^{-8} mol/cm^2 of electroactive ruthenium, which is equivalent to approximately 175 monolayers[12] of I in a layer ca. 0.25 μm thick.

The reductive polymerizations of monomers II and V are qualitatively similar to that of Figure 1. An example of the Pt/poly-V electrode, shown in Figure 2A, has $E^{\circ\prime}_{surf}$ = 0.935 V vs. SSCE, which is identical with $E^{\circ\prime}_{soln}$ = 0.93 V for the $Fe^{III/II}$ wave of monomeric V. Polymerizations of monomers III and IV as homopolymers also occur but yield lower coverages, probably reflecting the importance of cross-linking afforded by multiple vinyl groups.

Polymerization can be effected at constant as well as with scanned potential, and the quantity of polymer deposited on the electrode is controlled by the time of electrolysis and by the negative potential limit. Thus, in experiments conducted as in Figure 1A, varying the time of potential cycling from 5 to 120 min yields coverages of poly-I ranging from ca. 2×10^{-9} to 1.3×10^{-7} mol/cm^2 (e.g., ca. 24–1560 monolayers) as measured by the charge under the $Ru^{III/II}$ wave. Electrochemical properties

---

[7] Spiro, T.; Ghosh, P. *J. Am. Chem. Soc.* **1980**, *102*, 5543.

[8] Braddock, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 3158.

[9] Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

[10] Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3570.

[11] Woodward, W. S.; Rocklin, R. D.; Murray, R. W. *Chem., Biomed. and Environ. Instrum.* **1979**, *9*, 95.

[12] On the basis of packing hard spheres of radius 7.1 Å in a plane, a monomolecular layer of I is estimated as ca. 8.3×10^{-11} mol/cm^2, in a layer ca. 14.2 Å thick.

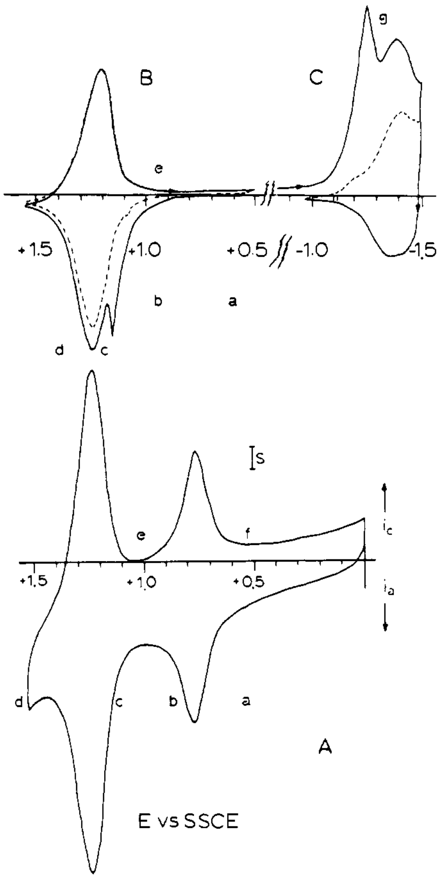

Figure 3. Cyclic voltammograms in 0.1 M Et_4NClO_4/CH_3CN of copolymer Pt/copoly-I,IV (curve A, 100 mV/s, S = 0.5 μA) and two-layer Pt/poly-I/copoly-I,IV (curve b, (—) first scan, (---) second scan, 20 mV/s, S = 10 μA; curve C subsequent negative scan, 50 mV/s, S = 25 μA). Oxidation states in the films, giving the state of I first, at the lettered potentials (a–g) are as follows: copolymer Ru^{II},Ru^{II} (a), Ru^{II},Ru^{III} (b), Ru^{II},Ru^{III} (c), Ru^{III},Ru^{III} (d), Ru^{II},Ru^{III} (e), Ru^{II},Ru^{II} (f); (—) bilayer Ru^{II}/Ru^{II} (a), Ru^{II}/Ru^{II} (b), Ru^{II}/Ru^{III} (c), Ru^{III}/Ru^{III} (d), Ru^{II}/Ru^{III} (e), Ru^{II}/Ru^{III} (f); (---) bilayer Ru^{II}/Ru^{III} (a), Ru^{II}/Ru^{III} (b), Ru^{II}/Ru^{III} (c), Ru^{III}/Ru^{III} (d), Ru^{II}/Ru^{III} (e), Ru^{II}/Ru^{III} (f), Ru^{II}/Ru^{III} (g).

of the films are well-defined over this coverage range; the thicker ($\geq 10^{-8}$ mol/cm^2) films show larger ΔE_{peak} values and broadened waves. Polymerization of I also proceeds, but more slowly, at potentials confined to the first monomer reduction wave only (e.g., −1.37 V). On the other hand, potentials oxidizing monomer I to the Ru^{III} state or simple exposure of the Pt surface to a solution of I does not result in polymeric accumulation of I on the Pt surface.[13] These results show that polymerization and electrode deposition is most favored by a highly reduced form of the complex, which is consistent with (but does not prove) the hypothesis (vide supra) associating a ligand-centered reduction with anionic polymerizability of 4-vinylpyridine.

The electrochemical polymerization mechanism has chain propagation character. A Pt electrode at −1.4 V vs. SSCE in a solution of IV accumulates no polymer on the surface; this potential is insufficient to reduce IV ($E^{\circ\prime}_{\text{soln}}$ = −1.49 V, Figure 1C). Monomer I, however, does form a polymer film at −1.4 V. A Pt electrode in a solution 0.08 mM in I and 0.25 mM in IV to which a potential of −1.4 V vs. SSCE is applied for 120 min, reducing only the smaller concentration of I, nonetheless incorporates a significant quantity of IV into the film as a copolymer constituent. See the Pt/copoly-I,IV film voltammogram in Figure 3A. In fact, formation of polymeric films of IV is aided by addition of a small concentration of I to the monomer solution, forming the copolymer film by reducing I at −1.4 V.

While our stability experiments are not exhaustive, these polymer films seem very durable to repeated potential cycling, and are stable and remain electroactive in other solvents such as CH_2Cl_2 and 1 M H_2SO_4. In 1 M H_2SO_4, for example, no measurable change in the $Ru^{3+}/^{2+}$ wave results from continuously cycling a Pt/poly-I electrode between −0.2 and 1.4 V vs. SSCE for 15 min or from soaking in the same solution for 16 h. Interestingly, the cyclic voltammogram in this case[14] shows, in addition to the $Ru^{III/II}$ polymer surface wave, the platinum oxide forming and stripping waves (Figure 2B). It is striking that oxide films can be formed and reduced repeatedly at the interface between the platinum and the polymer films without adverse effect on either the polymer's charging rate or stability. The ability to generate a stable polymer film containing $[Ru(bpy)_3]^{3+}$-like states in aqueous media is an important and encouraging result.

Immobilization of ruthenium complexes with highly oxidizing redox potentials on electrode surfaces has been actively pursued once it was recognized that such complexes could act as photosensitizers in solar energy conversion schemes.[15] Such complexes have also attracted interest because, on *n*-type semiconductors undergoing bandgap absorption, they could serve as electron-transfer mediators with greater oxidizing power than the presently used ferrocenes.[16] The complex $[Ru^{II}(bpy)_3]^{2+}$ is particularly attractive, having a high oxidation potential ($E^{\circ\prime}_{\text{soln}}$ = 1.29 V[17] and 1.02 V[18] vs. SSCE in Et_4NClO_4/CH_3CN and 1 M H_2SO_4, respectively), being chemically robust, and having an unusually long-lived ($\tau \approx 0.6$ μs) charge-transfer excited-state $[Ru(bpy)_3]^{2+*}$ thermodynamically capable[19,20] both of oxidizing water to oxygen and of reducing it to hydrogen at pH 7.

With this in mind and since the monomers I and II are close structural analogues of $[Ru(bpy)_3]^{2+}$, it was of interest to see whether polymeric films of these complexes could be deposited on *n*-type semiconductors. Since the flat band potentials of SnO_2 and TiO_2 in acetonitrile are both less negative than the potentials required to reduce I and II making their behavior metal-like in this potential region, deposition of polymeric films proved to be straightforward. These coated materials are being further studied.

Films deposited on Pt and on optically transparent SnO_2 are visibly colored, golden to orange, depending on thickness, and optical spectra of the polymers can be employed in their analysis. A spectrum of a polymer film of I on optically transparent tin oxide for example exhibits $\lambda_{\max}$ = 438 nm in acetonitrile which agrees with $\lambda_{\max}$ = 432 nm for dissolved monomer I. Elemental analysis of a sample of poly-I harvested from a thick coating on SnO_2 furthermore agrees with the expected stoichiometry.[21] These results plus the agreement of poly-I and monomer I formal potentials indicate that the ruthenium coordination sphere remains essentially intact upon polymerization and that poly-I can be regarded as nearly if not fully metalated. This latter aspect is of interest since attempts at binding metals to *preformed* polymer ligand backbones typically result in incomplete metalation.[3a,22]

---

[13] If a Pt electrode is immersed in an acetonitrile solution of $[Ru(bpy)_2(vinyl\text{-}py)_2]^{2+}$ for 4 h, some bonding occurs ($< 3 \times 10^{-11}$ mol/cm^2), presumably by interaction of the vinyl groups with the Pt surface.

(14) In Figure 2B, the waves at $E_{p,a}$ = +0.88 and $E_{p,c}$ = +0.49 V are associated with platinum oxide formation and reduction, respectively, while those at $E_{p,a}$ = +1.14 V and $E_{p,c}$ = +1.05 V are associated with the film of poly-I. The identity of the wave at $E_{p,c}$ = +0.80 V is unknown.

(15) (a) For recent reviews see: Meyer, T. J. *Acc. Chem. Res.* **1978**, *11* 94. (b) Sutin, N.; Creutz, C. *Adv. Chem. Ser.* **1978**, *No. 168*, *1*.

(16) Wrighton, M. S. *Chem. Eng. News* **1979**, 29 (Sept 3).

(17) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582.

(18) Lin, C. T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536.

(19) Creutz, C.; Sutin, N. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2858.

(20) $[Ru(bpy)_3]^{2+*/3+}$ (E° +0.84 V vs. NHE), $[Ru(bpy)_3]^{2+*/+}$ (E° = −0.84 V vs. NHE). The redox properties of this system can be further enhanced by ca. 0.4 V by oxidative or reductive quenching to give $[Ru(bpy)_3]^{3+}$ ($[Ru(bpy)_3]^{3+/2+}$, $E^{\circ\prime}$ = 1.29 V) or $[Ru(bpy)_3]^{+}$ ($[Ru(bpy)_3]^{2+/+}$, $E^{\circ\prime}$ = −1.32 V), respectively, see: (a) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815; (b) Anderson, C. P.; Salmon, D. J.; Meyer, T. J.; Young, R. C. *Ibid.* **1977**, *99*, 1980; (c) Maestri, M.; Graetzel, M. *Ber. Bunsenges. Phys. Chem.* **1977**, *81*, 504; (d) Mulazzani, Q. G.; Emmi, S.; Fuochi, P. G.; Hoffman, M. E.; Venturi, M. *J. Am. Chem. Soc.* **1978**, *100*, 981; Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83.

(21) Calcd: C, 49.6; N, 10.21; H, 3.65. Found: C, 49.3; N, 9.45; H, 3.49.

We should note that the present ruthenium polymer films differ from those described by Oyama and Anson[3a] in having a preformed monomer and thus a well-defined metal coordination in the polymer film. In addition, these films are probably cross-linked and thus insoluble in a range of solvents, are amenable to copolymerization, and achieve high oxidation potentials similar to $[Ru(bpy)_3]^{3+}$. With the synthetic versatility afforded by the monomer $[Ru(vinyl\text{-}bpy)_2Cl_2]$ (by analogy to $[Ru(bpy)_2Cl_2 \cdot 2H_2O]$), we hope to prepare copolymer films, with an array of formal potentials, which would serve as generalized outer-sphere electrocatalysts. Studies along this line are being pursued.

The Bilayer Scheme. When a pair of monomer metal complexes is simultaneously reduced to form a randomly mixed one-layer copolymer, the two types of monomer sites exhibit independent, facile electron-transfer reactions with the underlying electrode at the expected potentials.[23] This is demonstrated for a one-layer copolymer of II and V made by cycling the potential between 0.0 and −1.8 V vs. SSCE in an equimolar solution of monomers II and V in Figure 2C.

Consider now a bilayer electrode made from monomers I and IV by (i) potentiostatting a Pt electrode at −1.75 V vs. SSCE in 0.3 mM I for 60 min, (ii) washing, and (iii) potentiostatting this surface at −1.4 V in 0.017 mM I plus 0.25 mM IV for 60 min, all in 0.1 M Et_4ClO_4/CH_3CN. In (iii) the small amount of I facilitates polymerization of IV, forming an outer film copolymer, so the bilayer electrode is most precisely designated Pt/poly-I/copoly-I,IV.[24] Cyclic voltammetry of this bilayer electrode (Figure 3B) is strikingly different from the corresponding one-layer copolymer (Figure 3A). The "truth table" in the figure legend compares bilayer and one-layer copolymer ruthenium oxidation states at the indicated potentials. In the bilayer film, the (outer-film)-poly-IV sites, isolated from the Pt, are not oxidized at potential b. Instead, when potentials (c) generating a small population of Ru^{III} sites in the inner poly-I film are attained, (Ru^{II})poly-IV sites are oxidized by these through catalytic electron-transfer mediation at the poly-I-poly-IV interface. The inner-film-mediated oxidation of the outer film typically occurs as a sharp prewave,[25] which is followed by a wave for oxidation of the rest of the inner film (Ru^{II})poly-I sites. At potential d, the bilayer film is fully oxidized (all Ru^{III}).

When the potential scan is reversed, a current peak for reduction of Ru^{III} sites in the inner film (i.e., (Ru^{III})poly-I) is observed (Figure 3B), but the (Ru^{II})poly-I film is thermodynamically incapable of mediating the reduction of the outer (Ru^{III})poly-IV film. Furthermore, since these (Ru^{III})poly-IV sites are isolated from the Pt electrode by the inner poly-I film, no reduction wave for the outer poly-IV film is observed. The outer film sites remain trapped in the Ru^{III} state. As a consequence the prewave associated with the catalytic oxidation of the outer poly-IV film is greatly attenuated or entirely absent[26] in a subsequent anodic potential scan cycle (dashed curve, Figure 3B). These events demonstrate that electron transfer across the interface between the two polymer films of the bilayer is unidirectional (i.e., rectifying) for the outer, poly-IV ruthenium sites, mimicking an *n*-type semiconductor.

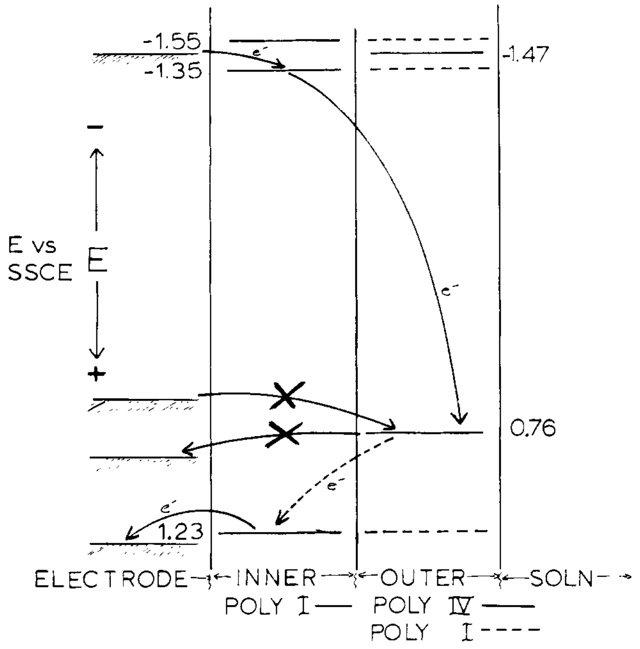

Figure 4. Schematic energy level diagrams for bilayer electrode Pt/poly-I/copoly-I,IV, showing the electron-transfer events of Figure 3.

Some of the most interesting potentialities of bilayer (or multilayer) modified electrodes arise from the manner in which trapped states are released. In the above experiment, trapped Ru^{III} sites in the outer poly-IV film in principle can be released by (i) exposure to a CH_3CN solution of monomer IV or other suitable reductant, (ii) scanning the electrode potential negatively to the bpy-localized reduction of poly-I, (iii) photogeneration of (Ru^{III}, $bpy^{-}\cdot$)poly-I excited states in the inner and outer film with subsequent electron-transfer quenching by trapped (Ru^{III})poly-IV sites, or (iv) electrolysis by a *second working electrode in contact with the outer film*. We have demonstrated trapped-site release for i and ii. For ii, Figure 3C shows a negative-going potential scan in which trapped (Ru^{III})poly-IV sites become reduced in a sharp catalytic prewave (potential g) by Ru^{II},$bpy^{-}\cdot$ sites generated in the poly-I film, analogous to the anodic catalytic prewave. An anodic potential scan following procedure i or ii quantitatively repeats the first scan result of Figure 3B. Note that in the bilayer Pt/poly-I/copoly-I,IV electrode, the normally reversible $Ru^{III/II}$ reactions of IV now occur in sharp oxidation and reduction peaks separated by a potential of 2.2 V. Also notable is that, at −1.0 V, trapped (Ru^{III})poly-IV sites in the outer layer are still not released even though the total potential drop across the inner layer, between the electrode and the $(Ru^{3+/2+})$poly-IV outer-layer electron level, can be estimated at ca. 10^5 V/cm.[27]

Essential to the functioning of the bilayer scheme is the ability of the inner layer to electrocatalytically oxidize (or reduce) species at its outer boundary. We have demonstrated this directly with one-layer Pt/poly-I and Pt/poly-II electrodes in solutions of $[Ru^{II}(bpy)_2pyCl]^+$, whose normal oxidation wave at $E^{\circ\prime}_{soln} = +0.79$ V vs. SSCE is suppressed by the polymer but occurs concurrently with the film's $Ru^{III/II}$ wave at +1.2 V. The reaction

$$\text{Pt/poly-II}(Ru^{III}) + [Ru^{II}(bpy)_2pyCl]^+ \rightarrow \text{Pt/poly-II}(Ru^{II}) + [Ru^{III}(bpy)_2pyCl]^{2+}$$

proceeds at the film's outer boundary just as in the bilayer electrode above. Reduction of the cation *N*,*N*′-dimethyl-4,4′-bipyridinium (methylviologen) is also suppressed at Pt/poly-II electrode surfaces, which shows that the polymer films are free from significant pinholes. This is important in preparing bilayer films whose inner layers are not "leaky". This result also demonstrates charge exclusion of cations by the anion-exchange

---

[22] (a) Calvert, J.; Meyer, T. J. *Inorg. Chem.*, in press. (b) Tsuchida, E.; Nischide, H. *Adv. Polym. Sci.* **1977**, *24*, 1.

[23] In Figure 3A, $E^{\circ\prime}_{surf}$ = +1.23 and +0.76 V vs. SSCE as compared to $E^{\circ\prime}_{soln}$ = +1.24 and +0.76 V for monomers I and IV, respectively. These electron transfers presumably occur via electron hopping between like neighbor complex sites and so extreme dilution of one site with the other may impede reactions of the dilute sites.

[24] $\Gamma_{poly\text{-}I} = 1.5 \times 10^{-8}$ (inner) + 1.3×10^{-8} (outer); $\Gamma_{poly\text{-}IV} \approx 1.3 \times 10^{-8}$ (outer) mol/cm^2.

[25] A preliminary theory has been developed which accounts qualitatively for the shape and sweep-rate dependence of the sharp prewave, in which the inner polymer layer is considered to be under Nernstian control with electron transfer between inner and outer layers taking place through a second-order chemical step. The rate of this reaction and its associated current thus increase as the inner layer is oxidized and fall off as the outer layer is depleted. P. Denisevich, University of North Carolina unpublished results, 1980.

[26] This results if the potential scan is repeated within a few minutes; background-electron-transfer reactions or bilayer imperfections otherwise slowly discharge trapped Ru^{3+} in poly-IV.

[27] Most of this potential drop actually occurs over the much thinner electrode/inner film double layer.

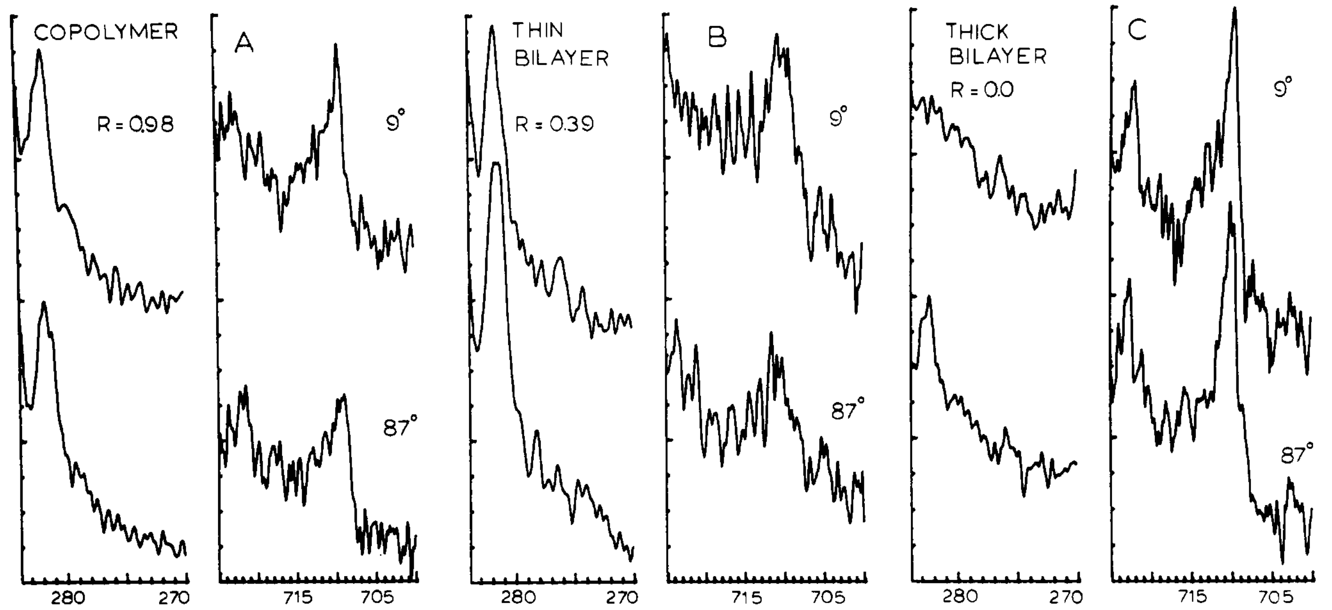

Figure 5. X-ray photoelectron spectra as a function of emission angle θ for Ru $3d_{5/2}$ (BE = 281 eV) and Fe $2p_{3/2}$ (BE = 710 eV) sites in one-layer copolymer Pt/copoly-II,V and bilayer Pt/poly-II/poly-V electrodes, where the poly-V film thickness d for the right-hand bilayer specimen is ca. 3× that of the middle bilayer. Intensity ratio numbers given as $R = [\text{Ru } 3d_{5/2}/\text{Fe } 2p_{3/2}]_{9°}/[\text{Ru } 3d_{5/2}/\text{Fe } 2p_{3/2}]_{87°}$ are (i) independent of θ for copolymer and (ii) smaller for larger d.

polymer films, which is important in avoiding intrusion of cationic monomer IV into the inner film during its polymerization in the bilayer film preparation.

The bilayer scheme for the Pt/poly-I/copoly-I,IV electrode is schematically presented in Figure 4 to emphasize the events discussed above. The essential criteria for successful operation of a bilayer-modified electrode are (i) the inner layer should insulate the outer layer from the electrode at all electrode potentials except those whereby redox reactions of the inner layer occur, which are placed so as to mediate electron transfer between the electrode and outer layer, (ii) the outer layer should be permeable to counterion flow demanded by the redox reactions of the inner layer, (iii) there should be minimal overlap of energy distributions of redox levels of inner and outer polymer film components, and (iv) for repetitive rectification events, release of trapped outer states should be feasible by one or more of the four procedures outlined above. These criteria are well satisfied in Figure 4.

Overlap of the energy distribution functions of inner- and outer-film redox states has a strong bearing on the *lifetime* of trapped outer-film states. For instance, the difference in $E^{\circ\prime}_{\text{surf}}$ of poly-II and poly-V is 0.10 V, as compared to the 0.47-V difference for poly-I and poly-IV. Thus, in a bilayer electrode made from II and V, Pt/poly-II/poly V, the first scan cyclic voltammetry is quite similar to Figure 3B, but on a second anodic potential scan cycle the sharp prewave for (Ru^{III})poly-II inner-film mediated oxidation of outer-film (Fe^{II})poly-V is only mildly suppressed. In the interval between the two scans, the distribution function overlap of (Ru^{II})poly-II and (Fe^{III})poly-V states has allowed the latter trapped states to slowly leak away. We have observed the behavior of additional polymer bilayer films to confirm that the magnitude of the difference in $E^{\circ\prime}_{\text{surf}}$ between the bilayer components is important in the perfection of the trapping process. For instance, a bilayer film made by evaporatively coating a Pt/poly-II electrode with a film of polyvinylferrocene can trap ferricenium outer layer states[28] for periods well in excess of 30 min without significant decay.

In the interest of directly demonstrating the bilayer spatial distribution of Ru and Fe sites in a Pt/poly-II/poly-V bilayer electrode, we have measured the relative X-ray photoelectron intensities from these sites as a function of emission angle (θ) relative to the surface plane[29] (Figure 5). Attenuation of poly-II Ru 3d photoelectrons by the poly-V film (of thickness d) depends exponentially on $d/\sin\theta$, so that in the spatially segregated bilayer film the intensity ratio for Ru 3d/Fe 2p photoelectrons decreases[30] substantially at low angle (θ = 9°) as compared to high angle (θ = 87°). In contrast and as ideally expected, the Ru 3d/Fe 2p intensity ratio is independent of θ for a randomly site-mixed copolymer Pt/copoly-II,V electrode.

These results are presented as supporting a scheme of rectifying and charge-trapping behavior for bilayer-modified electrodes which should be extendable to additional applications, including electrodes mimicking Zener diodes, transistors, optical switches, and solar collectors, among others. Experiments on such extensions will be described in future reports.

Acknowledgment. This research was supported in part by grants from the National Science Foundation and the Office of Naval Research. This is No. 27 in a series of Chemically Modified Electrodes.

---

[28] P. Denisevich, University of North Carolina, unpublished results, 1980.

[29] Fadley, C. S. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *5*, 725.

[30] The effect of angle θ is enhanced for a thicker poly-V film (compare Figure 5B,C), as expected for bilayer Ru/Fe site segregation.