to charging and discharging an imaginary capacitor.[28] The term "chemical capacitance" has been introduced to describe this capacitance contribution to the observed photovoltage.[8]

Incorporation of CdS into one side of a BLM appears, a priori, to be similar to the incorporation of a cyanine dye. The photoelectric behavior of these two systems is, however, completely different. In the semiconductor-coated BLM, unlike in that covered by the cyanine dye, electron transfer across the bilayer is permitted. Electron transfer products are formed in the solution bathing the opposite sides of the BLM during irradiation, with little depletion of the semiconductor. At the end of irradiation, the steady-state photovoltage simply decays by leakage through the membrane with its characteristic R_mC_m time constant, even though the electron-transfer products are stable in the cis and trans sides of the BLM.

Photoelectrochemistry has been investigated in several systems in which pigments were freely distributed in the BLM.[8,29-34] Chlorophyll and synthetic porphyrin derivatives have been used as pigments, while ferricyanide or MV^{2+} were typically introduced as electron acceptors. Pulsed light irradiation of such a pigmented BLM has resulted in charge separation, due to electron transfer in one of the membrane interfaces. This gave rise to a transient photovoltage signal which decayed as a result of charge recombination. The electron-transfer process for the magnesium octaethylporphyrin pigmented BLM was found to be dynamic; the risetime of the photovoltage signal depended on the concentration of the acceptor ($(Fe(CN_6)^{3-}$, MV^{2+}, or anthraquinone-2-sulfonate) present in the bathing solution.[31] This behavior is, of course, very different from that observed in the photoelectrochemistry of the CdS-coated GMO BLM system, studied in the present work. The photovoltage risetime has been found to be independent of the electrolyte concentration (Figure 7), as expected, since the electron transfer occurs on molecules absorbed on the semiconductor surface rather than at the BLM–water interface.

There is also a difference in the decay of the photovoltage signal. In the pigmented BLM, this decay has been found to be long and distinctly non-exponential.[30] The linearity of the plot of V against log T (where T is time elapsed after the pulse) and the insensitivity of the first half-life time on the intensity of the laser pulse is in accord with distributed rate constants arising from different distances (6.5–10 Å) between donors and acceptors at the BLM–water interface. In the CdS-incorporated GMO BLM system, the photovoltage decay followed a much more ideal second-order behavior. This reflects that recombination (eq 11) occurs with a uniform rate constant in a more constrained configuration at the surface of the semiconductor particles. The large magnitude of the observed photovoltage can be attributed to the large asymmetric potential existing across the CdS-containing BLM in our system.

Acknowledgment. Support of this research by the Department of Energy is gratefully acknowledged. We appreciate the critical and thoughtful comments made by the referees on an earlier version of this paper.

Chemical Phenomena in Solid-State Voltammetry in Polymer Solvents

L. Geng,[†] R. A. Reed,[‡] M.-H. Kim,[§] T. T. Wooster, B. N. Oliver,[‖] J. Egekeze,[⊥] R. T. Kennedy, J. W. Jorgenson, J. F. Parcher,[+] and Royce W. Murray*

Contribution from the Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290. *Received July 5, 1988*

Abstract: This paper, aimed at delineating significant chemical effects in solid-state voltammetry, describes electrochemical oxidations and reductions of electroactive monomer solutes dissolved in and diffusing through rigid and semirigid polymer electrolyte solvents. Sorption of organic monomer vapors into poly(ethylene oxide) films yields polymer solvents whose chemistry is dominated by that of the sorbed monomer as shown by coordination and precipitation effects. The dynamics of plasticization-induced changes in transport rates are quite rapid. Physical diffusion in the polymer solvent in slow enough that electron hopping reactions measurably enhance charge transport rates; the effect was used to estimate a lower limit for the $[Co(bpy)_3]^{2+/+}$ self-exchange rate constant of 2×10^9 M^{-1} s^{-1}. It is possible to erect polymeric film transport barriers at the electrode/polymer solvent interface and to measure the rate of permeation of monomer complexes from the polymer solvent into the polymer transport barrier film. Polymeric films of Os and Ru polypyridine complexes can be electropolymerized from polymer solutions of the corresponding monomers. Solid-state voltammetry can be extended to other polymer solvents including sulfonated polystyrene, poly(vinyl chloride), Nafion, and poly(acrylamide) gel.

This paper describes electrochemical oxidations and reductions of electroactive monomer solutes dissolved in and diffusing through rigid and semirigid polymer electrolyte[1] solvents. The use of polymers as rigid solvents for heterogeneous electron-transfer chemistry is a recent development[2-4] and little is as yet known about this form of solid-state chemistry. This paper describes experiments aimed at delineating significant chemical characteristics of electrochemical reactions in polymeric solutions, including how rigid solvent environments affect rates and mechanisms of electron-transfer reactions and mass transport rates. This paper will also demonstrate how molecular films can be used to

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[†] Brookhaven National Laboratories, Upton, NY 11973.

[‡] Dept. of Chemistry, Princeton University, Princeton, NJ 08544.

[§] Dept. of Chemistry, Old Dominion University, Norfolk, VA 23508.

[‖] Laboratory of the Government Chemist, Waterloo Road, London SE18XY.

[⊥] Dept. of Chemistry, Augusta College, Augusta, GA.

[+] Dept. of Chemistry, University of Mississippi, University, MS 38677.

(1) (a) Armand, M. B. *Annu. Rev. Mater. Sci.* **1986**, *16*, 245. (b) Vincent, C. A. *Prog. Solid State Chem.* **1987**, *17*(3), 145. (c) Ratner, M. A.; Shriver, D. F. *Chem. Rev.* **1988**, *88*, 109.

(2) (a) Reed, R. A.; Geng, L.; Murray, R. W. *J. Electroanal. Chem.* **1986**, *208*, 185. (b) Oliver, B. N.; Egekeze, J.; Murray, R. W. *J. Am. Chem. Soc.* **1988**, *110*, 2321. (c) Geng, L.; Reed, R. A.; Longmire, M.; Murray, R. W. *J. Phys. Chem.* **1987**, *91*, 2908. (d) Oliver, B. N.; Egekeze, J.; Murray, R. W., manuscript in preparation.

(3) Geng, L.; Longmire, M. L.; Reed, R. A.; Parcher, J. F.; Barbour, C. J.; Murray, R. W. *Chem. Mater.* **1989**, *1*, 58.

(4) (a) Skotheim, T. A. *Synth. Met.* **1986**, *14*, 31. (b) Skotheim, T. A.; Florit, M. I.; Melo, A.; O'Grady, W. E. *Mol. Cryst.* **1985**, *121*, 291. (c) Skotheim, T. A.; Inganas, O. *Mol. Cryst., Liq. Cryst.* **1985**, *121*, 285. (d) Skotheim, T. A.; Florit, M. I.; Melo, A.; O'Grady, W. E. *Phys. Rev. B* **1984**, *30*, 4846. (e) Inganas, O.; Skotheim, T. A.; Feldberg, S. W. *Solid State Ionics* **1986**, *18/19*, 332. (f) Raleigh, D. O. *Electroanal. Chem.* **1973**, *6*, 87.

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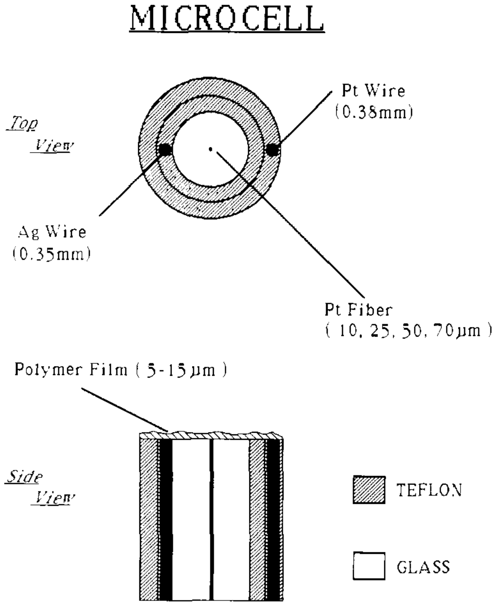

Figure 1. Schematic of microcell. A small-diameter Pt wire is sealed in a borosilicate glass capillary and larger Pt and Ag wires are attached to its perimeter with heat-shrink Teflon tubing. The polymer film is cast on top of the polished smooth platform in which the three disk electrodes lie in a common plane.

modify the interfaces of electrodes contacted by rigid solutions in ways analogous to those demonstrated for chemically modified electrodes in fluid media.[5]

There are both advantages and problems in using rigid solvents for experimental voltammetry. The cell solution needs no confining walls, can be shaped as a thin film that will sorb or desorb reagents from contacting bathing gases, and as a thin film can be used to confine reagents near the electrode surface with no special attachment chemistry.[5] Diffusion rates of redox solutes can be manipulated via polymer solvent plasticization[3] or temperature, and solid-state cells are readily miniaturized for sensor applications. The variety of useful rigid solvent media is furthermore potentially considerable, including ionically conducting polymers,[3] organic and inorganic gel polymers,[2] and ordered phases. The problems are that rigid solvents offer meager ionic conductivity, which requires compensation by use of miniaturized electrodes (microelectrodes[6]) and cells to make the currents and ionic transport distances small. Diffusion is slow in rigid media, making currents less sensitive to concentration and to rapid heterogeneous electron transfers and other kinetic events of interest. Polymer solvents can be inhomogeneous, due to reagent crystallization or polymer solvent microcrystallization or phase separation as exemplified by PEO[3] and Nafion.[7] Novel shapes of the cell solution and the electrode may require development of supporting mass transport theory. Solutions to such problems can be foreseen, however.

Our design[2] for voltammetric experiments in polymer solvents employs a disk microelectrode as working electrode, with wire tip reference and auxiliary electrodes lying in a common plane (Figure 1), over which is cast a film of an ionically conductive polymer containing the electroactive solute(s). The 1–50-μm-thick polymer film is readily equilibrated with a bathing gas. This way of adding or removing reagents to(from) the polymer solution proves to be a particularly potent tactic for invoking chemical effects in polymer solvents, as we will illustrate.

Experimental Section

Electrochemical Cells and Equipment. Construction of the microcell in Figure 1 and the high-sensitivity potentiostat have been described.[2,6b] The working, auxiliary, and reference electrodes are 10-μm-diameter Pt, 380-μm-diameter Pt, and 350-μm-diameter Ag wire tips, respectively. The potential of the Ag pseudo-reference electrode was calibrated vs the ferrocene$^{1+/0}$ potential where necessary. Experiments using poly(acrylamide) gels used an analogous cell design[2b] except that the working electrode was a macrosized (0.24-cm-diameter) edge-plane graphite (EPG) disk and the auxiliary electrode was a concentric Pt ring.

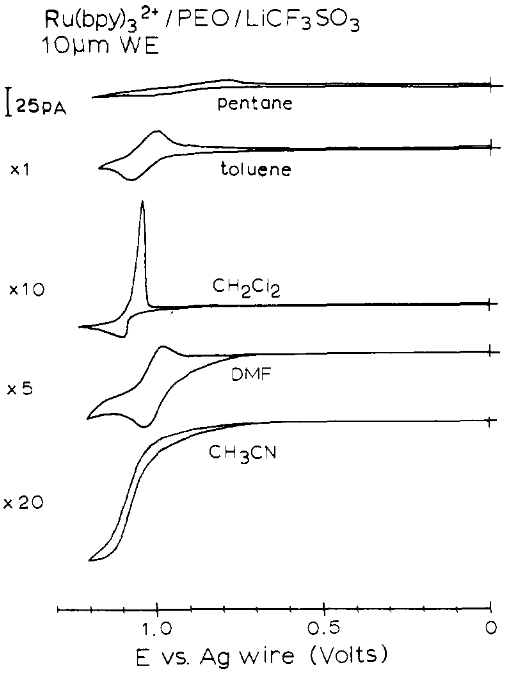

Figure 2. Cyclic voltammetry (v = 50 mV/s) of $[Ru(bpy)_3](PF_6)_2$ dissolved in a $PEO_{15}/LiCF_3SO_3$ film cast over a 10-μm Pt microdisk electrode with the electrode immersed in saturated (room temperature) vapors of indicated organic monomers.

Polymer Solutions. Purification[8] of MW 600 000 PEO and preparation[2b] of the lightly cross-linked polyacrylamide gels have been described. The casting solvent for PEO was 9:1 CH_3CN/CH_3OH, in which was dissolved the PEO, the $LiCF_3SO_3$ electrolyte in a 15:1 molar ratio of ether oxygen/Li^+, and the desired electroactive solute. The film is cast onto the microcell by evaporating enough 10–20-μL microdroplets of this solution to build up a film from 1 to 50 μm thick. These polymer films are denoted as $PEO_{15}/LiCF_3SO_3$.

The poly(acrylamide) gel was thoroughly washed after preparation[2b,d] and dried, and a slice of dry gel was cemented onto the EPG macrocell by wetting with a microdroplet of water or electrolyte solution.

Results and Discussion

Chemical Effects of Bathing Gases. The behavior of polymer solvents is strongly modified in the presence of bathing gases containing monomers that can sorb into the polymer. This is an important experimental tactic in exploring chemical effects in polymer solvents,[2,3] as we will illustrate with diffusion rate and film formation phenomena incited by bathing gas sorption.

Currents for the electrochemical oxidation of $[Ru(bpy)_3]^{2+}$ dissolved in $PEO_{15}/LiCF_3SO_3$ depend on the gas bathing the polymer as shown in Figure 2. A pentane (or dry N_2) bathing gas gives small, ohmically distorted oxidation currents which reflect a low mobility for both $[Ru(bpy)_3]^{2+}$ and $LiCF_3SO_3$ in this polymer. $PEO/LiCF_3SO_3$ is known[1] to be partially microcrystalline. The estimated room temperature diffusion coefficient of $[Ru(bpy)_3]^{2+}$ in dry PEO is ca. 10^{-10} cm^2/s.

Exposing the $[Ru(bpy)_3]^{2+}$/PEO solution to toluene, DMF, or acetonitrile vapor produces (Figure 2) progressively larger $[Ru(bpy)_3]^{2+}$ mobilities as reflected in the larger observed oxidation currents.[9] The increased mobilities are due to the lowered mi-

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(5) Murray, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 145.

(6) (a) Wightman, R. M. *Science* **1988**, *240*, 415. (b) Ewing, A. G.; Dayton, M. A.; Wightman, R. M. *Anal. Chem.* **1981**, *53*, 1842.

(7) Yeager, H. L.; Steck, A. *J. Electrochem. Soc.* **1981**, *128*, 1880.

(8) Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J. Phys. Chem.* **1981**, *42*, 493.

(9) There is a concurrent change in wave shape as the diffusion rate increases, which can be understood based on the changing relative magnitudes of $[Ru(bpy)_3]^{2+}$ diffusion path length, electrode radius, and PEO film thickness. This has been analyzed.[2c] Briefly, in toluene and in acetonitrile, diffusion is, respectively, slow and (relatively) fast, diffusion layers are, respectively, comparable to and larger than the electrode radius, and the voltammograms have the properties, respectively, of linear diffusion (peaked currents) and of radial diffusion (plateau currents[6a]).

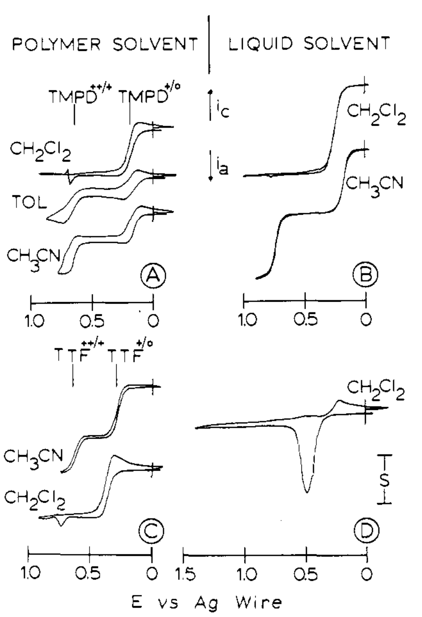

Figure 3. Cyclic voltammetry at 10-μm Pt microelectrodes of tetramethylphenylenediamine (TMPD) and tetrathiafulvalene (TTF). Panel A: 8×10^{-4} mol/cm^3 TMPD dissolved in $PEO_{15}/LiCF_3SO_3$ and immersed in room temperature saturated vapor pressures of the indicated organic monomers; S = 20, 10, 20 nA, v = 50 mV/s. Panel B: 6.2×10^{-6} mol/cm^3 TMPD dissolved in the indicated liquids containing 0.1 M Bu_4NClO_4; S = 20, 40 nA, v = 50 mV/s. Panel C: 1.7×10^{-4} mol/cm^3 TTF dissolved in $PEO_{15}/LiCF_3SO_3$ and immersed in room temperature saturated vapor pressures of the indicated organic monomers; S = 20, 10 nA, v = 50, 100 mV/s. Panel D: TTF in liquid CH_2Cl_2 containing 0.1 M Bu_4NClO_4.

croscopic viscosity (i.e., increased molecular segment mobility) of the polymer when the organic monomer partitions into the polymer phase. This so-called polymer "plasticization" depends both on the extent of partition[3] of organic monomer into the polymer and on the specific chemical interactions that it undergoes there. The importance of specific chemical interactions in plasticization is shown by the fact that, according to the currents in Figure 2, $[Ru(bpy)_3]^{2+}$ diffuses ca. 80× faster in $PEO_{15}/LiCF_3SO_3$ that has sorbed acetonitrile vs the sorption of toluene, yet the room temperature vapor pressure of acetonitrile is only ca. 3× that of toluene and gas chromatography experiments show that partition coefficients of acetonitrile and toluene into $PEO_{15}/LiCF_3SO_3$ are nearly identical.[10] We have analyzed the acetonitrile sorption process and proposed[3] that acetonitrile competitively displaces Li^+–polyether bonds with $Li^+–CH_3CN$ ones, with concomitant decrease in polyether–Li^+–polyether cross-linking. This chemical interaction should be insignificant for toluene, which is thereby a less effective plasticizer.

The oxidation of $[Ru(bpy)_3]^{2+}$ in $PEO_{15}/LiCF_3SO_3$ into which CH_2Cl_2 vapor is sorbed (Figure 2) is obviously different, exhibiting a sharp reduction peak during the negative potential sweep. A similar current–potential pattern is observed in voltammetry of $[Ru(bpy)_3]^{2+}$ solutions in liquid CH_2Cl_2. The explanation given such behavior is that $[Ru(bpy)_3]^{3+}$ salts are sparingly soluble in CH_2Cl_2 and are precipitated during the oxidative potential sweep and reduced in a current burst in the negative potential sweep. The current peak in Figure 2 corresponds to reduction of roughly 80 monolayers of oxidatively precipitated $[Ru(bpy)_3]^{3+}$ salt. Other metal polypyridine complexes dissolved in PEO bathed with CH_2Cl_2 vapor behave in an analogous manner, as does tetramethylphenylenediamine upon oxidation in Nafion bathed in water vapor. It seems generally that, when in a given liquid solvent the electrode reaction product is insoluble and precipitates on the electrode, use of vapors of that solvent as plasticizing bathing gas for $PEO_{15}/LiCF_3SO_3$ polymer solutions also leads to precipitation of films on the electrode from the polymer solution.

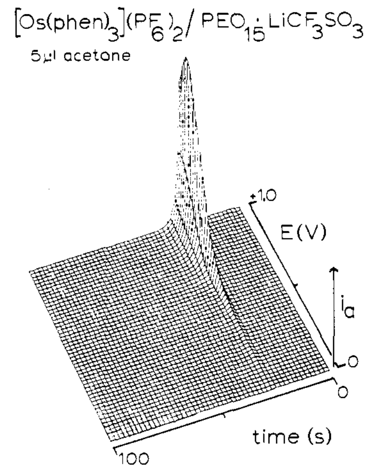

Figure 4. Cyclic voltammetry (100 mV/s) at a 70-μm Pt microelectrode of ferrocene and $[Fe(TPP)](PF_6)$ codissolved in a $PEO_{15}/LiCF_3SO_3$ film immersed in saturated vapors of the indicated organic monomers (S = 5nA). The voltage axis is adjusted to zero at the ferrocene wave.

Films precipitated as a result of electrochemical reactions in $PEO_{15}/LiCF_3SO_3$ solvent sometimes exhibit unusual chemical selectivity for electron transfers at the electrode/polymer interface. For example, while oxidation of TMPD and TTF from $PEO_{15}/LiCF_3SO_3$ exposed to acetonitrile vapors yields two well-defined voltammetric steps for the $TMPD^{+/0}$ and $TMPD^{2+/+}$ reactions and $TTF^{+/0}$ and $TTF^{2+/+}$ reactions, respectively, in a CH_2Cl_2 bathing gas, the second oxidation step in both cases, $TMPD^{2+/+}$ and $TTF^{2+/+}$, appears only as a small burst of current (Figure 3A,C) at the $TMPD^{2+/+}$ and $TTF^{2+/+}$ potentials. This small current burst apparently forms an inhibiting reaction product film at the electrode/polymer solvent interface, which is a chemically selective barrier in that it permits electron transfers for the $TMPD^{+/0}$ and $TTF^{+/0}$ reactions, apparently freely, while completely inhibiting passage of the second electron. Inhibition also occurs, with some changes in detail, for TMPD and TTF oxidations in liquid CH_2Cl_2 solutions (Figure 3B,D). It is clear from the comparison between acetonitrile and CH_2Cl_2 that formation of such films from $PEO_{15}/LiCF_3SO_3$ is governed not by the polymer solvent but by the sorbed bathing gas.

The general inference drawn from the preceding observations in $PEO_{15}/LiCF_3SO_3$ polymer solutions is that the chemical nature of the polymer solution is determined mainly by the sorbed organic rather than the resident polymer component of the solvent matrix. The PEO in a simple sense serves as a rigidifying framework for solutions of electroactive solutes in sorbed bathing gas. This statement is a useful generality for most (undoubtedly not all) electroactive solutes in $PEO_{15}/LiCF_3SO_3$ polymer but may not apply to more strongly coordinating polymer solvents.

The relatively neutral (chemically speaking) behavior of $PEO_{15}/LiCF_3SO_3$ as a polymer solvent means that chemical reactivity in the polymer solvent should be reasonably manipulable via choice of bathing gas. This has been done with a volatile acid to support solid-state oxygen electrocatalysis.[11] Figure 4 illustrates adjusting the axial coordination chemistry of $[Fe(TPP)](PF_6)$ dissolved in $PEO_{15}/LiCF_3SO_3$. The current peak at 0 volts in Figure 4 is due to ferrocene, which was added to establish a reference potential; the current peaks at positive potentials are presumed to be porphyrin oxidations but were not investigated, and the current peaks at negative potentials are at values expected for $[Fe^{III,II}TPP]$ reactions. While in acetonitrile or DMF vapor bathing gas, the $[Fe^{III,II}TPP)]$ voltammetric wave lies at −540 mV vs ferrocene$^{+/0}$, whereas when pyridine vapor is added to the DMF bathing gas the $[Fe^{III,II}TPP)]$ reaction potential shifts positively,

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(10) The capacity factors, which are porportional to partition coefficients, of acetonitrile and toluene vapor into $PEO_{15}/LiCF_3SO_3$ are 22 and 24, respectively, as measured by gas chromatography from the time to elute 5-μL samples of these compounds from a room temperature column packed with Chromosorb C coated with 10% by weight of $PEO_{15}/LiCF_3SO_3$.

(11) Bettelheim, A.; Reed, R. A.; Hendricks, N. H.; Collman, J. P.; Murray, R. W. *J. Electroanal. Chem.* **1988**, *238*, 259.

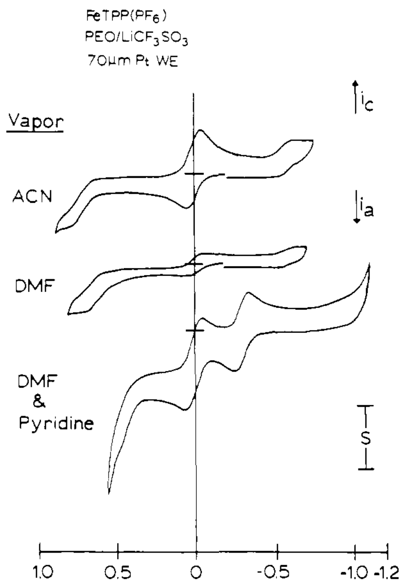

Figure 5. Current-potential responses for oxidation of 8.3 × 10^{-5} mol/cm^3 $[Os(phen)_3]^{2+}$ dissolved in a $PEO_{15}/LiCF_3SO_3$ film exposed to the vapors of a 5-μL sample of acetone eluted from a gas chromatographic column. The current-potential curves were taken at 1 V/s potential sweep rate with a 1-s rest at 0 V in between each sweep.

to −230 mV. This positive potential shift is consistent with strong diaxial coordination of pyridine to the metalloporphyrin. Such manipulation of coordination chemistry should be predictively possible whenever the polymer solvent does not itself introduce even more potent coordinating properties.

Dynamics of Bathing Gas Effects. A significant feature of bathing gas sorption is its rapidity (for thin polymer solvent films) and reversibility, both for plasticization and for coordination effects. For example, in Figure 4, removing the pyridine bathing gas component, leaving only DMF, causes an immediate shift of the $[Fe^{III,II}TPP)]$ reaction potential back to its original −540 mV value. Apparently, out-partitioning of pyridine rapidly depresses the pyridine concentration in the polymer solution below that required to sustain diaxial coordination to the iron porphyrin, completely reversing what is generally regarded as a very strong axial coordination.

Plasticization effects are also rapidly reversible. In Figure 2, changing the bathing gas from acetonitrile to dry N_2 environment results in a rapid diminution of the voltammetric currents back to those characteristic of dry N_2 bathing gas. The rapidity with which the rate of redox solute diffusion can be altered by sorption of an organic vapor is sufficiently great that the solid-state electrochemical cell can function as a gas detector[12] on the time scale of a gas chromatographic experiment. In the experiment shown in Figure 5, in which the electrode potential is cyclically scanned[12c] during chromatographic elution, the $[Os(phen)_3]^{2+}$ oxidation currents are small when the electrode is bathed only in carrier gas, but become large when the vapor band of the acetone sample emerges from the column. The current peak mirrors the chromatographic band shape, since the acetone sorbs and plasticizes the PEO solvent and $[Os(phen)_3]^{2+}$ transport rapidly on the chromatographic time scale. How rapidly the polymer solvent film equilibrates with a given bathing gas component will obviously depend on a variety of factors (including the bathing gas diffusion rate in the polymer film and the film thickness) and will not always be less than the chromatographic time scale. Thin polymer solvent films respond most rapidly; a 1-μm film and a sorbed bathing gas with $D = 10^{-8}$ cm^2/s would, for example, equilibrate in ca. 1 s, an estimate consistent with the observed behavior in Figure 5. The implication of course is that *chemical events in the polymer solvent that lead to plasticization occur on an even faster time scale.* Preliminary experiments have suggested that the kinetics of slow chemical steps, such as the off-rate of pyridine from the Fe metalloporphyrin in Figure 4, might be accessible to investigation using gas chromatography as a transient exposure method.

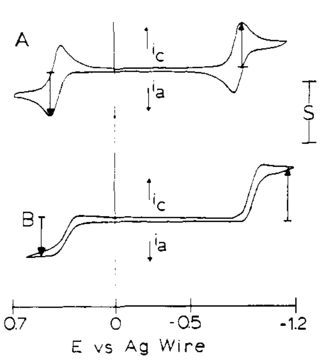

Figure 6. Cyclic voltammetry of the $[Co(bpy)_3]^{2+/3+}$ and the $[Co(bpy)_3]^{2+/1+}$ reactions of the following solutions. Panel A: 1.0 × 10^{-6} mol/cm^3 $[Co(bpy)_3]^{2+}$ in liquid CH_3CN containing 0.1 M Et_4NClO_4, at a 0.34-cm-diameter Pt disk macroelectrode; v = 50 mV/s, S = 80 μA. Panel B: 5.5 × 10^{-5} mol/cm^3 $[Co(bpy)_3]^{2+}$ in a CH_3CN vapor bathed $PEO_{15}/LiCF_3SO_3$ film cast over a 10-μm-diameter Pt microelectrode; v = 20 mV/s, S = 0.94 nA. The ratio of the currents for the $[Co(bpy)_3]^{2+/3+}$ and the $[Co(bpy)_3]^{2+/+}$ reactions is 1.00 in panel A and 1.35 in panel B.

Mechanisms of Charge Transport In Polymer Solvents. When redox species diffuse through a liquid electrolyte solution to an electrode surface, the net transport of chemical equivalents involves the parallel processes of physical diffusion and of electron self-exchanges between the reduced and oxidized redox species in the diffusion layer around the electrode. Electron self-exchange contributes to charge transport whenever the time scale for electron transfer between colliding reactants is shorter than that for a redox reactant to physically diffuse over a distance approximately equivalent to its diameter. Physical diffusion rates in liquid electrolytes are ordinarily much faster than electron-exchange-based charge transport, but as shown by Buttry and Anson,[13] the much slower rates of physical diffusion in solvent-wetted polymer films on electrodes can result in significant contributions from electron exchange events. This observation also applies to transport of electroactive solutes in polymeric solvents, where physical diffusion is again slow.

Enhancement of voltammetric currents by electron self-exhange is illustrated in Figure 6. Because the electron self-exchange rates[14] for $[Co(bpy)_3]^{3+/2+}$ and for $[Co(bpy)_3]^{2+/+}$ are very small (ca. 10 M^{-1} s^{-1}) and very large (>10^8 M^{-1} s^{-1}), respectively, currents in the oxidation wave for $[Co(bpy)_3]^{2+}$ are governed by physical diffusion, whereas those for $[Co(bpy)_3]^{2+}$ reduction can be enhanced by $[Co(bpy)_3]^{2+/+}$ self-exchange.[13] The enhancement is immeasurably small in voltammetry in liquid acetonitrile, because physical diffusion is fast there, and the oxidation and reduction currents are equal in size. In $PEO_{15}/LiCF_3SO_3$, where physical diffusion is slow, self-exchange enhances the $[Co(bpy)_3]^{2+/+}$ current by 35% relative to the $[Co(bpy)_3]^{3+/2+}$ reaction. Theory is available for such enhancement in the Dahms–Ruff[15] relation, which as modified by Buck[16] is

$$D_{exp} = D_{phys} + 10^3 k_{app} \delta^2 C/6$$

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[12] (a) An electrochemical detector for gas chromatography has been described[12b] that has a construction formally analogous to Figure 1 but is apparently not plasticization based. (b) Brina, R.; Pons, S.; Fleischmann, M. *J. Electroanal. Chem.* **1988**, *244*, 81. (c) White, G. G.; St. Claire, R. L.; Jorgenson, J. W. *Anal. Chem.* **1986**, *58*, 293.

[13] (a) Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 685. (b) Buttry, D. A.; Anson, F. C. *J. Electroanal. Chem.* **1981**, *130*, 333.

[14] (a) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (b) Baker, B. R.; Basolo, F.; Neumann, H. M. *J. Phys. Chem.* **1959**, *63*, 371.

[15] (a) Dahms, H. *J. Phys. Chem.* **1968**, *72*, 362. (b) Ruff, I.; Friedrich, V. J. *Ibid.* **1971**, *75*, 3297. (c) Ruff, I.; Friedrich, V. J.; Demeter, K.; Csaillag, K. *Ibid.* **1971**, *75*, 3303. (d) Ruff, I.; Korosi-Odor, I. *Inorg. Chem.* **1970**, *9*, 186. (e) Ruff, I. *Electrochem. Acta* **1970**, *15*, 1059.

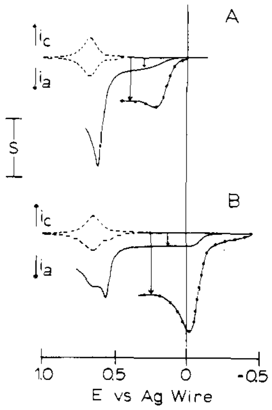

Figure 7. Permeation from polymer solutions into polymer films. Panels A and B: (- - -) current–potential responses at 50 mV/s of 7.4×10^{-9} and 6.4×10^{-9} mol/cm^2 poly[Os(bpy)$_2$(vpy)$_2$]$^{2+}$ films, respectively, on 25-μm Pt microelectrodes (S = 20 nA) contacted by liquid CH_3CN containing 0.1 M Et_4NClO_4, and of 6.8×10^{-5} mol/cm^3 [Co(bpy)$_3$]$^{2+}$ (S = 4 nA) and of 3.4×10^{-5} mol/cm^3 [Os(bpy)$_2$Cl$_2$] (S = 1 nA) dissolved in CH_3CN vapor bathed $PEO_{15}/LiCF_3SO_3$ films cast over (—) the above poly[Os(bpy)$_2$(vpy)$_2$]$^{2+}$ films and (–·–) over naked 10-μm Pt microelectrodes.

where D_{exp} and D_{phys} are diffusion coefficients measured from [Co(bpy)$_3$]$^{2+}$ reduction and oxidation, respectively, δ is the intersite distance upon reaction (1.3 nm), and C is [Co(bpy)$_3$]$^{2+}$ concentration (in mol/cm^3). The results give, for the polymer solvent experiment, an apparent rate constant $k_{app} = 1.12 \times 10^8$ M^{-1} s^{-1} for electron self-exchange between [Co(bpy)$_3$]$^{2+}$ and [Co(bpy)$_3$]$^+$. This rate constant is quite large and, given the slowness of physical diffusion in the polymer, occurs at a rate nearly at the collision rate limitation. Using the Smoluchowski equation,[17] we calculate from $D_{phys} = 5.67 \times 10^{-8}$ cm^2/s [obtained from the [Co(bpy)$_3$]$^{2+}$ oxidation] that the collision-limited rate constant k_d is 1.2×10^8 M^{-1} s^{-1}. This constant used in turn in the equation

$$1/k_{app} = 1/k_d + 1/k_{ex}$$

yields a lower limit for k_{ex} of 2×10^9 M^{-1} s^{-1}. This rate is entirely consistent with the prior data[14] on [Co(bpy)$_3$]$^{2+/+}$ self-exchange in acetonitrile solution. Put differently, the magnitude of the enhancement of the [Co(bpy)$_3$]$^{2+}$ charge-transport rate in its reduction to [Co(bpy)]$^+$ is consistent with a contribution from a very fast electron self-exchange.

The enhancement of currents for electroactive solutes in polymers should be a common effect given the generally slow diffusion to be expected in polymer solvents. The magnitude of current enhancement will depend on the relative values of electron self-exchange and physical diffusion for the solute, the concentration, and of course the effect of rigid environment on the self-exchange kinetics.

Polymeric Mass Transport Barriers in Polymer Solvents. A significant achievement of chemically modified electrodes[5] has been the capacity to rationally design the molecular nature of electrode surfaces contacted by fluid electrolyte media. These surfaces include polymer film coatings that mediate electron-transfer reactions of dissolved substances[18] and that act as selective transport barriers to dissolved permeants.[19] The same ideas should be useful in solid-state voltammetry in polymeric solvents, although the scope will be different because of slower transport rates in polymer solutions.

We will illustrate solid-state chemical modification with a transport barrier experiment (Figure 7) in which a barrier polymer film is interposed between a Pt electrode surface and $PEO_{15}/LiCF_3SO_3$ polymeric solvent containing a dissolved electroactive permeant. The barrier polymer is a 45-nm-thick poly[Os(bpy)$_2$(vpy)$_2$]$^{2+}$ film, which was prepared by reductive electropolymerization[20] of monomer from a fluid acetonitrile solution. Figure 7A,B (- - -) shows the poly[Os(bpy)$_2$(vpy)$_2$]$^{2+/3+}$ redox processes for two such films in liquid acetonitrile. The films were then coated with $PEO_{15}/LiCF_3SO_3$ polymer solutions containing two different permeant solutes, [Co(bpy)$_3$]$^{2+}$ and [Os(bpy)$_2$Cl$_2$]. Their voltammetry in Figure 7A,B (—) reveals that their oxidations occur at the proper potentials,[21] but the permeant oxidation currents are much smaller than those observed in an identical experiment in which the poly[Os(bpy)$_2$(vpy)$_2$]$^{2+}$ barrier film is absent [Figure 7A,B (–·–)]. The smaller currents reflect the slowness of permeation of [Co(bpy)$_3$]$^{2+}$ (panel A) and [Os(bpy)$_2$Cl$_2$] (panel B) through the poly[Os(bpy)$_2$(vpy)$_2$]$^{2+}$ film as compared to the diffusion rate of the permeant through the polymer solvent. The currents can be used to evaluate the barrier film permeability, PD_{pol}, with the relation[19]

$$[1/i_{lim}]^{-1} = [1/i_d]^{-1} + [1/i_{perm}]^{-1}$$

where i_{lim}, i_d, and i_{perm} are respectively, the limiting currents indicated for curves — and –·– and the hypothetical limiting current controlled *solely* by permeation, $i_{perm} = nFAPD_{pol}C/d$ where C, P, and D_{pol} are the concentration and partition and diffusion coefficients of the permeants in poly[Os(bpy)$_2$(vpy)$_2$]$^{2+}$ (film thickness d) and A is the microelectrode area. Application of this relation to the currents in Figure 7 gives similar values, $PD_{pol} = 1.4 \times 10^{-10}$ and 7.5×10^{-11} cm^2/s, for [Co(bpy)$_3$]$^{2+}$ and [Os(bpy)$_2$Cl$_2$] permeation through poly[Os(bpy)$_2$(vpy)$_2$]$^{2+}$, respectively.[22]

These results can be compared to prior permeation data[19] taken for polymer films contacted by solutions of these permeants. The

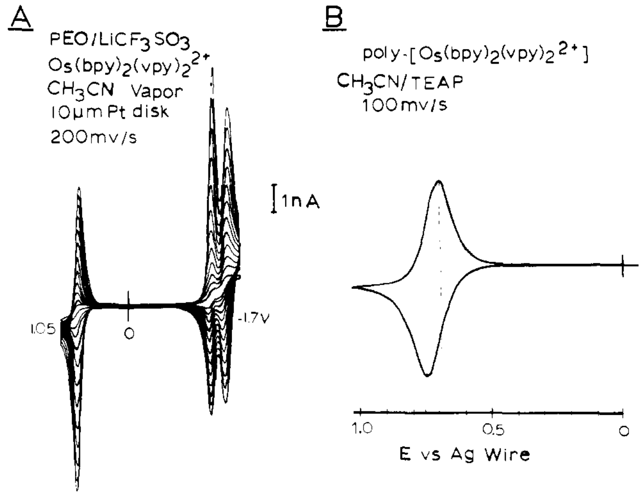

Figure 8. Panel A: electrochemical polymerization of [Os(bpy)$_2$(vpy)$_2$]$^{2+}$ dissolved in a CH_3CN vapor bathed $PEO_{15}/LiCF_3SO_3$ film cast over a 10-μm Pt microelectrode, by sweeping the electrode potential repeatedly through the (bpy)/(bpy$^-$) reduction waves; the increase in current reflects accumulation of an electroactive polymer film on the microelectrode. Panel B: the poly[Os(bpy)$_2$(vpy)$_2$]$^{2+/3+}$ wave for the film prepared in panel A, after rinsing off the PEO polymer with CH_3CN and immersing in liquid CH_3CN containing Et_4NClO_4.

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(16) Buck, R. P. *J. Electroanal. Chem.* **1988**, *243*, 279.

(17) von Smoluchowski, M. *Phys. Z.* **1916**, *17*, 557.

(18) (a) Ikeda, T.; Leidner, C. R.; Murray, R. W. *J. Electroanal. Chem.* **1982**, *138*, 343. (b) Leidner, C. R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1606.

(19) (a) Ewing, A. G.; Feldman, B. J.; Murray, R. W. *J. Phys. Chem.* **1985**, *89*, 1263. (b) Ikeda, T.; Schmehl, R.; Denisevich, P.; Willman, K.; Murray, R. W. *J. Am. Chem.* **1982**, *104*, 2683.

(20) (a) Denisevich, P.; Abruna, H. D.; Leidner, C. R.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1982**, *21*, 2153. (b) Calvert, J. M.; Schmehl, R. H.; Sullivan, B. P.; Facci, J. C.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1983**, *22*, 2151.

(21) The voltammetric scans in Figure 7A,B (—) exhibit sharp current peaks at potentials more positive than the permeation waves. These peaks represent mediated oxidation of remaining [Co(bpy)$_3$]$^{2+}$ and of [Os(bpy)$_2$Cl$_2$] at the poly[Os(bpy)$_2$(vpy)$_2$]$^{3+}$/$PEO_{15}/LiCF_3SO_3$ polymer–polymer interface, by Os(III) states generated there as the Os(III,II) reaction of the film is approached. This is a thermodynamically expected reaction and has been observed in solutions using acetonitrile liquid.[18]

(22) For comparison, the diffusion coefficients of [Co(bpy)$_3$]$^{2+}$ and [Os(bpy)$_2$Cl$_2$] in the acetonitrile-plasticized $PEO_{15}/LiCF_3SO_3$ polymer solvent are 1.2×10^{-7} and 6.2×10^{-8} cm^2/s, respectively.

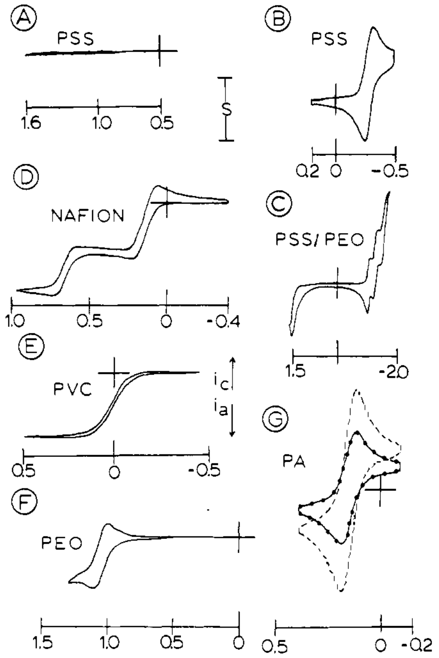

Figure 9. Cyclic voltammetry in various polymer electrolytes. Panel A: $[Ru(bpy)_3]^{2+}$ dissolved in a sulfonated polystyrene film bathed in CH_3CN vapor; 10-μm Pt microelectrode (S = 1 nA). Panel B: $[Ru(NH_3)_6]^{3+}$ dissolved in a sulfonated polystyrene film bathed in moist air; 10-μm Pt microelectrode (S = 5 nA). Panel C: $[Ru(bpy)_3]^{2+}$ dissolved in a 1:1 mixture film of PEO and sulfonated polystyrene bathed in CH_3CN vapor; 50-μm Pt microelectrode (S = 5 nA). Panel D: tetramethylphenylenediamine dissolved in a Nafion film bathed in CH_3CN vapor; 10-μm Pt microelectrode (S = 20 nA). Panel E: $[Co(bpy)_3]^{2+}$ dissolved in a poly(vinyl chloride) film containing Hx_4NClO_4 electrolyte, bathed in moist air; 10-μm Pt microelectrode (S = 2 nA). Panel F: $[Ru(bpy)_3]^{2+}$ dissolved in a $PEO_{15}/LiCF_3SO_3$ film, in N_2 at 80 °C; 10-μm Pt microelectrode (S = 2 nA). Panel G: $[Fe(CN)_6]^{3-}$ dissolved in a lightly cross-linked film of poly(acrylamide) containing 0.1 M KCl, after two successive additions of 5 μL of 0.3 mM $[Fe(CN)_6]^{4-}$ solution to N_2-dried gel film, drying the gel film between each addition (S = 1 nA).

permeability of films of the related polymer poly$[Ru(bpy)_2(vpy)_2]^{2+}$ to $[Os(bpy)_2Cl_2]$ from liquid acetonitrile solutions is similar (within a factor of 4X) to that measured for $[Os(bpy)_2Cl_2]$ from the polymer solvent. On the other hand, the permeability of poly$[Os(bpy)_2(vpy)_2]^{2+}$ to $[Ru(bpy)_3]^{2+}$ from liquid acetonitrile[19] is much smaller than the $[Co(bpy)_3]^{2+}$ polymer solvent result. Further data are needed, but the comparison suggests that the effect of co-ion charge exclusion in the case of $[Co(bpy)_3]^{2+}$ is less important in partition from the polymer solvent vs acetonitrile liquid.

Electropolymerization from Polymer Solutions. A number of reports have already appeared in which films of conducting polymers are electrochemically polymerized from polymeric electrolytes.[4a-e] Electropolymerization of a redox polymer from polymer solvents has not been previously reported and is illustrated in Figure 8 for formation of a film of poly$[Os(bpy)_2(vpy)_2]^{2+}$ from acetonitrile-plasticized $PEO_{15}/LiCF_3SO_3$ solutions. Compared to analogous electropolymerization from liquid acetonitrile, formation of poly$[Os(bpy)_2(vpy)_2]^{2+}$ films from the polymer solution is exceptionally rapid; thick films grow in only a few reductive cyclical potential sweeps (panel A). After the electropolymerization, the PEO solvent was removed by rinsing with acetonitrile and the coated microelectrode placed in a fresh liquid acetonitrile electrolyte solution, where the poly[Os(III/II)] cyclic voltammetry shown in panel B was obtained. Although the film appears to be quite thick, it exhibits remarkably rapid charging as reflected by the small ΔE_p of the voltammetric wave. It seems likely from this result that PEO polymer was entrapped in the poly$[Os(bpy)_2(vpy)_2]^{2+}$ film during its electropolymerization, and the entrapped polymer has usefully altered its charge transport characteristics. This is a potentially important effect, given widespread interest[5] in charge transport in localized-state polymers, and is under further study.

A second feature of the polymer solvent electropolymerization is an extensive spreading of the poly$[Os(bpy)_2(vpy)_2]^{2+}$ film out upon the glass shroud around the electrode. This spreading comes about because the supply of fresh monomer to the electrode is confined to lateral diffusion through the thin polymer solvent film (Figure 1). This also is a potentially important effect since it suggests that shapes and placement of electropolymerized polymer films might be usefully controlled and manipulated by control of the shape of a rigid solution medium that supplies the monomer.

Other Ionically Conducting Polymer Solvents. Many ionically conducting polymers have been reported[1] since the initial report by Armand et al.,[23] and with exceptions for undesirable polymer electroactivity or impurities, most of these should be useful as polymeric solvents. The diversity of the choices is illustrated in Figure 9 by examples from a series of exploratory experiments. Sulfonated polystyrene (Na^+ salt) in acetonitrile vapor bathing gas gives no discernable voltammetry for the $[Ru(bpy)_3]^{2+/3+}$ reaction (curve A), but exposure of that polymer to moist air produces a well-defined reduction reaction for $[Ru(NH_3)_6]^{2+}$ (curve B), and admixture with PEO (curve C) reveals the oxidation and reduction reactions for metal and ligand, respectively. No electrolyte was added in curves A–C, so the sulfonated polystyrene polymer serves as its own electrolyte with the cation presumably having unit transference number. The perfluorinated sulfonate polymer Nafion likewise can serve as both polymer solvent and electrolyte as illustrated by the TMPD voltammetry in Figure 9, curve D. Poly(vinyl chloride) would not ordinarily be considered as a useful ionic medium, but it dissolves fatty electrolytes like Hx_4NClO_4 and in moist air gives good voltammetry for $[Co(bpy)_3]^{2+}$ (curve E). Dry $PEO_{15}/LiCF_3SO_3$ can also be employed if heated above the temperature required for it to become amorphous (curve F).

The above ideas also apply to gel-forming polymers such as poly(acrylamide). This material can be prepared as dry (nonconducting) films on electrodes, which will readily sorb aqueous microdroplets of electroactive solutions.[2d] Figure 9, curve G, shows voltammetry (---) for the $[Fe(CN)_6]^{4-/3-}$ reaction, obtained after sorbing a 5-μL droplet of ferricyanide solution into a dry gel film. Drying this gel and sorbing a second 5-μL droplet of ferricyanide solution gives a current (---) exactly double the first current, since twice the quantity of ferrocyanide is now "immobilized" on the electrode. This easy immobilization in a gel solvent that is also biocompatible gives access to redox protein reactions[2b] and electron transfers of enzyme couples[2d] in aqueous solutions self-confined by the semirigid gel structure.

Acknowledgment. This research was supported in part by grants from the National Science Foundation, the Department of Energy (DE-FG05-87ER13675, charge transport and gas chromatographic studies), and the North Carolina Biotechnology Center [poly(acrylamide) gel studies]. M.-H.K. and J.E. were faculty participants in an NSF-sponsored Summer Institute (CHE-8701080). We thank S. Creager for preparation of the sample of $[FeTPP](PF_6)$.

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(23) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. In *Fast Ion Transport in Solids*; Mundy, J. N., Shenoy, G. K., Eds.; Pergamon Press: New York, 1979; p 131.