sidered here which are known to be active in the photooxidative process at CdS. It thus seems that a beneficial surface modification could involve either a chemisorbed species which would lower the rate of surface recombination while being most probably inert in the process of charge transfer (21, 22), or it would involve a chemisorbed species with high surface capture cross sections, which may serve as an effective charge transfer mediator as seems to be the case for the $CdS/S^{=}$, $Sn^{=}$ system. Whether this model of photocharge mediation by adsorbed anions (or by other forms of surface states) is more or less general, should be verified by further similar measurements on other semiconductor-electrolyte interfaces.

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Polymer Films on Electrodes

XIX. Electrochemical Behavior at Polypyrrole-Nafion and Polypyrrole-Clay Thin Films on Glassy Carbon Electrodes

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ABSTRACT

Biconductive films, involving the incorporation of an electronically conductive phase within an ionically conductive one, on glassy carbon electrode surfaces have been prepared by electropolymerization to form polypyrrole (PP) in matrices of Nafion and the clay, hectorite. These films display electronic conductivity and higher stability than films of PP alone. Electrochemical studies of several species at these electrodes ($Fe(CN)_6^{3-}$, $Ru(NH)_6^{2+}$, methyl viologen) are described. Freestanding PP/Nafion and PP/hectorite films have also been prepared.

Polymer-modified electrodes involving films of either ionically or electronically conductive materials have been investigated (1, 2). For example, the electronic conductor polypyrrole (PP) can be prepared by electrochemical oxidation of pyrrole and forms highly conductive films with good stability (2). However, the mechanical properties of these films are poor, and attempts have been made to improve these by electropolymerizing pyrrole in a poly(vinylchloride) matrix (3). We have also been interested in incorporation of an electronically conductive phase into ionically conductive polymer films to improve the charge transfer rates in such films and to grow unique conductive structures. Thus, tetrathiafulvalenium (TTF^+) was incorporated into Nafion (4, 5) and TTFBr structures formed by electrochemical cycling.

We report here an electrochemical method for producing flexible co-polymer films from ionically conductive Nafion and PP. These films have good electronic conductivity (*ca.* one order less than pure PP films) and a much higher cation exchange capacity as compared to $PP^+ BF_4^-$ films. These films also possess high mechanical strength. Copolymerization of clay and pyrrole is also possible. The electrochemical responses at glassy carbon (GC) electrodes coated with these films in aqueous solutions containing various redox couples are also presented. Recently, Penner and Martin (6) have described the incorporation of PP into Nafion and Gore-tex-impregnated Nafion by electrochemical means.

Experimental

All chemicals, if not otherwise mentioned, were reagent grade and were used without further purification. Pyrrole (Alfa Products) was purified by distilling from CaH_2 under N_2. Tetra-n-butylammonium fluoroborate ($TBABF_4$) was recrystallized twice from methanol. Ca-hectorite (SHCa-1, University of Missouri, Columbia, Missouri) was exchanged to the Na-form and dried by the standard method (7). N,N′-dimethyl-4,4′-bipyridinium (MV^{2+}) dichloride (Sigma Chemicals) was recrystallized from MeOH/acetone. Distilled water for all experiments was from a millipore water reagent system.

Electrode preparation.—$PP^+BF_4^-$ films were deposited electrochemically (2b) onto GC electrodes (Atomergic) (0.071 cm^2) from MeCN (spectrograde) solutions containing $0.2M$ $TBABF_4$ and 50 mM pyrrole by sweeping continuously between -0.6 and 1.0V *vs.* Ag until a total of *ca.* 42 mC/cm^2 of charge was consumed. The films were then thoroughly rinsed with MeCN. Na-hectorite films were prepared by dropping a known volume (50 μl) of aqueous clay colloid (2.5 g/l) onto the GC substrate. The films were dried under ambient conditions. Nafion films were prepared by dropping a known volume (50 μl) of an ethanolic Nafion (E.W. 1100, 2 g/l) (C.G. Processing, Incorporated, Rockland Delaware) solution onto the GC electrode. The films were dried in air at room temperature.

Hectorite-PP films were prepared by sweeping the potential of Na-hectorite-coated GC electrodes between -0.6

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and 1.0V *vs*. Ag in MeCN solutions containing 0.2*M* $TBABF_4$ and 50 m*M* pyrrole until *ca*. 42 mC/cm^2 of charge was consumed. The films were then thoroughly rinsed with MeCN and dried under ambient conditions. Two different methods were employed to prepare Nafion-PP films. Type A films were prepared by the same procedure as used for PP deposition with Nafion-coated GC used as a substrate. Type B films were prepared by sweeping GC electrodes in 25 ml of mixed EtOH:MeCN (1:5 by volume) solutions containing 50 m*M* pyrrole and 10 meq. Nafion (E.W. 1100) over the potential range −0.8 to 1.0V *vs*. Ag until *ca*. 42 mC/cm^2 of charge was collected.

Instrumentation for electrochemical experiments consisted of a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat and PAR Model 179 digital coulometer. All electrochemical experiments were performed in an undivided three-electrode cell containing Pt counter- and Ag wire quasireference electrodes in nonaqueous solution and SCE reference electrode in aqueous solution. All experiments were performed in deoxygenated solutions and under nitrogen throughout the experiment, unless mentioned otherwise.

Results and Discussion

Film structure.—The deposition of PP involves oxidation of pyrrole to form cationic centers that polymerize with solution anions (*e.g.*, BF_4^-) as counterions (2). When Nafion is used as a substrate, the sulfonate groups attached to the polymer backbone play the role of anions, and, upon oxidation, the cationic PP polymer probably forms within the Nafion matrix with the expulsion of Na^+. We thus propose as the polymerization reaction (where $\sim SO_3^-$ represents Nafion and P^+ oxidized pyrrole centers in PP)

$$(\sim SO_3^-Na^+)_x + xP - xe \rightarrow (\sim SO_3^-\ P^+\!\sim)_x + xNa^+ \quad [1]$$

Although the structure of the interwoven Nafion and PP chains has not yet been investigated, we assume that this dual chain structure of the copolymer is what leads to better mechanical stability, as discussed below. In a similar way, the anionic oxygen sites in the clay film probably play the role of the counterion in hectorite/PP films. The electrochemical behavior of these films was examined by cyclic voltammetry (CV) in aqueous 0.5*M* Na_2SO_4 solution in the absence and presence of additional redox couples.

Nafion-pyrrole films.—As shown in Fig. 1, both types of Nafion-PP thin films show the characteristic large background currents in the potential region where PP is not completely oxidized or reduced (−0.6 to 1.0V *vs*. SCE). These currents were smaller (by a factor of *ca*. 2 for an equivalent thickness) than those found with $PP^+BF_4^-$ films. The smaller background current of the Nafion-incorporated PP thin film paralleled a total lower conductivity (electronic and ionic) (*i.e.*, the conductance of a dry freestanding Nafion-PP film was about ten times smaller than the same thickness $PP^+BF_4^-$ film).[1] The incorporation of Nafion, as shown in Fig. 1, also affected the peak potentials for the reduction and reoxidation of the PP films, which on occasion were shifted by *ca*. ±100-200 mV.

The electrochemical activity of Nafion-PP thin film electrodes was examined in the presence of several one-electron reversible redox couples, which span a potential range from −0.68 to 0.22V *vs*. SCE and carry different kinds of charges. At a simple Nafion-coated GC electrode, $Fe(CN)_6^{3-/4-}$ is essentially electrochemically inactive, since penetration of the highly charged anion through the Nafion film *via* a membrane process is strongly hindered (Fig. 2a). However, reversible cyclic voltammograms are observed on both types of Nafion-PP electrodes (Fig. 2b). The voltammograms are consistent with a diffusion-controlled reaction ($i_p \propto v^{1/2}$), and

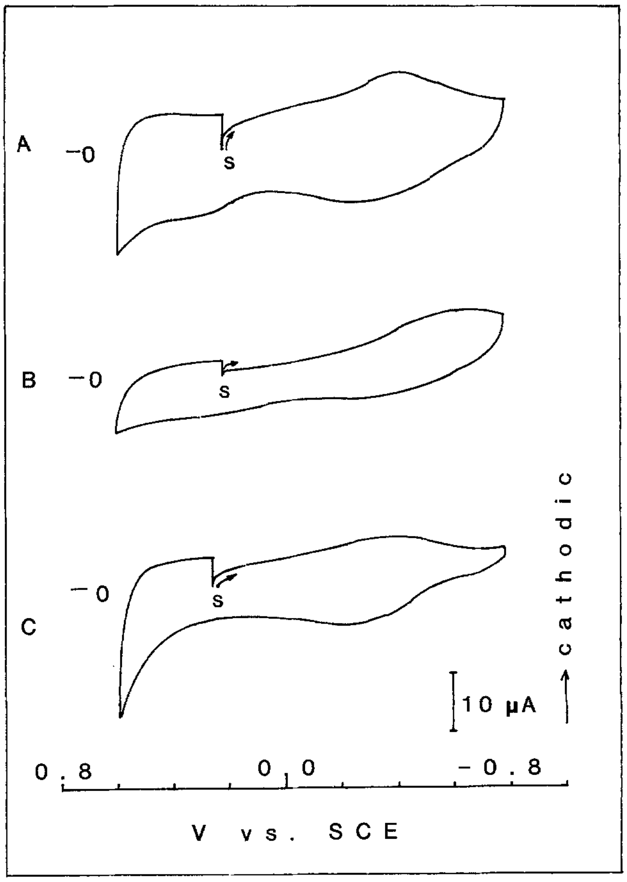

Fig. 1. Voltammetric curves in 0.5*M* Na_2SO_4 aqueous solution at scan rate 20 mV/s for (a) PP-coated GC electrode; (b) Type A Nafion-PP-coated GC electrode; (c) Type B Nafion-PP-coated GC electrode. PP deposition charge = 42 mC/cm^2.

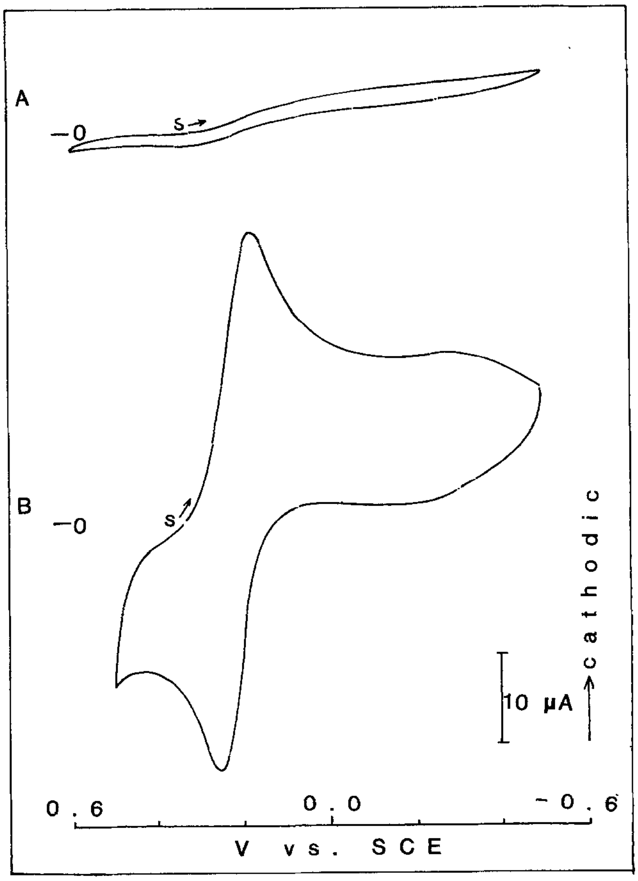

Fig. 2. Voltammetric curves in 0.5*M* Na_2SO_4 aqueous solution containing 10 m*M* $Fe(CN)_6^{3-}$ at scan rate 20 mV/s for (a) Nafion-coated GC electrode and (b) Type B Nafion-PP-coated GC electrode. PP deposition charge = 42 mC/cm^2.

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[1] Type B Nafion-PP films were found less conductive (*ca*. one order of magnitude) than $PP^+BF_4^-$ films. No attempt was made to measure the exact conductivities of those films.

there is no evidence of a specific interaction between films and the redox species (*e.g.*, as signaled by a change in the peak potentials). With couples, such as $Ru(NH_3)_6^{3+/2+}$, that carry positive charges and have redox potentials positive of the potential at which the film is completely reduced (*ca.* −0.5V *vs.* SCE), reversible cyclic voltammograms were obtained. However, the voltammograms, as shown in Fig. 3, were not purely diffusion-controlled (*e.g.*, peak current, i_p, was not proportional to the square root of scan rate, v) suggesting that some interaction occurs between the film and $Ru(NH_3)_6^{3+/2+}$. Higher peak currents and more symmetric cyclic voltammograms were observed at Nafion-PP electrodes, as compared with uncoated GC electrodes. After extensive cycling between −0.8 and 0.2V *vs.* SCE in a $Ru(NH_3)_6^{3+}$ solution, a Nafion-PP electrode, when transferred to 0.5*M* Na_2SO_4 alone, showed some current corresponding to the redox reaction of $Ru(NH_3)_6^{3+/2+}$ couple. Thus, some incorporation of $Ru(NH_3)_6^{3+/2+}$ (*ca.* 20-30% of that of a Nafion-coated GC electrode) into the film appears possible. For positively-charged redox species such as $MV^{2+/+}$ with redox potentials negative of −0.5V *vs.* SCE, the cathodic peak current was only about 5% of that obtained on bare GC electrodes on the first several scans (Fig. 4a). The low electrochemical activity of MV^{2+} on these electrodes indicates that the permeability of MV^{2+} through these polymer films is very low and is consistent with the nonconductive nature of PP in this potential region. Note that a single reduction wave of MV^{2+} is observed at a potential where the reduction of MV^{2+} is supposed to occur, but two reoxidation waves are observed. In addition to the normal reoxidation wave at *ca.* −0.6V *vs.* SCE, a second reoxidation wave is observed at a potential (−0.3 to −0.4 V *vs.* SCE) where PP is partially reoxidized and its conductivity is restored. The small reduction current demonstrates that the incorporation of MV^{2+} into these films is initially very low. However, extensive cycling of the Nafion-PP-film-coated GC electrodes between −0.9 and 0.3V *vs.* SCE in a 0.5*M* Na_2SO_4 solution containing 5 m*M* MV^{2+} increased substantially the amount of MV^{2+} incorporated (Fig. 4b). The incorporated MV^{2+} is held in these films when they are transferred to supporting electrolyte alone, as shown in Fig. 4c. The MV^{2+} diffusion coefficient in these Nafion/PP films has not yet been determined, because of the high background current and the uncertainty in the film concentration of MV^{2+}.

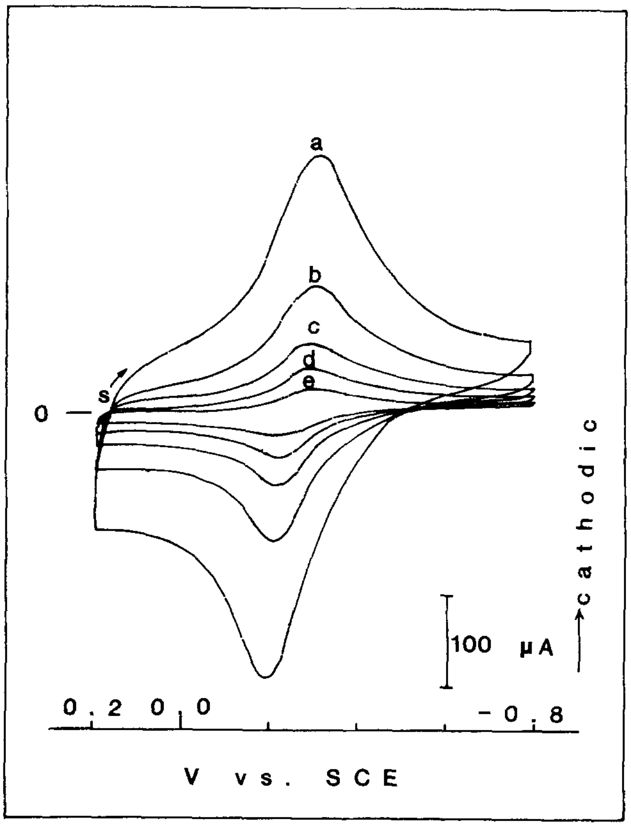

Fig. 3. Voltammetric curves in 0.5*M* Na_2SO_4 aqueous solution containing 5 m*M* $Ru(NH_3)_6^{3+}$ at Type B Nafion-PP-coated GC electrode at various scan rates: (a) 500, (b) 200, (c) 100, (d) 50, and (e) 20 mV/s PP deposition charge = 42 mC/cm^2.

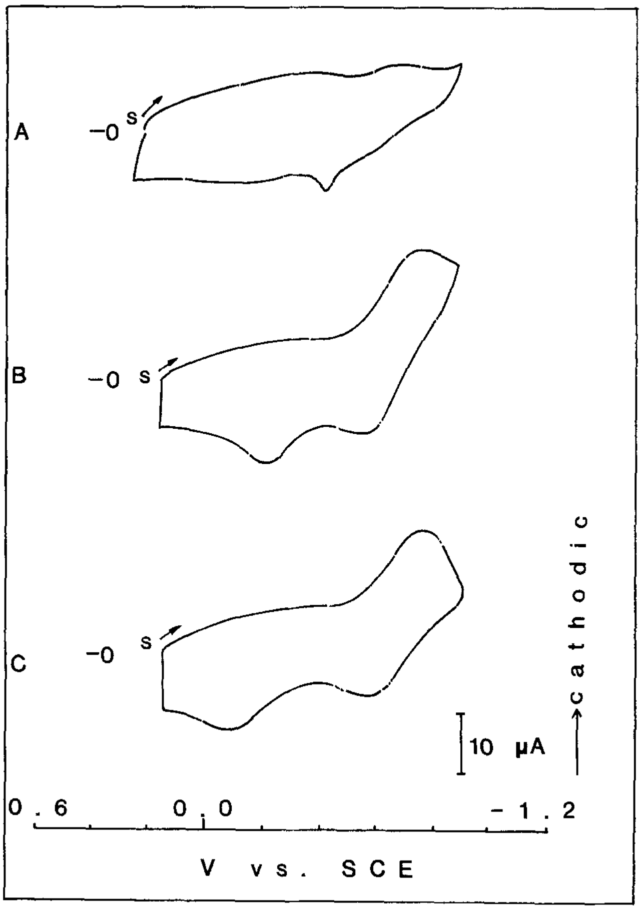

Fig. 4. Voltammetric curves at Type B Nafion-PP-coated GC electrode at scan rate 20 mV/s. (a) First several scans in 0.5*M* Na_2SO_4 solution containing 5 m*M* MV^{2+}; (b) the same electrode after sweeping at 20 mV/s between −0.9 and 0.3V vs. SCE in the same solution for 20 min; (c) the same electrode after (b) in 0.5*M* Na_2SO_4 solution but at scan rate 50 mV/s.

Clay-pyrrole films.—Na-hectorite-coated GC electrodes in 0.5*M* Na_2SO_4 solution show a low flat background current over a potential region of −0.8 to 1.0V *vs.* SCE, so the electrode is suitable for studying various electrochemical reactions. These electrodes, after further coating with 42 mC/cm^2 of PP, show the characteristic large background current of a PP film. The shape (both magnitude and peak position) of the voltammograms, as with $PP^+BF_4^-$ films, varies with film thickness. The peak potential separation of the polymer redox reaction increased with film thickness.

The hectorite-PP film on a GC electrode is electronically conductive in the potential range where a large background is present (−0.6 to 1.0V *vs.* SCE in 0.5*M* Na_2SO_4 solution). The conductance of a dry freestanding clay-PP film was 10-100 times smaller than the same thickness $PP^+BF_4^-$ film. The film can be used as an electrode to drive various electrochemical reactions, as shown in Fig. 5. The hectorite-PP film behaves well for both negatively and positively charged species, and the redox peaks appear superimposed on the background current with redox potentials close to the values measured with a Pt electrode. In contrast to the hectorite-PP film, an unswollen Na-hectorite-coated GC electrode shows low electrochemical activity for $Fe(CN)_6^{4-/3-}$ (compare Fig. 5a and 5b); in this case, the anionic species penetrates the clay layer through small interparticle channels (7b). Electrochemical activity of clay-modified electrodes can be en-

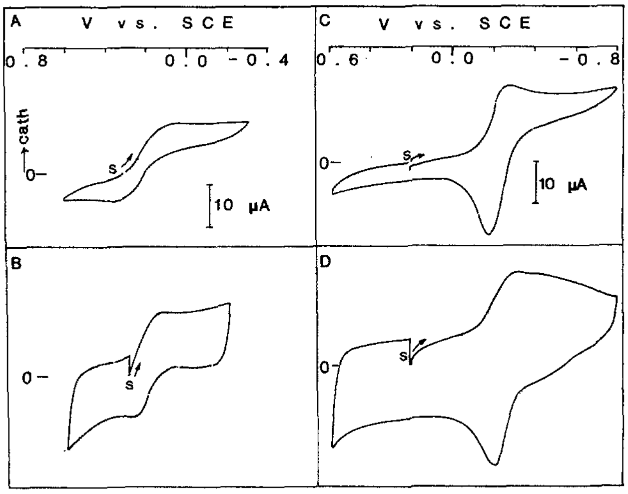

Fig. 5. Voltammetric curves at scan rate 20 mV/s. (a) At hectorite-coated GC electrode in 0.5M Na_2SO_4 solution containing 10 mM $Fe(CN)_6^{3-}$; (b) at hectorite-PP-coated GC electrode in the same solution; (c) at hectorite-coated GC electrode in 0.5M Na_2SO_4 solution containing 5 mM $Ru(NH_3)_6^{3+}$; (d) at hectorite-PP-coated GC electrode in 0.5M Na_2SO_4 solution with 5 mM $Ru(NH_3)_6^{3+}$.

hanced dramatically by swelling the clay film in aqueous solution (7b). Note that the peak current observed on a hectorite-PP electrode for $Fe(CN)_6^{3-}$ reduction is only about 1/2 of that found with a bare GC electrode, although hectorite-PP shows a smaller peak separation ($\Delta E_p \sim 100$ mV) compared to a GC electrode ($\Delta E_p \sim 150$ mV). This is very different from a Nafion-PP electrode which shows an active area for electrochemistry of a solution species that is the same as that of the GC electrode. This can be attributed to a poor swelling of the clay in acetonitrile[2] so that the deposition of PP occurs only at the grain boundaries of the clay particles; the molecularly homogeneous mixing that probably characterizes Nafion-PP does not occur with hectorite. For a positively charged species, such as $Ru(NH_3)_6^{3+/2+}$, there seems to be strong interaction between the clay film and the redox species, as manifested by the highly asymmetric shape of the voltammetric wave (Fig. 5c). The incorporation of PP into the clay film appears to reduce the extent of this interaction, and the voltammograms appear closer to those of a diffusion-controlled reaction (Fig. 5d).

The mechanical strength of a PP film is greatly enhanced by the incorporation of Nafion. A freestanding Nafion-PP film can be obtained by preparing the Nafion-PP film on a GC substrate (*ca.* 50 μm thick) and then peeling it from the GC with a razor blade. The resulting black film shows high flexibility. Clay-PP films are quite brittle. However, the mechanical strength of a clay-PP film might be improved, if a suitable solvent that is capable of swelling the clay and of dissolving pyrrole could be found, or if the clay is pillared (7c). Further research on the elucidation of the structure of these copolymers, and the application of such films as potential-controllable ion exchange membranes (8) are underway.

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[2] A poorer swelling capability of clay in MeCN as compared in H_2O is manifested by the much lower rate of incorporation of redox species such as $Os(bpy)_3^{2+}$ into a clay film in MeCN. F.-R. F. Fan and A. J. Bard, Unpublished results.