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A Poly-*p*-nitrostyrene on Platinum Electrode. Polymer Charging Kinetics and Electrocatalysis of Organic Dihalide Reductions

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Abstract: Platinum electrodes were modified by dip coating them with poly-*p*-nitrostyrene from a *N,N*-dimethylformamide solution. The coated electrodes were dried and then used for electrochemical studies in dry acetonitrile containing tetraalkylammonium fluoroborate electrolytes. Cyclic voltammetry showed that cycling the potential of these electrodes from −1.0 to −1.8 V vs. a $Ag/AgNO_3$ reference produced some initial desorption and formation of a stable polymer layer which was charged and discharged with peak potentials of −1.6 V. The peak shapes and the dependence of the voltammograms on the sweep rate, electrolyte cation, and amount of adsorbed polymer provided evidence about the structure and about the kinetics and thermodynamics of charging. The catalyzed reduction of 1,2-dibromo-1,2-diphenylethane to stilbene was investigated using cyclic voltammetry and preparative electrolysis. It was shown that the efficiency of catalysis increased to a limiting value as the amount of chargeable polymer increased. High efficiencies for reduction of this dihalide (3 mm) in acetonitrile could be obtained with layers corresponding to a surface charge of 4 nM cm^{-2}. The turnover number for catalyst sites was estimated to be 10^4.

Considerable attention has recently accrued to "chemically modified electrodes".[1] These devices are constructed by binding organic or organometallic species to the surfaces of conductors. The *molecular* structure of the modified surface endows these electrodes with specific physical and chemical properties not otherwise attainable. Our research in this area has emphasized the invention of techniques for synthesizing useful electrode surfaces, provided tests for surface structure and stability under electrochemical conditions, and demonstrated that such devices could be used to achieve greater selectivity in preparative reactions. Although our initial studies demonstrated the feasibility of producing and using surfaces modified by covalent binding, our attention has since moved to polymer modified electrodes. It was anticipated that such surfaces would have unique properties and some advantages over covalently modified materials. This anticipation has begun to be realized and there are now a number of research groups pursuing this approach.[2-9] The goal of all this work, and the present study in particular, is generalizable as selective electrocatalysis.

Electrocatalysis with chemically modified electrodes can occur by several (somewhat arbitrarily defined) mechanisms. An electroinactive modifier, which is not capable of accepting or donating electrons, can interact with incoming substrate molecules to alter their chemical reactions or electrochemical reaction rates. Alternatively, an electroactive modifier can act to relay charge from the underlying conductor to a solution species. This is a two-step process first involving (for reductions) electron transfer from the conductor to the modifier. The reductions of solution species can then take place either by an outer-sphere electron transfer from the modifier to the substrate or by an inner-sphere reaction in which nuclei as well as electrons move between modifier and substrate. The latter seems most interesting from the viewpoint of selectivity, but it also seems difficult to accomplish because of the greater mechanistic complexity. We have, therefore, chosen to test some ideas concerning the preparation, structure, stability, and catalytic efficiency of polymer modified electrodes using materials and a process which are chemically more simple. In this report we detail and amplify a preliminary communication concerning the use of a Pt/poly-*p*-nitrostyrene surface.[4] Evidence is provided concerning the charging of the polymer and the first example of preparative-scale electrocatalysis by an electroactive modifier is described.

Results and Discussion

Electrode Preparation and Voltammetric Characterization. Poly-*p*-nitrostyrene/Pt electrodes, as previously described,[4] were prepared from solutions of the polymer in *N,N*-dimethylformamide (DMF). Unless otherwise noted, the concentration was 1% w/v. These solutions were sufficiently stable to be used over a period of 1 week. Platinum disk electrodes (3×10^{-3} cm^2) set in soft glass were dipped in the solution for 10 min. The electrodes were then removed, shaken to remove the excess solution droplet, and dried in an oven at 130 °C for 30 min. Electrodes so prepared are referred to as electrode I. As shown below, the quantitative reproducibility of this dip-coating procedure as determined voltammetrically is usually obscured by the complexity of the electrochemistry. A few X-ray photoelectron spectra (X-ray PES) were obtained for electrodes which had not received any electrochemical treatment, but these are insufficient to provide any quantitative assessment. We have, therefore, reserved spectroscopic studies from this paper. In studies with other polymers[2] we have found

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Table I. CV Data for Electrode I[a]

electrolyte	cycle no.	Q_c, nF cm^{-2}	$-E_p^c$, V	i_p^c, mA cm^{-2}	δ^c, mV	Q_a, nF cm^{-2}	$-E_p^a$(N)	i_p^a	δ^a, mV
Et_4NBF_4 (0.1 M)	1	42	1.58	3.5	120	8.1	1.55	0.58	140
	5	7.8	1.60	0.56	140	7.0	1.58	0.53	130
	10	6.2	1.60	0.52	120	6.2	1.58	0.52	120
Bu_4NBF_4 (0.1 M)	1	34.8	1.65	2.9	120	15.6	1.53	0.78	200
	20	9.9	1.60	0.52	190	5.5	1.56	0.55	170
		(1) (2)	(1) (2)	(1) (2)	(1) (2)				
Me_4NBF_4 (satd)	1	10.0 32.0	1.50 1.74	0.91 1.43	110 225	49	1.43	5.5	90
	5	16.9 20.0	1.51 1.68	1.69 1.04	100 190	40	1.43	4.4	90

[a] Sweeping from −1.0 to −1.9 V vs. Ag|AgNO$_3$ at $\nu = 0.1$ V s^{-1}. Q_c = cathodic charge, E_p^c = cathodic peak potential, i_p^c = cathodic peak current, δ^c = peak width at half-height.

surprisingly good reproducibility, considering the method of removing the excess solvent.

Cyclic voltammetry (CV) was performed using dried acetonitrile, degassed with nitrogen, containing either tetramethylammonium fluoroborate (Me_4NBF_4) or the corresponding tetra-*n*-butyl (Bu_4NBF_4) and tetraethylammonium (Et_4NBF_4) salts as supporting electrolytes. The reference electrode was Ag|0.1 M $AgNO_3$ in acetonitrile. As detailed below, the water content of the solvent is an important variable, and, unless otherwise noted, activated alumina was added to the electrolyte solution in the cell to dry it. In a few experiments Pt flags were used. The shapes of the voltammograms obtained for flags were identical with those for disks.

The following discussion first treats the behavior observed during the first few voltammetric sweeps and describes the stable polymer modified electrodes which result. Somewhat different electrochemical behavior was observed on initial sweeps with each electrolyte. The most thorough studies were performed using 0.1 M Et_4NBF_4 solutions. Using electrode I in such solutions the first sweep (sweep rate $\nu = 0.1$ V s^{-1}) from −1.0 to −1.9 V gave a large cathodic peak $E_p^c = -1.58$ V and a much smaller anodic peak $E_p^a = -1.55$ V (see Table I). On following cycles these peaks diminished in size until after six or seven sweeps an identical trace (0–3% decrease in current) was obtained (see Figure 1). This electrode (Ia) could then be removed from the cell, washed, dried, and replaced in the same or fresh electrolyte solution and it would again give an unchanged voltammogram. A more thorough discussion of the CV behavior is presented below. It is only noted here that at $\nu < 0.1$ V s^{-1} the peak separation, ΔE_p, was 10–25 mV in various samples, the peak widths at half-height, δ, were typically 120 mV, and the ratio of the cathodic and anodic charges Q_c and Q_a was 1.0 ± 0.1. A typical value of Q_c is 6 nF/cm^2. The voltammograms do not change if the solution is stirred. All the data are consistent with charging and discharging a tightly held polymer layer.

The potential for charging the polymer corresponds closely to the potential for the reversible reduction of nitrobenzene ($E_p^c = -1.60$ V) to its radical anion. It is proposed that polymer charging involves a similar reduction of the nitroaromatic moieties along the polymer chain. We have no evidence for the proportion of moieties actually charged. A necessary condition for the estimation of surface charge by CV is that the current trace returns to background. This does not, however, ensure that all the groups are charged. An independent (presumably spectroscopic) technique is required. In the present case the current would return to background at $\nu < 0.1$ V s^{-1} and some values for the charge, Q_c, are reported in Table II. These data were assembled in order to demonstrate an unexpected aspect of the surface preparation method. As shown there the value of the cathodic limit during the first few sweeps makes a substantial difference in Q for the resulting Ia. A more negative switching potential produces an electrode with a smaller Q after ten sweeps. The variation in Q_c from sample to sample is evident here and it is clear that a precise electrochemical treatment is vital to reproducibility. A further disconcerting discovery of some importance is that the electrode preparation method requires the heating step. Electrodes prepared by dip-coating and drying at room temperature gave no CV waves under the usual conditions.

Table II. Effect of Switching Potential on Stable Surface Charge[a]

switching potential, V[b]	Q_c, nF/cm^{-2} [c]	switching potential, V[b]	Q_c, nF/cm^{-2} [c]
−1.75	9.5	−1.9	4.5
−1.75	8.7	−1.9	5.8
−1.8	7.4	−2.00	2.6
−1.8	8.8	−2.20	2.0
−1.9	5.5	−2.20	2.8

[a] Determined in 0.1 M Et_4NBF_4–acetonitrile. $\nu = 0.1$ V s^{-1}. Individual electrodes prepared from a 1% solution in DMF. [b] First cycle switching potential in CV. [c] Surface charge for stable electrode, Ia.

The observations that cycling diminishes the amount of chargeable material on the surface can be explained by desorption of some charged polymer. There are, however, two observations which suggest that further changes occur which bind the remaining polymer more tightly to the platinum surface. (a) As already described, not all the charged polymer desorbs. That which disappears does so rapidly, and then the remainder is permanently attached. (b) When electrode Ia was dipped in DMF for 30 min, rinsed, and dried, it was found by CV not to have lost any polymer from the surface. By contrast, an electrode I prepared normally, but not voltammetrically cycled, then soaked in DMF for 30 min, rinsed, and dried, showed an infinitesimal charging peak. The latter experiment indicates that the electrode I had lost all of its adsorbed polymer and demonstrates the increased adhesion of the polymer on electrode Ia, which was developed by the electrochemical treatment. These observations would seem to require that cycling in Et_4NBF_4 solution produces some subtle structural modification of the polymer or the polymer–platinum interface. The nature of this change is unknown but one possibility is that cross-linking takes place to some extent leading to a less soluble polymer. This reaction could involve the small amount of residual water in the electrolyte solution. It is known that reduction of nitrobenzene in the presence of water can lead to the formation of azo and azoxy compounds.[10] These moieties would act to cross-link the polymer and could interact with the platinum surface.

The absence of substantial amounts of water in the electrolyte solution is, indeed, critical to the electrochemical performance of these electrodes. All experiments which describe the charging and discharging of stable polymer layers refer to electrolyte solutions which have been dried by treatment of the

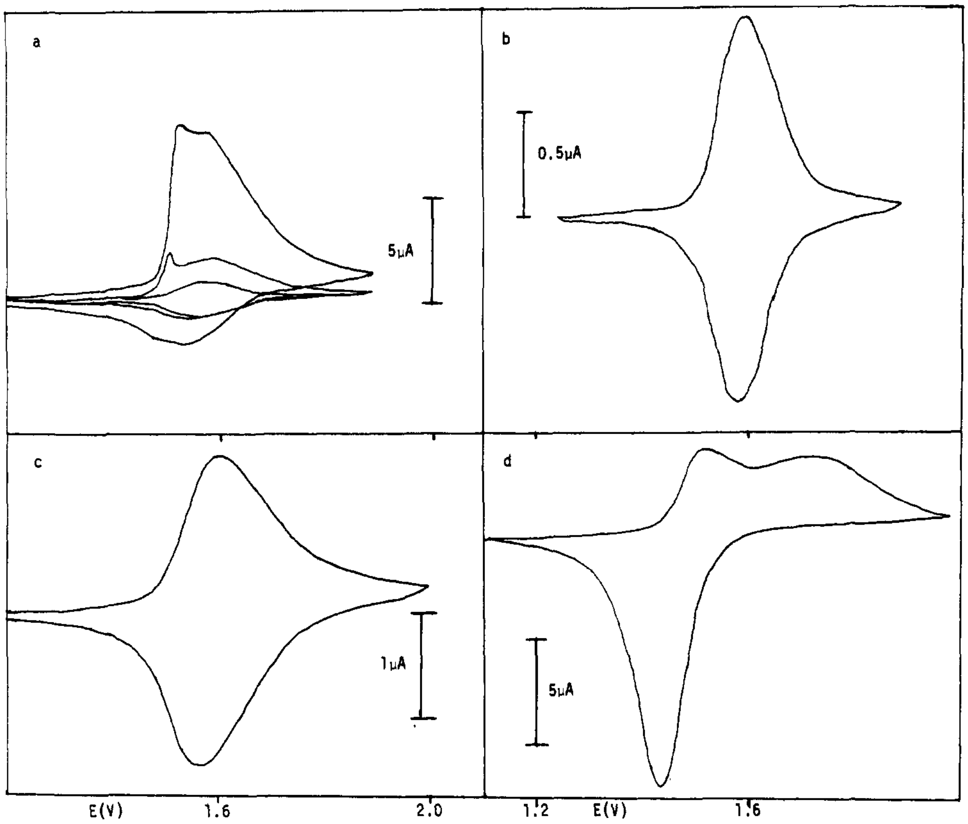


Figure 1. Cyclic voltammograms at $\nu = 0.1$ V s^{-1} for I in acetonitrile: (a) Et_4NBF_4 sweeps 1, 2, 5; (b) Et_4NBF_4 sweep 10; (c) Bu_4NBF_4 sweep 10; (d) Me_4NBF_4 sweep 2.

solvent with calcium hydride and by the addition of activated alumina to the cell. If these precautions are not taken, the acetonitrile contains about 0.3% water. Voltammograms measured using such solutions demonstrate that the charging process rapidly becomes less reversible and the total amount of charge accepted tends to decrease until eventually no electroactivity can be discerned. Again, the formation of the more difficultly reduced hydroxylamine, azo, and azoxy moieties is expected.

A study of the dependence of the amount of adsorbed polymer (determined spectroscopically) and the amount of charge accepted has not yet been undertaken. In Table III are, however, some data obtained with flag electrodes which demonstrate that the total acceptable charge can be increased by increasing the concentration of the dip solution. Perhaps more interesting is the fact that after voltammetric cycling in Et_4NBF_4 solution a "redip" will deposit more polymer which can in turn be stabilized electrochemically. In this way the stable surface charge could be increased to large values. Repeated dip-coatings without the electrochemical treatment did not result in a large increase in the stable surface charge.

One further observation concerning electrode Ia is that it could be used in 0.1 M Et_4NBF_4-DMF solution and it appeared to be stable. At 0.1 V s^{-1} a voltammogram with the shape of curve b of Figure 1 was obtained: $\delta = 120$ mV; $\Delta E_p = 10$mV at $\nu = 0.1$ V s^{-1}. Again, it seems clear that cycling the electrode produces important changes in the polymer adhesion.

Electrode I in Bu_4NBF_4-acetonitrile solution behaves similarly (see Table I). Thus, the first few cycles produce a dramatic decrease in the amount of charge accepted by the layer. After five to ten cycles at 0.1 V s^{-1} between -1.0 and -2.0 V a stable surface is achieved. A typical voltammogram is shown in Figure 1c. This stable surface behaved qualitatively like Ia. Quantitatively, at 0.02, 0.05, and 0.1 V s^{-1} ΔE_p was 30-40 mV, $i_p{}^c/i_p{}^a = 1.0 \pm 0.1$, Q_c was typically 6×10^{-9} F cm^{-2}, δ was typically 170 mV, and i_p was proportional to ν. At higher ν the peaks broaden and E_p increases regularly.

Table III. Surface Charge for Electrode I Prepared from Solutions of Varying Concentrations[a]

soln concn, %[b]	Q_a, nF Me_4NBF_4[c]	Q_c nF Et_4NBF_4[d] sweep 1	sweep 10
0.01	2.2	2	1.6
0.05	4.1	6	2.7
0.1	5.5	12	5.2
0.5	18	>35	17
1.0	25	>40	20

[a] Flag electrodes (2 cm^2). [b] Polymer concentration in DMF dip solution, w/v. [c] Electrodes initially cycled in Me_4NBF_4-acetonitrile, anodic current integral. [d] After *c*, electrodes cycled in Et_4NBF_4-acetonitrile. Cathodic current integral. First sweep values are poorly reproduced estimates.

Since some difference between Et_4NBF_4 and Bu_4NBF_4 was noted it was of obvious interest to study electrolytes with other cations. Me_4NBF_4 was used even though it is not very soluble in dry acetonitrile. It is estimated that the saturated solution used here contained 0.01 M Me_4NBF_4. This causes interpretational problems because of the uncompensated solution *iR* drop. The results are, however, quite interesting as shown in Figure 1d and Table I. Thus, the first cycle ($\nu = 0.1$ V s^{-1}) shows two cathodic peaks $E_p{}^c = -1.50, -1.74$, followed by one anodic peak $E_p{}^a = -1.43$. The total cathodic charge was equal to that of the anodic charge. The second cycle gave again two cathodic peaks, but the relative peak heights changed slightly. The total Q_c was unchanged. Subsequent sweeps were essentially retraces. Thus, there is no substantial diminishment of electroactivity like that found for Et_4NBF_4 and Bu_4NBF_4. Sweeping the potential of this electrode at 0.01 V s^{-1} gave similar behavior ($E_p{}^c = -1.47, -1.61$, $E_p{}^a = -1.46$) except

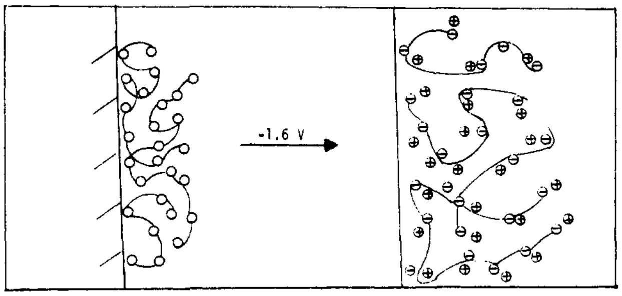


Figure 2. Model of electrode Ia. ○ ≡ *p*-nitrobenzene group. ⊖ ≡ *p*-nitrobenzene anion radical. ⊕ ≡ tetraethylammonium.

that the second cathodic peak was somewhat narrower. Although the charging process with Me_4NBF_4 takes place in the same voltage range as with Et_4NBF_4, the observation of two cathodic peaks and one anodic peak is unexpected. This is not due to the low concentration since 0.01 M Et_4NBF_4 gave a voltammogram with the same shape as that for 0.1 M Et_4NBF_4. One rationale is that there are two electroactive sites in the uncharged polymer. One of these sites is more difficult to charge, but the reduction product at that site (an anion radical in a spectral environment?) rapidly converts to the more stable reductive product formed at the first peak. On the return half-cycle this is then rapidly oxidized only at the more positive potential. An analogy can be found in the recent work of Evans and Nelson and their co-workers.[11] They have found cases in which two neutral conformers oxidize at different potentials, but the two cation radical products rapidly interconvert giving the more stable cation radical conformer. Only one reduction peak is then seen on completing the cycle. An alternative explanation is that the second peak is due to dianion formation promoted by Me_4NBF_4 ion pairing. This seems unlikely since nitrobenzene has its second wave at −2.5 V and ion pairing would have to shift this by about 1 V. One would also expect to see two anodic peaks from such a process. Therefore, the second peak could be due to dianion formation, but only if there is some additional kinetic complication of the kind cited above.

Because of its low solubility, extensive studies using Me_4NBF_4 were not undertaken. We did however, determine the effect of 0.01 M Me_4NBF_4 on a voltammogram taken with 0.1 M Bu_4NBF_4. Addition of the Me_4NBF_4 sharpens the peaks substantially and reduces ΔE_p. There is, however, no evidence for two cathodic peaks as seen for 0.01 M Me_4NBF_4 alone.

Since the data suggested that the use of Et_4NBF_4 led to desorption, but that Me_4NBF_4 did not, an experiment in which these electrolytes were used sequentially was of interest. An electrode I was first cycled in Me_4NBF_4 solution giving curve d of Figure 1 (Q_a = 40 nF cm^{-2}), then placed in Et_4NBF_4 solution giving curves with the shape of a of Figure 1. After several cycles in this Et_4NBF_4 solution a CV identical with that of electrode Ia was obtained. When the electrode was then returned to the Me_4NBF_4 solution, a CV with the same shape as Figure 1d, but with smaller currents, was observed. Indeed, Q_a = 6 nF cm^{-2} from this voltammogram and Q_c = 6 nF cm^{-2} for its chronological precursor in an Et_4NBF_4 solution. Thus, it again seems clear that the electrochemical treatment in Et_4NBF_4 irreversibly diminishes the amount of chargeable material held on the surface, as well as *subtly* changes the remainder.

Polymer Charging. The experimental CV data reveal several interesting aspects of the nature of the charged polymer and the charging mechanism. We are not aware of theories explicitly designed to handle such data and they are, therefore, treated in an empirical manner using theories designed for submonolayers with some discussion of useful qualitative models.

Consider first a structural model for electrodes coated with electroactive polymer (see Figure 2). From nonelectrochemical studies of adsorbed polymers[12] it is known that in most situations of interest the polymer will not lie flat on the surface, but will loop out in solution. The density of polymer within the layer will likely depend on the amount adsorbed. Thus, higher Q may suggest both a denser layer and one which extends further into solution. It should be swollen with electrolyte solution when uncharged, but *must* incorporate electrolyte cations when charged. Thus, the charged polymer "layer" is in reality a very concentrated solution. Association of cations with the proposed anion radical sites must be important and electronic disproportionation of anion radicals (to give a dianion plus neutral) should be enhanced in this region. Polymer motion could be important for charging and even the extension of the polymer layer into solution will change during charging. It may be true that there is a gradient of charge density as one moves out from the conductor surface.

Consider now the data for ν <0.2 V s^{-1} using Et_4NBF_4 and electrode Ia with $1 \leqslant Q \leqslant 16$ nF cm^{-2}. It is found that ΔE_p = 10–25 mV in various samples and the value for any one electrode is independent of ν. This value decreased only from 15 to 10 mV as the electrolyte concentration was quadrupled. The peak widths at half height, δ, are typically 120 mV and the individual peaks are nearly symmetrical about E_p. The data, especially the constancy of $E_p{}^c$ and $E_p{}^a$ with changing ν, suggests reversible electrochemistry. Previous theoretical studies[13,14] have predicted that the CVs for reactions involving reversible electron transfer to adsorbed monolayers or submonolayers where both the oxidized and reduced forms are confined to the surface show $\Delta E_p = 0$ and a symmetrical shape. The peak width, δ, for this situation is affected by interactions between adsorbed species. Thus, for example, in a case where neutral adsorbents are reduced to anions, theory indicates that repulsion between neighboring anions, which is not present between the neutrals, can lead to broadening of the peak. The voltammogram for electrode Ia in Et_4NBF_4 solution can to a good approximation be understood by applying the monolayer theory[13-15] and suggesting that the peak width >90 mV is due to repulsive interaction between moieties in the charged layer. One might alternatively suppose that there could be a distribution of sites with varying reversible potentials. The primary reason for such inhomogeneity, however, would seem to be a variable distance from the electrode. Since the peak shape is invariant from 1 to 16 nF cm^{-2} this seems an unlikely explanation. The concept of repulsions between sites in a dynamic layer can, however, nicely accommodate the δ results if the density of charged moieties within the layer is independent of Q. This theory does not, however, accommodate the $\Delta E_p > 0$.

Consider now the rather similar situation for Bu_4NBF_4 solutions. The ΔE_p and δ are constant and i_p is proportional to ν at ν = 0.02, 0.05, and 0.1 V s^{-1} for a variety of electrodes with Q = 1–13 nF cm^{-2}. This again suggests that at these sweep rates the electrochemistry is reversible. The δ = 170 mV at small ν can again be explained by repulsive interactions within the charged layer. These might be expected to be more serious when the bulkier Bu_4N^+ is involved. The situation cannot be so simple, however, since the peaks are asymmetric about E_p. Both the anodic and cathodic peaks have more charge at potentials negative to E_p than at potentials positive to E_p. The ΔE_p is also substantially greater than zero. Thus, the shape of the voltammogram is far from the theoretical one for simple, reversible electron transfer to a homogeneous layer with noninteracting electroactive groups.

We turn now to the behavior at high sweep rates. The qualitative observation, using either electrolyte, is that ΔE_p increases and the peaks broaden with increasing sweep rate. Using Et_4NBF_4 under all conditions, the peak shapes closely resemble those expected for slow electron exchange with a bound monolayer.[15-17] Some quantitative data for electrodes with three different Q values are displayed in Figure 3. It can be qualitatively concluded from this data that layers with larger Q give slower apparent charging rates and that electrodes charge slightly more slowly in Bu_4NBF_4 solutions than in Et_4NBF_4 solutions. This again suggests the importance of electrolyte cations to the charging process.[18] The importance of counterions for the charging of modified electrodes has previously been suggested by Wrighton and co-workers for ferrocenylsilane modified electrodes[19] and by Oyama and Anson[8] for ruthenium-polyvinylpyridine electrodes.

It has been previously noted that polymer layers often have an inhibiting effect on electron transfer at the underlying metal.[2] In this case, the uncharged polymer acts similarly. The test compound was ferrocene (1 mM) in 0.1 M Et_4NBF_4–CH_3CN and $\nu = 0.1$ V s^{-1}. Electrodes coated from more concentrated solutions gave more inhibition. In one example an electrode was coated from a 5% solution of polymer in DMF. Compared to the value on clean platinum this coating depressed the peak current for ferrocene oxidation by 90%. After cycling to −1.8 V the peak current for ferrocene returned to its uninhibited value. This reinforces the conclusion that cycling in Et_4NBF_4 solution causes desorption. Inhibition by the polymer was found to be more effective when a water–ethanol mixture was used as solvent. An electrode I prepared from a 0.5% polymer solution inhibited the peak current of ferrocene (1 mM) in water–ethanol (50:50) containing 0.1 M $LiClO_4$ by 40% at 0.1 V s^{-1}. In acetonitrile the inhibition was less than 5% for the same electrode. It is thus clear that the uncharged polymer inhibits electrochemical events on platinum[20] and that the extent of inhibition is solvent dependent, as well as being dependent on the amount of material on the surface. It is shown below that the charged polymer actually catalyzes certain electrode processes. This disparate behavior of the charged and uncharged polymer can be thought of as a potential-dependent change in "conductivity". As such, it should have some interesting applications.

It was also of interest to examine a reversible couple with an $E_{1/2}$ more negative than −1.55 V and benzophenone ($E_p^c = -2.35$ V) was chosen. On clean platinum it shows a reversible couple. Using electrode Ia, the first sweep shows polymer charging and a benzophenone peak at ca. −2.3 V. There is, however, no anodic peak at either −2.3 or −1.5 V on the reverse half-cycle. The second cycle shows no peak for polymer charging. It seems clear that the benzophenone radical anions react rapidly with the polymer.

Electrocatalysis. Exploration of the use of electrode Ia for catalyzed reductions has been undertaken. Most of this work was directed toward halide reductions and it is instructive to first describe some aspects of the reduction of organic halides on platinum. Carbon tetrachloride, for example, reduces with E_p −1.95 V. Using CV there is no anodic peak on the return half-cycle. The electrode becomes rapidly passivated so that preparative reductions are not possible and, indeed, the reduction peak is severely distorted even on the second sweep. As indicated below, this inefficient reaction could be catalyzed by the polymer layer of electrode Ia. It should be realized that the reductions of halides can be performed adequately on other metals and a chemically modified electrode is not necessary. This system seemed, however, to provide a useful testing ground.

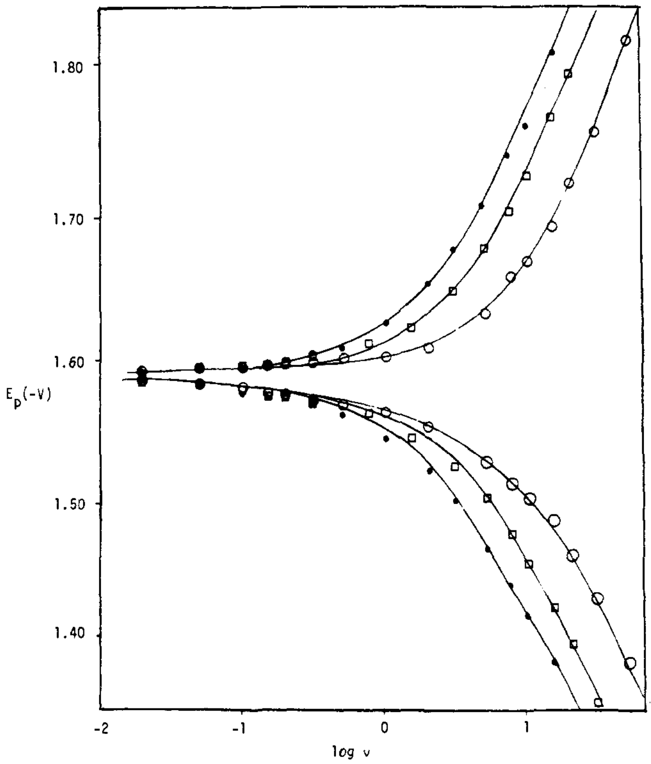


Figure 3. Charging kinetics for Ia in 0.1 M Et_4NBF_4–acetonitrile: ○, Q = 3.7 nF cm^{-2}; □, Q = 7.6 nF cm^{-2}; ●, Q = 10.4 nF cm^{-2}.

Based upon numerous literature reports, halide reductions are expected to be chemically irreversible and kinetically slow. The reduction has a high activation energy (overpotential) related to the interplay of a concomitant carbon–halogen bond cleavage and electron transfer. There are also numerous reports which demonstrate that these reductions can be mediated by other solution species.[21-23] As initially studied by Fry and by Lund and their co-workers, and later thoroughly expounded by Saveant and his co-workers, a simplified scheme is

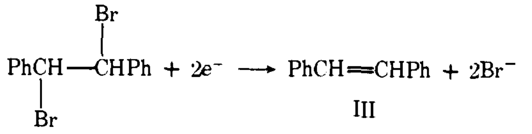
$$e^- + A \rightleftarrows A^{-}\cdot$$

$$A^{-}\cdot + RX \rightarrow A + R\cdot + X^-$$

$$R\cdot \rightarrow \text{products}$$

A is chosen so that it reduces reversibly at potentials more positive than those for the irreversible RX reduction. Upon reduction of A at the electrode, $A^{-}\cdot$ is formed, diffuses out into the solution, and donates an electron to RX. The resulting radical, R·, has many possible fates depending on its structure and the conditions, but eventually it leads to protonated or coupled products. A practical advantage of using a mediator is that RX can then be reduced at a more positive potential. This, in essence, diminishes the activation energy for RX reduction. Transference of the qualitative concept to modified electrodes is straightforward, since one should be able to simply bind the mediator to the surface. The quantitative aspects of transfer are, however, not at all clear. Several examples of catalysis using covalently modified electrodes have appeared[24] and one study has been performed using a "plasma polymerized vinylferrocene" surface to catalyze the electrochemical oxidation of ascorbic acid.[25] No detailed investigation of mediation kinetics with a modified electrode has appeared and only one brief note concerning the theory for such a process is available.

Our studies have concentrated on the reduction of *meso*-1,2-dibromo-1,2-diphenylethane (II), which is expected to be reduced to stilbene (III) in a two-electron process. This com-



$$\text{PhCH(Br)–CH(Br)Ph} + 2e^- \longrightarrow \text{PhCH=CHPh} + 2\text{Br}^-$$

II

III

pound was chosen in the hope that any intermediates formed in its reduction would rapidly go on to form the alkene and not

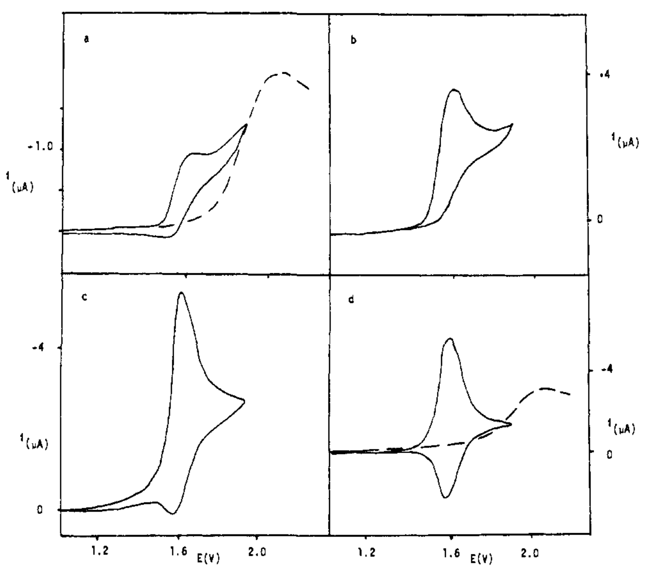


Figure 4. Cyclic voltammograms for Ia in 0.1 M Et_4NBF_4-acetonitrile containing 3 mM II, $\nu = 0.1$ V s^{-1}. - - - represents a partial voltammogram for 3 mM II on clean platinum. (a) $Q = 1.1$ nF cm^{-2}, CAT EFF = 0.3. (b) $Q = 4$ nF cm^{-2}, CAT EFF = 0.8. (c) $Q = 7$ nF cm^{-2}, CAT EFF = 0.8. (d) $Q = 15$ nF cm^{-2}, CAT EFF = 0.7.

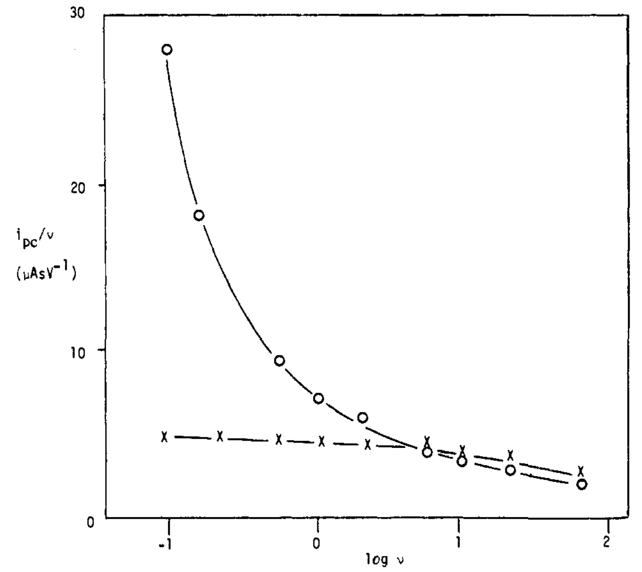


Figure 5. Dependence of cathodic peak current on sweep rate: ○, Ia; ×, Ia + 3 mM II.

attack the polymer. It has been previously reported that the reduction of II on mercury is clean and that the reduction can be mediated by chloranil or quinoxaline anion radicals.[26]

The CV of II (3 mM) on clean platinum in dry acetonitrile containing alumina and 0.1 M Et_4NBF_4 shows a peak at −2.02 V ($\nu = 0.1$ V s^{-1}), Figure 4a. The reduction is chemically irreversible. Using polymer electrode Ia ($Q = 1.1$ nF cm^{-2}) in this same solution at $\nu = 0.1$ V s^{-1} gives the voltammogram in Figure 4a in which the cathodic current at the polymer peak is greatly enhanced and the anodic current almost entirely suppressed. The usual peak due to II at −2.02 V is not seen, but a reversible couple due to *trans*-stilbene at −2.6 V is present. It is, therefore, evident that the polymer mediates the reduction of II. The ν dependence is shown graphically in Figure 5 where i_p^c/ν is plotted against ν for the polymer electrode Ia in the presence of II. At 10 V s^{-1} there is no evidence for catalysis indicating that the electron transfer to II is slower than the time scale of the experiment.

The catalytic component of the current, i_p^{CAT}, is of interest with regard to mechanism and to measurement of the efficiency. It is defined here as the difference between the peak cathodic current measured at −1.59 V with II present and absent. Measured at $\nu = 0.1$ V s^{-1}, i_p^{CAT} varied linearly when the bulk concentration of II was changed from 0.3 to 5 mM. No change in E_p was observed upon addition of II. Bu_4NBF_4 gave very similar results to $EtNBF_4$.

It is of great interest to know the dependence of the catalytic efficiency on the "thickness of the polymer layer".[26] In this case, the amount of polymer present on the surface is unknown. The charge Q_c accepted by the polymer in the absence of II is, however, known and can be compared to the catalytic efficiency CAT EFF = i_p^{CAT}/i_p^{II}, where i_p^{II} is the peak current for 3 mM II on clean platinum in dry acetonitrile. Quite a large number of examples were investigated. Although the CAT EFF for one electrode used in several experiments was good, the reproducibility of the data for different electrodes was, unfortunately, not sufficiently good to provide a quantitative correlation. The voltammograms shown in Figure 4 are representative and demonstrate the qualitative conclusion which can be unequivocally drawn from the data. At $Q = 1$ nF cm^{-2} the catalytic efficiency (CAT EFF) is ca. 0.3. As Q rises to 4 nF cm^{-1} so does CAT EFF. Above 4 nF cm^{-2} a limiting value of CAT EFF of 0.8 ± 0.3 is reached. The shapes of the voltammograms are quite rational. Thin layers generally give no anodic peak on the return cycle. Thicker layers show the anodic peak, and indeed, for $Q = 16$ nF cm^{-2} the voltammogram shape at 0.1 V s^{-1} is only slightly distorted from that in the absence of II. It is thus clear that the kinetics for catalysis of a 3 mM solution of II are not improved when Q is greater than about 4 nF cm^{-2}.

A brief report containing a theoretical treatment germane to this data has appeared.[27] It predicts that the catalytic efficiency will increase with the "number of equivalent monolayers" as our data for $1 < Q < 4$ nF cm^{-2} demonstrate. If it is rather arbitrarily assumed that an equivalent monolayer takes up 0.5 nF cm^{-2}, optimum efficiency is obtained in this case with about eight equivalent layers.

A comparative study of the mediated reduction of II by nitrobenzene in solution was also undertaken. Nitrobenzene, $E_p^c = -1.60$ V, catalyzes the reduction of II in a similar fashion to the polymer electrode. The CAT EFF = 0.35 at $\nu = 0.1$ V s^{-1} for a solution 4 mM in nitrobenzene and 5 mM in II. Thus, as expected, concentration of the mediator at the surface by adsorption enormously reduces the quantities required.

Turning to preparative-scale experiments, it is first noted that reduction of II at clean platinum, as at mercury,[26] gave high yields of *trans*-stilbene. Mediated reduction of 0.1 mmol of II with a 4 mM nitrobenzene solution on platinum in acetonitrile was also successful. Gas-liquid chromatography demonstrated a 98% yield of *trans*-stilbene, with only a trace of the cis isomer. Electrodes Ia (2 cm^2) were used in the same manner to reduce II. *cis*- and *trans*-stilbene (~5/95) were formed in high yield (Table IV). Examination of the electrode by CV in a separate acetonitrile solution after a preparative run showed a substantial decrease in the amount of chargeable polymer. This decrease allows an estimate of catalyst turnover as 10^4 (Table IV). The catalyst lifetime seems primarily limited by residual water since it was found that simply polarizing the electrode to −1.6 V for 30 min without II present also led to a substantial decrease in the number of electroactive groups. Since most of the catalyst is consumed during these preparative experiments, it is difficult to unequivocally establish that none of the reduction takes place on the underlying metal of a partially decomposed electrode surface. In one case, therefore, an electrode with a large Q was employed to reduce a small amount of II. After the run the electrode was reexamined as usual by CV. The curve had the usual reversible shape and the calculated turnover was again 1×10^4. It should be empha-

Table IV. Preparative Reductions of *meso*-1,2-Dibromo-1,2-diphenylethane at Electrode Ia [a]

stilbene yield,[b] mol × 10^5	q, F × 10^5 [c]	Q_c init,[d] mC	Q_c final[e]	turnover[f] × 10^{-4}
2.1 (6.6)	4.25	0.63	0.25	1.0
1.4 (18)	3.16	0.25[g]	trace	1.2
2.4 (6.6)	4.46	0.42	0.14	1.5
1.7 (15)	4.41	0.85	0.28	0.75
0.9 (14)	2.12	0.74	0.27	0.43

[a] 5 mM II in 0.1 M TEABF$_4$, CH$_3$CN. E = 1.50–1.55 V. [b] Analyzed by GLC. The trans/cis ratios are in brackets. [c] Total number of faradays passed in the electrolysis. [d] Charge accepted by polymer before adding II. [e] Charge accepted by polymer after electrolysis and in the absence of II. [f] Turnover = $q/Q_{c_{init}} - Q_{c_{final}}$. [g] Electrode from previous experiment.

sized, however, that the catalytic efficiencies and turnovers depend strongly on having dry acetonitrile. The catalysis of other organic halides has also been accomplished. A list of these is given in Table V, together with their reduction peak potentials at clean platinum, the catalytic efficiency, and the surface charge of the electrode with which the catalysis was carried out. The numbers there are, however, of limited value since the peak potentials for the halides were difficult to accurately reproduce.[28] It was found that the peak potential varied substantially with the amount of water present in solution.

Finally, the previously reported effect of the polymer upon the reduction of oxygen in acetonitrile[4] was investigated using Et$_4$NBF$_4$. On platinum the oxygen reduces to superoxide. At 0.1 V s^{-1} $E_p{}^c = -1.5$ V and ΔE_p is ca. 500 mV. The presence of the polymer substantially improves the reversibility of this couple. Indeed, because the cathodic peak shifts to positive potentials, it appears at a potential (−1.3 V) positive of the polymer charging peak. Thus, it is not clear that this reduction is mediated via electron transfer through the polymer.

Experimental Section

Cyclic and linear sweep voltammetry were carried out using a Princeton Applied Research (PAR) potentiostat, Model 173, in conjunction with a PAR 175 Universal Programmer. Voltammograms were recorded on a Varian F-80A X-Y recorder or a Tektronix 5111 storage oscilloscope. Coulometry and preparative electrolyses were performed with the same potentiostat coupled with a PAR 179 digital coulometer.

Acetonitrile (Burdick and Jackson UV) was used as received. Tetraethylammonium fluoroborate (Southwestern Analytical Chemicals), tetra-*n*-butylammonium perchlorate (G. F. Smith), and tetramethylammonium fluoroborate were used without further purification. Neutral alumina, activity grade 1 (Fischer Scientific), was used for drying. It was established by GC analysis that this led to electrolyte solutions 0.006 M in water. That level was not improved by predrying the acetonitrile.

Platinum electrodes were cleaned before use by soaking in concentrated HNO$_3$ for 1-2 h, followed by soaking in concentrated KOH (aqueous) for 1 h. The electrodes were cycled five times in 0.5 M H$_2$SO$_4$ from 0 to 1.5 V vs. SCE, stopping at 0 V. Electrodes were also polished mechancially on a regular basis before the chemical cleaning.

The organic halides were either commercial samples or were synthesized using the literature procedure.[29] The purity was ascertained using NMR and melting point. Poly-*p*-nitrostyrene (Polysciences) gave a satisfactory elemental analysis and was used without purification. The viscosity was measured in DMF over the concentration range 0.5-5.0 g/dL and [η] = 0.13. A weighed amount of polymer was dissolved in a known volume of DMF, which had been dried by passing it through an alumina column. Platinum disk electrodes prepared by sealing a wire into soft glass and grinding it flat were dipped into this solution, usually for 10 min. They were removed, quickly shaken four times (nurse/thermometer style) to remove the excess solvent, and baked at 130 °C for 30 min. After voltammetric cycling, electrodes Ia were quite stable and could be used in several different experiments in different electrolyte solutions. An attempted electrodeposition from DMF-0.1 M Et$_4$NBF$_4$ failed as judged by the absence of CV peaks when the electrode was transferred to acetonitrile-0.1 M Et$_4$NBF$_4$. Repetitive dipping and heating did not produce electrodes with larger amounts of adsorbed polymer, but repetitive dip, bake, and CV treatments did work. In a typical example, four of these treatments would increase i_p from 1.2 to 4 μA. The quantitative reproducibility of Q for Ia was usually ±10%. There were, however, occasions when much less polymer was bound.

Table V. Catalytic Reductions of Organic Halides[a]

compd	$-E_p$, V	Q, nF cm^{-2}	CAT
dl-PhCHBrCH(Ph)Br	2.24	8.1	0.08
PhCHBrCH$_2$Br	2.20	3.4	0.24
(Ph)$_2$CBrPhCHBr	2.29	2.2	0.04
CCl$_4$	1.95	5.0	0.25
o-iodobromobenzene	1.85	2.2	0.3

[a] Electrode Ia in 0.1 M Et$_4$NBF$_4$, ν = 0.1 V s^{-1}.

The cell for cyclic voltammetry was a single-compartment cell containing the reference electrode (Ag|0.1 M AgNO$_3$ in CH$_3$CN), which was separated from the main compartment by a cracked glass tube, and the platinum counterelectrode. The volume of solution was generally 25 mL. A Luggin capillary was used to reduce the uncompensated resistance of the cell, which was nominally 300 Ω. Degassing with argon was performed in every case.

Preparative electrolysis was performed in the same cell with about 20 mL of solution but the cathode was separated from the anode and reference electrode by a glass frit. The anode used in this case was platinum gauze or a sheet (12.5 cm^2).

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Use of Chemically Derivatized n-Type Silicon Photoelectrodes in Aqueous Media. Photooxidation of Iodide, Hexacyanoiron(II), and Hexaammineruthenium(II) at Ferrocene-Derivatized Photoanodes

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Abstract: n-Type Si can be derivatized using (1,1′-ferrocenediyl)dichlorosilane yielding a photoanode that can be used in aqueous electrolyte solutions under conditions where the naked (nonderivatized) n-type Si undergoes photoanodic corrosion yielding an insulating SiO_x surface layer. Derivatized electrodes in aqueous electrolyte solution exhibit chemically reversible oxidation of the surface-confined, ferrocene-centered redox reagent when the electrode is illuminated. Oxidation is not detectable in the dark, consistent with the fact that n-type semiconductors are blocking to oxidation in the dark. At sufficiently high light intensity, the surface-confined material can be oxidized at more negative potentials than when the same material is confined to the surface of a reversible electrode material such as Pt or Au. Light intensity of ~40 mW/cm^2 at 632.8 nm is typically sufficient to effect oxidation 200-400 mV thermodynamically uphill for electrodes exhibiting coverages of 10^{-10}-10^{-9} mol/cm^2 of electrochemically active material. Such electrodes can be used to effect the persistent oxidation of I^-, $[\mathrm{Fe(CN)_6}]^{4-}$, and $[\mathrm{Ru(NH_3)_6}]^{2+}$. The current efficiency for $3\mathrm{I}^- \rightarrow \mathrm{I_3}^-$ and $[\mathrm{Fe(CN)_6}]^{4-} \rightarrow [\mathrm{Fe(CN)_6}]^{3-}$ is measured to be >90% and these oxidations can be effected thermodynamically uphill, but with low efficiency. The formal potential of $[\mathrm{Ru(NH_3)_6}]^{3+}/[\mathrm{Ru(NH_3)_6}]^{2+}$ is sufficiently negative, −0.2 V vs. SCE, that oxidation cannot be effected thermodynamically uphill with n-type Si. Oxidation of $\mathrm{H_2O}$ using derivatized n-type Si does not occur under any conditions used. The oxidation of the three reductants used occurs by (1) photogeneration of electron-hole pairs by absorption of band-gap irradiation by n-type Si (band gap = 1.1 eV); (2) oxidation of the surface-confined ferrocene-centered redox reagent by the photogenerated holes; (3) oxidation of the solution reductant (I^-, $[\mathrm{Fe(CN)_6}]^{4-}$, $[\mathrm{Ru(NH_3)_6}]^{2+}$) by the surface-confined ferricenium oxidizing reagent. This mechanism is established by cyclic voltammetry. Current-time plots show that ferrocene-ferricenium turnover numbers exceed 10^5 and constant (within 10%) photocurrents can be obtained for >5 h, whereas naked electrodes give photocurrents which decay by >90% within 5 min. Energy conversion efficiency for $[\mathrm{Fe(CN)_6}]^{4-}$ oxidation or I^- oxidation at 632.8 nm is of the order of 1%.

Substantial improvement in n-type semiconductor-based cells for light to electricity energy conversion has been possible through judicious choice of aqueous and nonaqueous electrolyte/redox systems.[1-8] We have recently adopted a strategy involving chemical derivatization of the surface of n-type semiconductor photoanodes in order to design photosensitive interfaces for use in a large number of thermodynamically uphill oxidation processes. The essence of our strategy is to bind redox reagents to the surface of the n-type semiconductor. The bound reagents can be oxidized in a thermodynamically uphill fashion by irradiation of the semiconductor and the oxidized form can then oxidize solution species. The point is that the surface-confined material serves two functions: (1) photogenerated holes are transferred to the attached redox reagent to preclude semiconductor decomposition and (2) the photooxidized, surface-confined material oxidizes solution species that may or may not be directly competitively oxidized at the naked electrode. Just what species in solution can be oxidized does not depend on the kinetics of hole transfer from semiconductor to the solution species, but rather on the nature of the surface-confined material. Thus, electrodes can be "designed" to oxidize certain species selectively. In energy conversion applications what can be oxidized, overall efficiency, and durability are parameters of central importance. Our earlier articles have been concerned with the preliminary aspects of derivatized n-type Si,[9] Ge,[10] and GaAs[11] characterized in nonaqueous media by electrochemical techniques. In this article we wish to amplify our results[9c] on the use of derivatized n-type Si in aqueous electrolyte solutions. These are important measurements inasmuch as naked Si is useless in aqueous electrolytes and yet has a band gap, E_{BG}, of 1.1 eV[12] that is nearly optimal from the point of view of solar energy conversion. Our new results show that the uphill oxidation of I^- to $\mathrm{I_3}^-$ can be sustained using an n-type Si photoelectrode derivatized with (1,1′-ferrocenediyl)dichlorosilane.

Results and Discussion

A. Characterization of Naked and Derivatized n-Type Si Electrodes in Aqueous Electrodes. Freshly HF-etched, single-crystal, n-type Si photoanodes in aqueous 0.1 M $\mathrm{NaClO_4}$ (pH 0-6) are not durable, and we have been unable to observe any sustained photoanodic reaction other than that represented by the equation

$$x\mathrm{H_2O} + \mathrm{Si} \xrightarrow{h\nu} \mathrm{SiO}_x + 2xe^- + 2x\mathrm{H}^+ \qquad (1)$$

Note that the surfaces of Si used here are not pure Si; the surfaces invariably have a thin air oxide.[13] Irradiation of the

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