

studies. Thus, the tidy relationship between the stoichiometric and catalytic reactions, as outlined in Scheme I, is also incorrect. In particular, the immediate precursor and the route to chlorobenzene in the catalytic reaction remain to be identified.

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### Stabilization of n-Type Silicon Photoelectrodes to Surface Oxidation in Aqueous Electrolyte Solution and Mediation of Oxidation Reaction by Surface-Attached Organic Conducting Polymer

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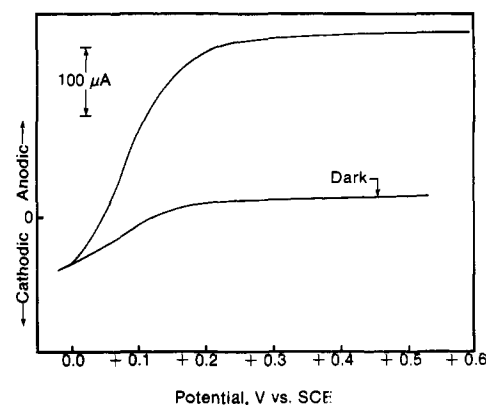
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A major impediment to the exploitation of photoelectrochemical cells in solar energy conversion and storage is the susceptibility of small bandgap semiconductor materials to photoanodic and photocathodic degradation.<sup>1-3</sup> We have found that the photoanodic degradation of n-type Si can be greatly suppressed in aqueous solution by electrodeposition of an organic conducting polymer (polypyrrole) on the surface of the electrode. The conducting polypyrrole film protects the n-type Si electrode against  $\text{SiO}_2$  formation, presumably by covering potential oxide-forming sites and efficiently directing photoinduced charge in the semiconductor across the film before the charge has an opportunity to react with the semiconductor electrode. These effects are similar to those reported<sup>4</sup> for n-type Si derivatized with ferrocene complexes, but the nature of the modified surface is quite different. The degree of stability produced and the ease of film deposition are quite remarkable and provide encouragement for the potential application of organic conducting polymer films to practical photoelectrochemical devices for solar energy conversion.

Previous work<sup>5</sup> on n-type GaAs coated with polypyrrole also shows stabilization of the semiconductor against photocorrosion; however, the polymer film exhibited poor adhesion in aqueous electrolyte. Other interesting papers have been published on the nature of polypyrrole-coated metal electrodes; electrochemical synthesis of polypyrrole having conductivities in the range of  $10\text{--}100\ \Omega^{-1}\ \text{cm}^{-1}$  on platinum electrodes have been reported.<sup>6</sup> We have carried out photoelectrochemical studies of polypyrrole deposited on n-type crystalline and polycrystalline Si in aqueous solution. The photoelectrochemical behavior of the crystalline and polycrystalline materials are similar, although the surface treatment and morphology of the electrodes necessary to form the film may differ. In this communication we shall report results only on the n-type polycrystalline Si.

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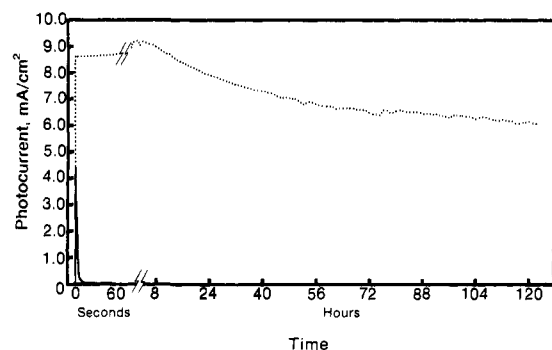
**Figure 1.** Current-potential curves (50 mV/s) of polypyrrole-covered polycrystalline n-type Si electrode in the dark and in the light in 0.15 M  $\text{FeSO}_4$ , 0.15 M  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and 0.1 M  $\text{Na}_2\text{SO}_4$  in water at pH 1 under He at 295 K. Illuminated with tungsten-halogen light at 87 mW/cm<sup>2</sup>.

The polypyrrole films were synthesized potentiostatically under illumination on the n-type silicon surfaces in a three-electrode, three-compartment cell containing 1.0 M pyrrole and 0.3 M tetraethylammonium fluoroborate in a helium-bubbled acetonitrile solvent which was stirred mechanically.

Electrodes were fabricated from polycrystalline n-type Si (20–30- $\Omega\text{-cm}$  resistivity) with a grain size of about 1.5 mm  $\times$  4 mm. Ohmic contacts were made with an alloy solder of 10% silver and 90% indium. The wire leads were encased in a glass tube for mounting and insulated with epoxy to expose only the Si surface. The electrodes were etched for 10 s in concentrated HF at room temperature immediately prior to electrodeposition of the polypyrrole film. Deposition on n-type Si begins ca 0.45 V vs SCE under illumination (ca. 200 mW/cm<sup>2</sup>) with a tungsten-halogen lamp. Films were formed at constant potential at voltages between 0.6 and 0.9 V. During the synthesis, the current remained practically constant at 100  $\mu\text{A}/\text{cm}^2$ . On the basis of charge density passed (between 1 and 10 mC/cm<sup>2</sup>), and assuming 2.2 F mol<sup>-1</sup> of pyrrole,<sup>6</sup> the films typically were 140–1200- $\text{\AA}$  thick. Illumination of the electrodes was carried out with a 100- or a 250-W tungsten-halogen lamp; unless otherwise noted, the radiation was unfiltered.

Polypyrrole-covered n-type Si was characterized by cyclic voltammetry in 0.15 M  $\text{FeSO}_4$ , 0.15 M  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , and 0.1 M  $\text{Na}_2\text{SO}_4$  in aqueous solvent at pH 1. Figure 1 shows the current-potential characteristics of polypyrrole-covered n-type Si in the dark and under illumination. The polypyrrole-covered electrode exhibits typical n-type behavior. The oxidation wave of the coated electrode is strongly dependent on the incident light intensity, whereas the cathodic current is relatively unaffected by light. The onset potential of the photoanodic current corresponds to the flatband potential of n-type Si (ca. 0.1 V), which was determined independently by capacitance measurements. The current-potential data in Figure 1 are the average of ca. 50 scans at 50 mV/s; little difference was observed between the first and last scan. In marked contrast, the photoanodic current of the naked (film-free) n-type Si electrodes diminishes rapidly to nearly zero after 1–2 scans.

The power characteristic of a polypyrrole-covered n-type Si electrode in an iron sulfate solution of the same composition referred to above was examined under nonoptimal conditions (i.e., with respect to the separation distance between the working and the counter electrodes, the potential of the redox couple, the electrolyte concentration, etc.) and with no IR compensation. The electrode was illuminated with a tungsten-halogen lamp that delivered 24.5 mW/cm<sup>2</sup>; this radiant power has been corrected for the infrared absorption (mainly,  $\lambda \geq 1200\ \text{nm}$ ) of a 4-cm length water filter and absorption due to the electrolyte solution. The power conversion efficiency of the cell was 3%, corresponding to a short-circuit current of 2.9 mA/cm<sup>2</sup>, an open-circuit voltage of 0.39 V, and a fill factor of 0.6. This efficiency can be compared



**Figure 2.** Photocurrent-time behavior of naked (—) and polypyrrole-coated (· · ·) polycrystalline n-type Si electrodes illuminated with tungsten-halogen light at  $143 \text{ mW/cm}^2$  under short-circuit conditions. Solution containing  $0.15 \text{ M FeSO}_4$ ,  $0.15 \text{ M FeNH}_4(\text{SO}_4) \cdot 12\text{H}_2\text{O}$  and  $0.1 \text{ M Na}_2\text{SO}_4$  in water at pH 1 was stirred continuously. No precaution was taken to exclude air.

with an average conversion efficiency of 10% at AM 1 reported<sup>7</sup> for polycrystalline silicon grown similarly to that used in this work and employed in a solid-state p-n junction cell. The thickness of the film was calculated to be  $1200 \text{ \AA}$ . Presumably, a thinner film would result in a higher current density.

The current-time behavior (Figure 2) of the polypyrrole-coated n-type Si photoanode in aqueous solution containing a  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple contrasts dramatically with that of unprotected naked n-type Si. The photocurrent of the naked electrode drops precipitously to zero from its initial value in less than 30 s. However, the photocurrent of the polypyrrole-coated n-type Si first increased by ca. 6% over the first 5 h followed by decay. During 122 h of irradiation ( $143 \text{ mW/cm}^2$  of unfiltered light from a tungsten-halogen lamp) the photocurrent decayed by only ca. 30%. No precaution was taken to exclude air from the photoelectrochemical cell, and there were no signs that the polypyrrole film was peeling off the electrode or dissolving into solution after the passage of ca.  $3100 \text{ C/cm}^2$  at a current density between 6 and  $9.2 \text{ mA/cm}^2$ . The magnitude of the charge density is particularly noteworthy, since less than  $10 \text{ mC/cm}^2$  is required to form the film. The detailed mechanism for the stability<sup>8</sup> produced by polypyrrole films is currently being investigated. The good adhesion and induced stability characteristics of the electrode system are also representative of other polypyrrole-covered electrodes that we have studied.

In conclusion, polypyrrole polymer films have been shown to produce a dramatic improvement in the stability of n-type Si against photooxidation in aqueous electrolyte. The polymer film is very easy to apply to the semiconductor electrode and exhibits excellent adhesion. Other n- and p-type semiconductors are being examined with polypyrrole films. The mechanism by which the conducting polymer films stabilize semiconductors is also under investigation.

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(8) A referee proposed that the stability of the polypyrrole-coated electrode arises from iron-pyrrole complexes which produce a high concentration of oxidizable  $\text{Fe}^{2+}$  ions at the film-electrode interface. The  $\text{Fe}^{2+}$  ions compete with oxide formation, and the film behaves only as an inert matrix that does not conduct photogenerated holes. The suggestion of a complex with polypyrrole can be dismissed because polypyrrole-coated n-GaAs exhibits stability with  $\text{Fe}(\text{CN})_6^{3-/4-}$  and with  $\text{Fe}^{\text{III}}\text{EDTA}/\text{Fe}^{\text{II}}\text{EDTA}$  redox couples as described in ref 5. We believe, however, that both charge conduction by the film and the availability of oxidizable  $\text{Fe}^{2+}$  species are important in the stabilization of n-type Si.

## Low-Valent Molybdenum Porphyrin Derivatives: Synthesis and Structure of a $\pi$ -Bonded Diphenylacetylene Adduct of Molybdenum(II) (*meso*-Tetra-*p*-tolylporphyrin)

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Metalloporphyrin derivatives in which olefins or acetylenes are  $\pi$  bonded to the central metal have been postulated as transient intermediates during the formation of  $\sigma$  carbon-metal bonds with metalloporphyrins.<sup>1</sup> To our knowledge no such compound has ever been characterized. We report now the preparation and structural characterization of a novel molybdenum(II) porphyrin derivative  $[\text{MoTTP}(\text{PhC}\equiv\text{CPh}) \cdot \text{C}_6\text{H}_5\text{CH}_3$  (**1**) in which a diphenylacetylene molecule is  $\pi$  bonded to the metal atom enclosed in the porphyrin ring. Moreover, the acetylenic carbon-carbon and the carbon-to-metal bond distances present in **1** indicate by comparison with the same structural parameters present in  $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{PhC}\equiv\text{CPh})$  (**2**)<sup>2</sup> that the acetylenic group acts as a four-electron donor in **1**. It can only act as a two-electron donor in **2**.<sup>3</sup>

Reduction by lithium aluminum hydride of a toluene solution (50 mL) containing  $\text{Mo}^{\text{IV}}(\text{TTP})\text{Cl}_2$  (100 mg), an excess of diphenylacetylene (100 mg), and a few drops of THF led to a green solution after 1 h of vigorous stirring. After the solvents were evaporated under vacuum, the residue was eluted on alumina with toluene. A violet compound **1**  $[\text{MoTTP}(\text{PhC}\equiv\text{CPh}) \cdot \text{C}_6\text{H}_5\text{CH}_3$  was crystallized from this solution by addition of pentane (25 mL). [Visible spectral data in benzene:  $\lambda$  (log  $\epsilon$ ) 426 (5.20), 544 (3.98), 624 nm (3.36)]. Complex **2**  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{PhC}\equiv\text{CPh})]$  was prepared by the method of A. Nakamura and S. Otsuka.<sup>2</sup>

Crystals suitable for X-ray studies were obtained for complex **1** by slow diffusion of pentane into a toluene solution of the complex and for compound **2** by slow diffusion of pentane into a chlorobenzene solution.<sup>5,6</sup>

The structure of **1** is shown in Figure 1. The geometry about the metal is best described as pseudo square pyramidal with the four porphyrinato nitrogens  $\text{N}_p$  constituting the basal plane and the middle of the acetylenic carbon-carbon triple bond occupying the apical position. The molybdenum(II) atom is displaced out of the 4-nitrogen  $\text{N}_p$  plane by  $0.63 \text{ \AA}$  and by  $0.73 \text{ \AA}$  from the mean plane of the 24-atom core. Thus a net doming is present; yet two opposite pyrrole rings  $\text{N}_1$  and  $\text{N}_3$  tilt upward out of the mean plane toward the molybdenum(II) atom, while the  $\text{N}_2$  and  $\text{N}_4$  pyrrole rings tilt downward.<sup>7</sup> The conformation of the core presents thus

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(5)  $\text{Mo}(\text{TTP})(\text{PhC}_2\text{Ph})(\text{CH}_3\text{C}_6\text{H}_5)$  crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 21.815$  (4),  $b = 16.414$  (3),  $c = 15.055$  (3)  $\text{ \AA}$ ;  $\beta = 94.08$  (6) $^\circ$ ;  $Z = 4$ ,  $V = 5377 \text{ \AA}^3$ . The calculated density based on four molecules ( $\text{C}_{69}\text{H}_{54}\text{N}_4\text{Mo}$ ,  $M = 1035.2$ ) per unit cell is  $1.28 \text{ g/cm}^3$ . The data were collected in the range  $2.5 < \theta < 57^\circ$  by a flying spot scan technique using Cu  $K\alpha$  radiation on a Philips PW1100 diffractometer. Independent reflections (5825) corrected for absorption were coded as observed [ $I > 3\sigma(E)$ ]. All nonhydrogen atoms were given anisotropic temperature factors to yield, after introduction of the hydrogen atom positions,  $R = 0.075$ ,  $R_w = 0.105$ .

(6)  $\text{Cp}_2\text{MoC}_2(\text{C}_6\text{H}_5)_2$  belongs to the orthorhombic space group  $Pbcn$  with  $a = 22.042$ ,  $b = 13.017$ ,  $c = 12.689 \text{ \AA}$ ;  $V = 3640.7 \text{ \AA}^3$ ,  $Z = 8$ . Data were collected by using Cu  $K\alpha$  radiation in the range  $2^\circ < \theta < 60^\circ$  with a Philips PW1100 diffractometer. Reflections (1902) with  $I > 3\sigma(I)$  were used in refinement ( $R = 0.050$ ,  $R_w = 0.079$ ).