differ by 180° rotations about one of the heme pseudo-C_2 axes. In addition, an earlier report of two forms of cytochrome b_5 is further evidence of the generality of this phenomenon and suggests the possibility that such heme asymmetry could modulate electron-transfer properties as well as ligand binding.[10]

We have not yet observed such heterogeneity in native CcP but, Figure 1 demonstrates that reconstituting CcP with deuterohemin IX produces such heterogeneity. Consider Figure 1A, the spectrum of native CcP. It is similar to that of most other met-aquo heme proteins. The four intense resonances between 45 and 90 ppm downfield from 2,2-dimethyl-2-silapentane-5-sulfonate[11] were previously assigned to the peripheral methyl substituents of protohemin IX (IA).[1] Reconstitution doubles the number of methyl resonances in this region, indicating heme asymmetry. Comparison of the cyanide-ligated forms of the native and reconstituted protein (Figure 1C,D) makes this clearer.

In Figure 1D the spectrum of the cyano-native protein displays two of the protohemin methyls[12] which are shifted away from the diamagnetic envelope (30.4, 27.4 ppm). Reconstitution (Figure 1C) produces twice the number of downfield methyl resonances (31.8, 26.9, 26.4, 20.2 ppm). In the upfield region where the 2,4 protons of deuterohemin characteristically resonate[7,10] the reconstituted protein displays four resonances instead of the expected two (−9.5, −17.4, −19.7, −31.3 ppm). The peak at −5.6 ppm is assigned to a single hemin meso proton based on its integrated intensity and assignments made in model compounds. These peaks may be assigned to one component or the other on the basis of their temperature-dependent intensities, and those of the minor components at 28 °C are indicated by arrows.

Besides demonstrating that the relative concentrations of each component depend upon temperature, our preliminary work indicates their sensitivity to pH and treatment of the apoprotein. Work currently under way is designed to quantitate this behavior, elucidate the mechanism by which the heme asymmetry is established, and define the nature of the asymmetry. Whether such asymmetry exists in the native protein is particularly important. Although its presence has not yet been established, if the concentration of the asymmetric component were small, as in the case of sperm whale myoglobin, it may be difficult to detect except under more severe treatment of the protein.

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(10) Keller, R.; Groudinsky, O.; Wuthrich, K. *Biochim. Biophys. Acta* **1976**, *427*, 497.

(11) All shifts reported here are relative to external 2,2-dimethyl-2-silapentane-5-sulfonate.

(12) Resonances were assigned by integration and comparison with the spectra of other cyanide-ligated hemes and heme proteins.

Silicon Photocathode Behavior in Acidic V(II)–V(III) Solutions

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The p-Si/VCl_3–VCl_2–HCl/C cell shows 2.8% light-to-electrical conversion efficiency at 101 mW cm^{-2} of natural sunlight with improved output retention relative to previous aqueous Si-based photoelectrochemical cells. Over a 0.5-V range, the open-circuit photovoltage follows the redox potential of the solution, ruling out, for this system, pinning of the p-Si surface Fermi level as proposed by Bocarsly et al.[1]

Photocathode-based semiconductor–liquid junction solar cells differ fundamentally from photoanode-based cells in that illumination confers cathodic protection rather than intensifying the problem of anodic photocorrosion. Reductive degradation of silicon (as to SiH_4) is kinetically difficult. n-Si photooxidizes in acid solution to form an insulating SiO_2 layer which makes Si photoanodes inactive in short order. Derivatization of the surface leads to increased stabilization but, so far, not to efficient cells.[2] For p-Si, Bookbinder et al. have shown that stable currents may be drawn for at least 24 h in mixed acetonitrile–water–NaI with organic redox couples and 2.4% conversion efficiency for 6328-Å light[3] can be reached.

According to these groups[1-4] higher efficiencies (i.e., photovoltage) cannot be reached because of "pinning" of the Fermi level at the interface. We find this explanation inconsistent with several well-established features of the surface chemistry of silicon. Si, upon exposure to air or water, readily forms an oxide layer which "unpins" the surface Fermi level.[5] A wide literature and technology of Si MIS and MOS (metal–insulator–semiconductor and metal–oxide–semiconductor) solar cells amply demonstrate that there is no pinning at the Si/SiO_x/SiO_2 interface. Indeed, modern silicon technology is highly dependent on the quality of this interface with respect to a low density of surface states in the forbidden gap.

Recently we reported that, by using a relatively concentrated V^{2+}/V^{3+} redox couple with p-InP, we could achieve 9.4% solar-to-electrical conversion efficiency. With p-InP, as Si, pinning is likely to be overcome by an air-formed interfacial layer (possibly also by adsorbed cations in solution). Measurements of the voltage of the p-InP/VCl_2–VCl_3–HCl/C cell as a function of the redox potential of the solution, while varying the latter, indicate that the surface Fermi level is substantially unpinned. We show that the same holds also for p-Si and, in addition, that the interface is more stable than in any other previously reported Si-based photoelectrochemical cell. We note that effects of solvents other than water[1] may produce different results and are concerned here only with aqueous environments. Indeed, in some solvents, an interfacial oxide may not be produced.

The open-circuit voltage of the cell p-Si/V^{n+}–$V^{(n+1)+}$–HCl/C, under tungsten–halogen illumination equivalent to AM1 solar, was recorded while the $n/(n+1)$ species ratio was being increased by zinc metal or decreased by access to air. Since vanadium has three (V^{3+}/V^{2+}, V^{4+}/V^{3+}, V^{5+}/V^{4+}) well-defined one-electron couples, each separated by about 0.5 V over its 2+ to 5+ oxidation states, the redox potential could be varied with ease over a wide range. Reduction by zinc metal produces equivalently concentrated Zn^{2+} solutions which may have small effects on equilibria and redox potentials. The result of the experiment is shown in Figure 1. A simple linear dependence of cell photovoltage on solution redox potential is found over a Nernst potential range of −0.4 to +0.1 V vs. SCE. Slices of a standard semiconductor grade p-Si wafer B-doped to 7×10^{15} cm^{-3}, with bulk resisivity of 3 Ω cm have been used as photocathodes. (100) faces were employed after conventional slicing and polishing, with 30% HF or with CP-4, an etchant consisting of 25 mL of HNO_3, 15 mL of CH_3COOH, 15 mL of HF, and 1% bromine. When the redox potential in a 0.35 M total vanadium solution was −0.47 ± 0.01 V vs. SCE (adjusted by access of air or by zinc reduction, as necessary), no weight loss (±10 mg cm^{-2}) was detectable after

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(1) Bocarsly, A. B.; Bookbinder, D. C.; Dominey, N. R.; Lewis, N. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 3683.

(2) Bocarsly, A. B.; Walton, E. G.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 3390.

(3) Bookbinder, D. C.; Lewis, N. S.; Bradley, M. G.; Bocarsly, A. B.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7721.

(4) Bard, A. J.; Bocarsly, A. B.; Fan, F.-R. F.; Walton, E. G.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 3671.

(5) Wagner, L. F.; Spicer, W. E. *Phys. Rev. B* **1974**, *9*, 1512.

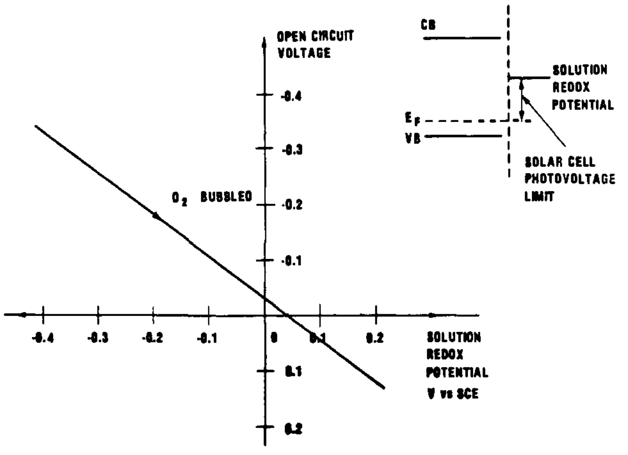

Figure 1. p-Si/VCl_3-VCl_2-HCl/C cell open-circuit voltage under tungsten-halogen illumination recorded against the solution redox potential. Insert on top right shows theoretical expectation for ordinate with no pinning by surface states and sufficient light intensity to flatten the bands. The silicon Fermi level intercept shown on the abscissa is negative of the true flat-band condition to the extent that the ordinate values are below the light intensity saturation limit.

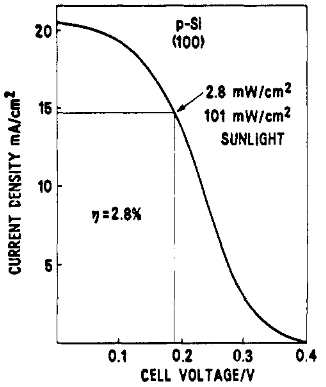

Figure 2. Current-voltage characteristics of the cell ⟨100⟩ p-Si/0.35 M total V(II) + V(III), 4 M HCl (E_{soln} = -0.47 V vs. SCE)/C, under 101 mW cm^{-2} sunlight.

passage of 20 000 C cm^{-2} under tungsten-halogen illumination over a 120-h period. The cell was placed under a 10-Ω load, wherein the p-Si potential was ~+80 mV from its short-circuit value throughout. Dissolution by 2 e/mol in that time would correspond to a loss of 2800 mg cm^{-2} and by 4 e/mol to 1400 mg cm^{-2}. In this experiment the initial current was 66.7 mA cm^{-2}, which declined after 120 h to 37.5 mA cm^{-2} (56% of initial). These approximate 2 and 3 times, respectively, the levels observed at short circuit under AM1 solar illumination. In a 116-h run with total vanadium and HCl increased to 1.8 and 6 M, respectively, and more focused white light, an initial 71.7 mA cm^{-2} reading declined to 51.7 (72% of initial) after passage of 23 700 C cm^{-2}.

Figure 2 shows the current-voltage curve of the cell, p-Si/0.35 M total V(II)-V(III), 4 M HCl (E_{soln} = -0.47 V vs. SCE)/C, at 101 mW cm^{-2} irradiance of natural sunlight. The maximum power output is 2.8 mW cm^{-2} for a solar-to-electrical power conversion efficiency of 2.8%. The short-circuit current of 20.4 mA cm^{-2} may be compared to the theoretical limit of ~43 mA cm^{-2} for the 1.1-eV band gap of Si.[6]

The initial condition of the Si surface is critical to cell performance. The highest current is observed after a 10-30-s CP-4 etch. The current drops, however, over a short time (~1 min) to a relatively stable level. During this period some H_2 evolution is detected when the electrode is held within +100 mV of the short-circuit potential. After a 30% HF etch the current is at the level to which the CP-4-etched electrode drops after the first minute. No H_2 evolution, even at short circuit, is observed after this etch.

The respectable stability and quantum efficiency obtainable with silicon in these strongly acidic environments, a shift of photovoltage as expected by Schottky models without pinning, and the variations in behavior observed with the two etchants and with cell cycling can be reconciled with the properties of the Si interface. Since SiO_2 is an excellent insulator whose presence is responsible for failure of n-Si photoanodes in aqueous environments, the thickness of any SiO_2 film must be limited to tunneling dimensions, permitting significant currents to be drawn, as is the present case for p-Si.

Ellipsometry shows that the surface of silicon exposed to air can be schematically represented as $Si/SiO_x/SiO_2$.[7] The composition denoted by SiO_x is apparently not removed by HF, but is removed by CP-4, and is reformed rapidly in the acidic solution, even in the presence of a strong reducing agent. A thicker (SiO_2) film forms on standing near open circuit, as is evident from hysteresis in the I-V curves, if the voltage is allowed to approach open circuit. However, even on long operation at high light near short circuit, or even near the maximum power point, the thickening of the SiO_2 layer is extremely slow and approaches a steady-state value. Exhaustive stability runs would be required to establish the limit of the maintenance of output current. Weight loss measurements establish that surface attack is restricted to minimal dimensions in the sense of removal of electrode material.

The shifts in cell voltage with solution redox potential indicate that, in spite of the involvement of electrode films shown by the cyclic cell and etching results, the interface is responsive to solution Nernst potentials. This observation is consistent with recently reported results for p-InP[8] and in contrast to recent publications asserting wide applicability of pinning of surface Fermi levels for p-Si and other covalent semiconductors.[1-4] While the p-Si/VCl_2-VCl_3-HCl/C cell is not as stable or as efficient as that with a p-InP photocathode, the stability and efficiency are the best for any Si-based photoelectrochemical cell so far.

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(6) Hovel, H. J. *Semicond. Semimetals* **1975**, *11*, 38.

(7) Aspnes, D. E.; Theeten, J. B. *J. Electrochem. Soc.* **1980**, *124*, 1359.

(8) Heller, A.; Miller, B.; Lewerenz, H. J.; Bachmann, K. J. *J. Am. Chem. Soc.* **1980**, *102*, 6555.

Absence of Internal Return in the Reaction of (4-Nitrophenyl)nitromethane with Amine Bases in Toluene Solution. Implication on Unusually Large Isotope Effects Reported for This Reaction

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Very large isotope effects have been reported for the acid ionization of (4-nitrophenyl)nitromethane in nonpolar solvents in the presence of strongly basic amine proton acceptors (eq 1).[1]

$$ArCH_2NO_2 + B \rightleftharpoons ArCHNO_2^-HB^+ \qquad (1)$$

Some of these rate ratios are as great as k_H/k_D = 50 at 25 °C, which exceeds by a considerable margin the maximum value attributable to complete loss of all of the zero-point energy of a C-H bond. These isotope effects were therefore interpreted in terms of quantum-mechanical tunneling through the reaction barrier, and they soon came to be regarded as among the best evidence for the tunnel effect in proton-transfer reactions.[2]

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(1) (a) Caldin, E. F.; Mateo, S. *J. Chem. Soc., Chem. Commun.* **1973**, 854-855. (b) *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1876-1904. (c) *Ibid.* **1976**, *72*, 112-121.