

nally consistent parameters extending over at least ten years are needed, absolute calibration not being essential. Such a satellite-derived reference climatology has not yet been created. The development of an operational monitoring and prediction system entails a substantial material commitment. This is something that deserves to be considered seriously in the light of the demonstrated predictability of northeast Brazil droughts and their social and economic impact.

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Evidence against surface state limitations on efficiency of p-Si/CH₃CN junctions

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We report here the first efficient p-type Si-based semiconductor-liquid junction system. p-Type Si photocathodes have been previously reported to yield open circuit photovoltages, V_{oc} , of 0.38-0.40 V with several redox systems¹⁻⁸. Photocurrent-voltage studies of p-Si cathodes in CH₃CN solvent have demonstrated 2.5% efficiency for conversion of 632.8-nm light to electricity with the N,N' -dimethyl-4,4'-bipyridinium^{2+/+} redox system¹, and 0.5-2.4% with other macrocyclic complexes^{7,8}. Such modest energy conversion efficiencies for small band gap semiconductors have been attributed to surface states which pin the semiconductor Fermi level⁶⁻⁹ and promote recombination processes¹⁰. However, we find that p-type Si/CH₃CN interfaces can yield solar conversion efficiencies in excess of 10%, and can display open circuit photovoltages within 0.08 V of the theoretical limit for an ideal junction.

We have chosen the cobaltocene⁺⁰ (CoCp₂⁺⁰)/1.0 M [(C₂H₅)₄N]⁺[BF₄]⁻/CH₃CN redox system to probe the interface behaviour of p-Si in CH₃CN solvent. (CoCp₂)⁺(PF₆)⁻ is sufficiently soluble in CH₃CN to be used in concentrations which minimize mass transport polarization losses at the working electrode. In addition, the electrochemically reversible^{11,12} CoCp₂⁺⁰ system possesses an $E^{0'}$ (-0.95 V/SCE) sufficiently negative to effect a large degree of band bending at the semiconductor-liquid interface. Uncompensated ohmic resistance losses can be minimized with proper cell design in this highly conductive

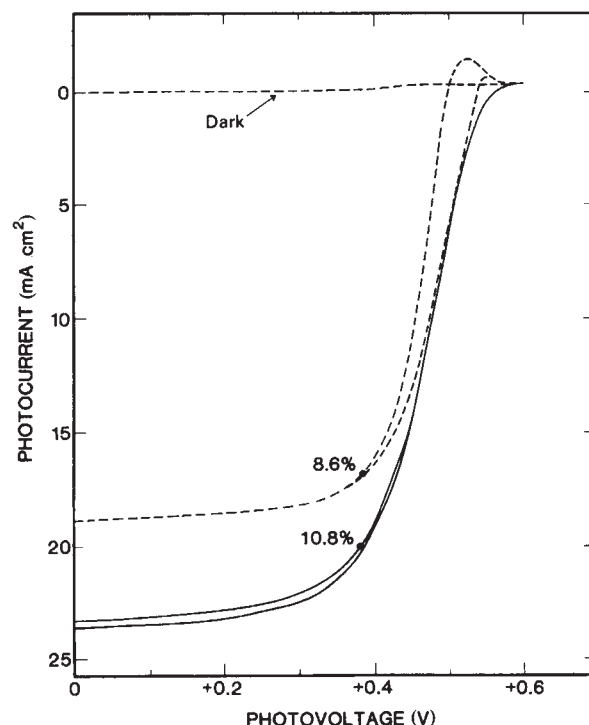


Fig. 1 Current-voltage properties of a single crystal p-type Si photocathode in a stirred CH₃CN/1.0 M [(C₂H₅)₄N]⁺[BF₄]⁻/0.2 M cobaltocenium/0.5 mM cobaltocene solution. Light intensity is 70 mW cm⁻² from an ELH-type tungsten-halogen solar simulator, and photocurrent-voltage curves are uncorrected for any losses due to optical reflection or solution absorption. —, Shiny Si surface obtained from a 10-s etch in 48% aqueous HF, followed by a 10-s rinse with H₂O, then a 10-s rinse with CH₃CN. —, Matte-textured surface¹³ in identical illumination conditions. Both current-voltage curves were measured potentiostatically (50 mV s⁻¹) versus a Pt reference electrode (-0.82 V/SCE) through a Luggin capillary, and represent photoelectrode efficiencies of the semiconductor cathode.

($\rho = 18 \Omega\text{-cm}$) electrolyte; thus, all current-voltage parameters have been measured under potentiostatic control versus a Pt reference electrode in a 0.2-mm outer diameter Luggin capillary. Only when all of the above criteria are met might one conclude that any inefficiencies are due to surface states at the interface.

Use of a mirror-finished p-type Si electrode (HF-etched, 1.5 $\Omega\text{-cm}$ resistivity, (100) oriented) in the optimized 1.0 M [(C₂H₅)₄N]⁺[BF₄]⁻/0.2 M CoCp₂⁺/0.5 mM CoCp₂/CH₃CN system with 70 mW cm⁻² of ELH-type tungsten-halogen irradiation¹³⁻¹⁵ yields V_{oc} of 0.48-0.52 V, short circuit photocurrent densities, J_{sc} , of 20-21 mA cm⁻², fill factors of 0.52-0.55, and photoelectrode efficiencies for conversion of incident light to electricity of $8.5 \pm 0.8\%$ (Fig. 1). Texturing of the photoelectrode surface to expose (111) planes and produce a matte black surface yields decreased reflectivity¹³ and produces a system with $V_{oc} = 0.49-0.53$ V, $J_{sc} = 23-26$ mA cm⁻², and efficiencies of $10.5 \pm 1.0\%$. Actual direct sunlight yields similar behaviour, and at 70 mW cm⁻² of insolation on matte-etched surfaces, we observe $V_{oc} = 0.49-0.53$ V, $J_{sc} = 23-26$ mA cm⁻², and efficiencies of $10.5 \pm 1.0\%$.

The photocurrents depicted in Fig. 1 are certainly not due to cathode corrosion. With suitable precautions to exclude air and water from the cell, we have maintained stable ($\pm 10\%$) short circuit currents at AM2 photocurrent densities (> 20 mA cm⁻²) for passage of $> 2 \times 10^3$ C cm⁻² through the interface. Longer term stability of this system has not been investigated because of the documented photodecomposition processes of CoCp₂ (ref. 11); however, other soluble, outer-sphere redox couples should be available which would yield similar photocurrent-

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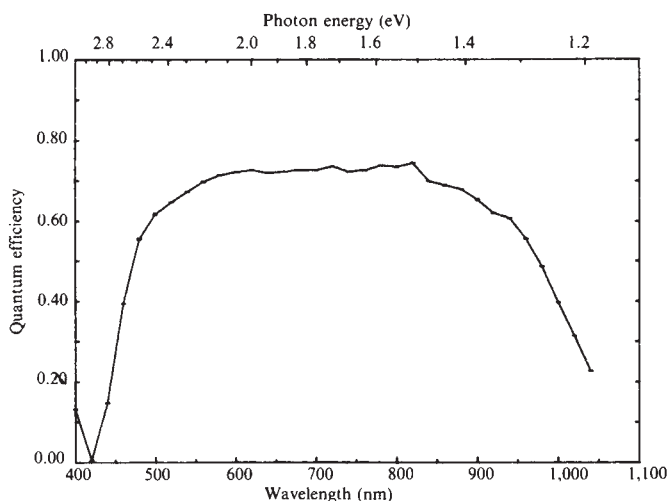


Fig. 2 Spectral response of the short circuit quantum yield plotted against wavelength of incident photons for the p-Si/CH₃CN/cobaltocene^{+/0} system. Average incident light intensity is 1 mW cm⁻², and quantum efficiencies ($\pm 10\%$) are uncorrected for losses due to optical reflection or solution absorption of light. Shiny p-Si cathodes yield 20–30% less current than a matte-textured surface, but both electrodes exhibit excellent response over a broad spectral range.

voltage parameters. Our stability and efficiency measurements represent photoelectrode efficiencies of the working electrode only, and do not represent actual operating two-electrode solar cells. However, the system certainly illustrates that it is possible to observe excellent junction behaviour for p-Si photocathodes in the proper conditions.

The photocurrent response versus incident photon energy for mirror-finished p-Si cathodes is depicted in Fig. 2. The onset of photocurrent is in accord with the 1.1-eV absorption edge of Si, and the high-energy cutoff is attributable to solution absorption of light. An integration of the spectral response properties in Fig. 2 with the solar spectral input yields short circuit photocurrent densities which are in excellent agreement with experimental J_{sc} values. The observation of significant photocurrent near the Si absorption edge implies that unthermalized hot carriers do not provide the sole source of photocurrent flow at these p-Si/CH₃CN junctions. In addition, the high absolute value of the short circuit quantum efficiency, both at low light intensities and solar irradiance levels, yields little evidence for surface recombination sites at the p-Si/CH₃CN interface.

We view these results as consistent with observations in our laboratory^{13,17} and by others^{18,19} that the chemistry of the Si/SiO₂ interface will preclude substantial carrier recombination by surface states. With a minority carrier diffusion length of 300 μ m and a dopant density of 2×10^{15} carriers cm⁻³, photocurrent densities of 20 mA cm⁻² imply a bulk diffusion-limited open circuit voltage of 0.59 V (refs 20–22). Thus, the V_{oc} of 0.48–0.52 V at 20–21 mA cm⁻² for the p-Si/CH₃CN system is within 0.08 V of the maximum attainable value for any junction fabricated with our semiconductor samples. Furthermore, the V_{oc} of p-Si/CH₃CN junctions substantially exceed V_{oc} values typically found for direct p-Si/Au or p-Si/Pt Schottky barriers ($V_{oc} < 0.20$ – 0.25 V)²³. In fact, the V_{oc} values at high light intensity (> 1 W cm⁻²) for the p-Si/CH₃CN system (> 0.55 V) exceed reported values of barrier heights for p-Si Schottky barriers with metals such as Ag, Au, Cr, Cu, Mo, Ni, Pb, Pd, Pt and W (ref. 20). Clearly, intrinsic surface states do not dominate the chemistry at both the semiconductor/liquid and semiconductor/metal interfaces.

Our data on the p-Si/CH₃CN interface yield no evidence for surface state limitations which would prevent the rational design and study of efficient semiconductor–liquid junctions. Investigations of the p-Si system are thus consistent with recent studies

of other common, small band gap semiconductors (n-Si (ref. 13), n-GaAs (ref. 24), n-GaAs_{1-x}P_x (ref. 25)) which suggest that control of bulk electrode properties and of solution overpotential losses can eliminate most inefficiencies previously ascribed to surface states at the semiconductor–liquid interface. Extension of the CoCp₂^{+/0} redox system, and similar metallocenes, to other photocathode materials is underway.

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Photochemical dehydrogenation of ethanol in dilute aqueous solution

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The need for alternative sources of energy has stimulated research into the storage of sunlight as chemical potential. Many systems have been investigated but photogeneration of H₂ seems to be the most practical. The cyclic photodissociation of water has yet to be realized in homogeneous solution using visible light, although heterogeneous photosystems are known^{1–3}. Efficient photogeneration of H₂ in homogeneous conditions can be achieved^{4–7} at the expense of an added electron donor but such systems have little application in practical devices. Replacement of the sacrificial donor with waste material, for example sulphide⁸, offers a route for improving these systems and, here we describe efficient H₂ photogeneration from a system using aqueous ethanol, as available from low grade fermentation, as donor. To couple the photoproduction of H₂ to the oxidation of ethanol we have used NADH/alcohol dehydrogenase as a relay.

Dichloro tin(IV) *meso*-tetrakis (*N*-methyl-4-pyridyl)porphyrine (SnTMPyP⁴⁺) dissolves readily in water throughout the entire pH range and such solutions absorb strongly all light