oxygen mobility at low temperatures. Thus, the plateaus may be 'smeared out' in nonequilibrated samples and even absent in samples rapidly quenched from high temperatures. Second, the apparent phase separation at $x = 6.90$ could also be caused by nonuniform oxygen uptake during the slow cooling because there is an appreciable oxygen pressure in the apparatus at this stoichiometry. (This caution does not apply to the $x = 6.65$ sample.) Third, because electron diffraction examines an exceedingly small portion of each sample, it would be useful to see if complementary measurements of the structure and properties of the bulk material also provide evidence for phase separation at the same stoichiometries. We note, however, that phase separation between phases with only small differences in oxygen content may be difficult to detect using bulk techniques. Alternatively, the ordered structures and T_c plateaus could be determined in $YBa_2Cu_3O_x$ derivatives to see if similar correlations are found. □

Received 19 June; accepted 1 August 1989.

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ACKNOWLEDGEMENTS. We thank R. Sinclair for the use of his electron microscope, J. H. Turner for help with image processing of the electron diffraction patterns, and P. Grant, F. Herman and J. Torrance for their comments.

Efficient photovoltaic devices for InP semiconductor/liquid junctions

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AN alternative to conventional solid-state photovoltaic devices is the semiconductor/liquid junction. Liquid-junction cells not only offer the possibility of integrating energy conversion and storage functions[1], but also may exhibit electrical properties that are fundamentally different from those in solid-state systems[2]. We have investigated the photovoltaic behaviour of n-InP/metal and n-InP/liquid junctions. We have found that the electrical properties of these semiconductor/liquid junctions are superior to those of n-InP/metal (Schottky barrier) systems, and that the current-voltage characteristics are a strong function of the electrochemical potential of the liquid phase. Liquid contacts thus provide a possibility for the construction of more efficient photovoltaic devices than those available at present from Schottky barriers.

The n-InP samples were 300-μm-thick, 2×10^{16} cm^{-3} Si-doped crystals oriented along the (100) plane obtained from Crystacomm Inc., Mountain View, California. After mounting[3] and etching[4], the samples were immersed in the appropriate electrolyte solution and current-voltage (I-V) data were collected. The redox potential $E(A^+/A)$ of the $LiClO_4$-CH_3OH electrolyte was varied by use of several different pairs of oxidized (A^+) and reduced (A) ions. Because of their different electron affinities and solvation properties, addition of these redox pairs (A^+/A) to the liquid produced changes in the electrochemical potential (that is, the Fermi level) of the solution phase. On the electrochemical potential scale, more positive redox potentials indicate that the Fermi level of the solution is further away from the vacuum level. Thus, the difference in energy between the conduction band of an n-type semiconductor and the redox potential of the solution (that is, the barrier height) should be larger for more positive solution redox potentials. The molecules used included: cobaltocene$^{+/0}$ (with a standard electrochemical potential $E^{0\prime} = -0.9$ V relative to the reference level of a standard calomel electrode (SCE) ($CoCp_2$); decamethylferrocene$^{+/0}$ ($E^{0\prime} = -0.08$ V relative to SCE) ($Me_{10}Fc$); 1,1′-dimethylferrocene ($E^{0\prime} = +0.26$ relative to SCE) (Me_2Fc).

Figure 1 displays the dark I-V properties of n-InP/Au Schottky contacts and n-InP/0.20M Me_2Fc-0.10M Me_2Fc^+-1.0M $LiClO_4$-CH_3OH junctions. In accord with previous reports, we observed that the Schottky contacts exhibited ohmic behaviour at moderate current densities and were poor rectifying contacts with high reverse-saturation-current (J_0) values[5-9]. By contrast, the dark I-V properties of the dimethylferrocene-CH_3OH liquid contact had excellent rectifying characteristics and low J_0 values ($J_0 = 10^{-9}$ A cm^{-2}).

This difference in rectification implies that more efficient photoelectrochemical behaviour should be obtainable from the n-InP/liquid interface. Figure 2 displays the potentiostatic photoelectrode I-V properties of the n-InP/0.20M Me_2Fc-0.5mM Me_2Fc^+-1.0M $LiClO_4$-CH_3OH junction under simulated Air Mass 2 conditions (62 mW cm^{-2}) and under lower-level illumination. At Air Mass 2 conditions, we observed short-circuit current densities of 14–15 mA cm^{-2}, open-circuit voltages (V_{oc}) of 0.59–0.61V and photoelectrode efficiencies of 6.5–7.0%, which are quite excellent properties for an n-InP surface-barrier device. The modest fill factors (rectangularity of the I-V curves[10]) arise from residual concentration overpotentials and uncompensated series-resistance losses in the test-cell design[11], both of which can be minimized by optimal electrode-electrolyte configurations[12]. The I-V properties at lower light levels (<10mW cm^{-2}) show (Fig. 2*b*) that improved fill factors are obtained when

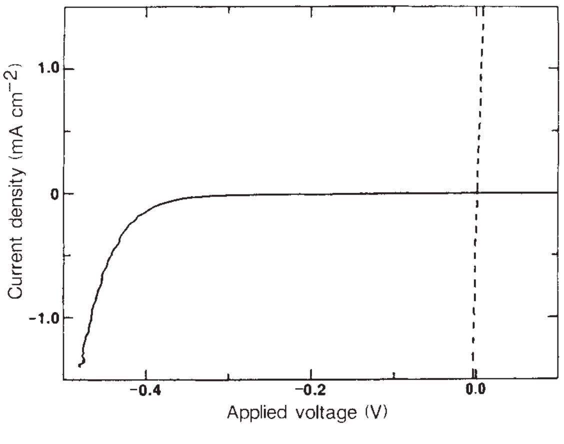

FIG. 1 Dark I-V properties of the n-InP/CH_3OH-0.20M Me_2Fc-0.10M Me_2Fc^+ semiconductor/liquid junction (solid line) and of the n-InP/Au Schottky barrier (dashed line). Negative voltages are forward biases and anodic currents are positive. n-InP Schottky barriers were made by filament evaporation of the metal in a vacuum of base pressure $<5 \times 10^{-6}$ torr.

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these losses are minimized. Photoelectrode stability was confirmed for charge passed $>10^2$ C cm^{-2}, which is in agreement with previous rotating ring-disk studies on a related n-InP/CH$_3$OH interface[13] and indicates that the observed photovoltages are not an artefact of a corrosion potential acting in series with the regenerative cell photovoltage.

The I-V properties of the n-InP/CH$_3$OH junction were also found to be sensitive to the redox potential of the electrolyte. Figure 3 depicts the I-V behaviour of n-InP/Me$_{10}$Fc$^{+/0}$-LiClO$_4$-CH$_3$OH-tetrahydrofuran and n-InP/CoCp$_2^{+/0}$-LiClO$_4$-CH$_3$OH junctions. The CoCp$_2^{+/0}$ system has the most negative redox potential (that is, the Fermi level that is closest to the vacuum level), and this solution produced poor rectification properties with n-InP samples. The n-InP/Me$_{10}$Fc$^{+/0}$ system had higher V_{oc} values and better dark-rectification properties, in accord with expectations for an unpinned semiconductor surface Fermi level over this range of solution redox potentials. This behaviour is consistent with dark-current cyclic-voltammetry studies of related n-InP/CH$_3$CN interfaces[14] but contrasts with the low barrier heights found for various n-InP/metal contacts[5-9].

The three metallocenes used in this study are sufficiently similar in their charge-carrier capture properties (that is, their solvent reorganization energies and heterogeneous electron-capture rates)[15-18] that the most reasonable explanation for the differences between Figs 2 and 3 is a large change in the barrier height of the n-InP/liquid contacts with changes in the value of the solution redox potential. The changes in the reverse saturation current are in good agreement with expectations based on increasing barrier heights with more positive solution redox potentials. Furthermore, the data for the lowest J_0 system, n-InP/CH$_3$OH-Me$_2$Fc$^{+/0}$, cannot readily be rationalized by assuming that the barrier height of the semiconductor/liquid contact is pinned at the 0.3–0.5 V value of n-InP semiconductor/metal junctions. Using a 0.4 V barrier height in the thermionic-emission expression[5-9,19], we calculate that $J_0 =$ 0.16 A cm^{-2} for the Schottky contact; thus, J_0 for the liquid contact would have to be decreased by over eight orders of magnitude to yield the observed dark I-V properties of Fig. 1 and to produce the V_{oc} values depicted in Fig. 2.

To explain the very low value of J_0 for the n-InP/Me$_2$Fc$^{+/0}$

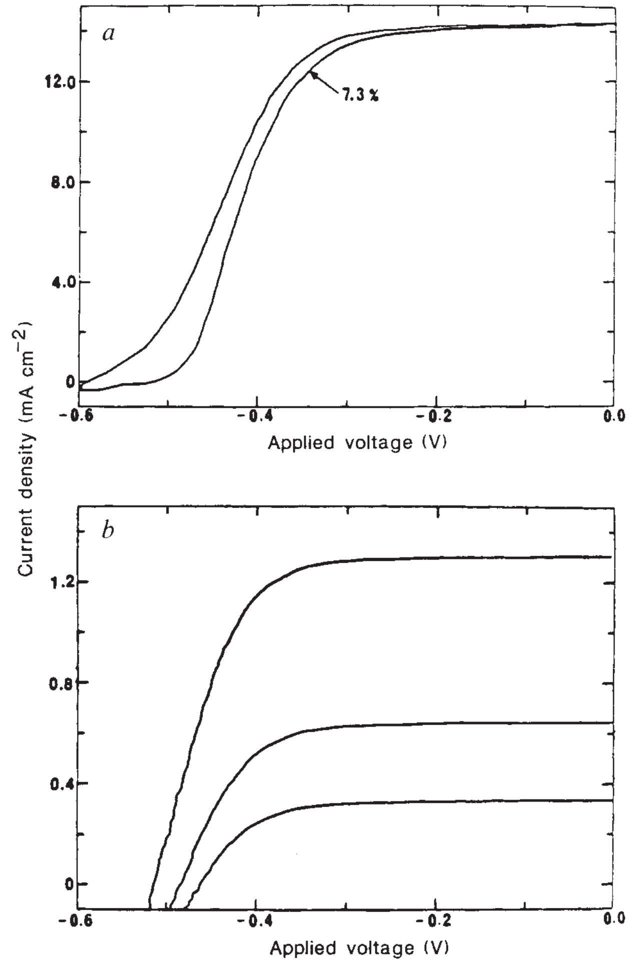

FIG. 2 *a*, I-V properties of the n-InP/CH$_3$OH-1.0M LiClO$_4$-0.20M Me$_2$Fc-0.5mM Me$_2$Fc$^+$ junction under Air Mass 2 conditions (62 mW cm^{-2}). The electrode was mirror-finished (100)-oriented n-InP and the solution was magnetically stirred. The CH$_3$OH was distilled from Mg and stored over 3-Å molecular sieves. The LiClO$_4$ was fused *in vacuo* at 280 °C. Illumination was provided by an ELH-type 3,200-K, 100-W tungsten-halogen lamp[3]. The photoelectrode properties were obtained under potentiostatic control relative to a reference electrode at the nernstian potential of the cell (E=0.15 V relative to SCE). The hysteresis between forward and reverse direction scans was largely due to mass-transport limitations of the ions in the solution. The energy conversion efficiency of this particular interface was 7.3%. *b*, I-V properties at lower photocurrent densities showing the improved I-V behaviour at lower concentration overpotentials and series-resistance losses.

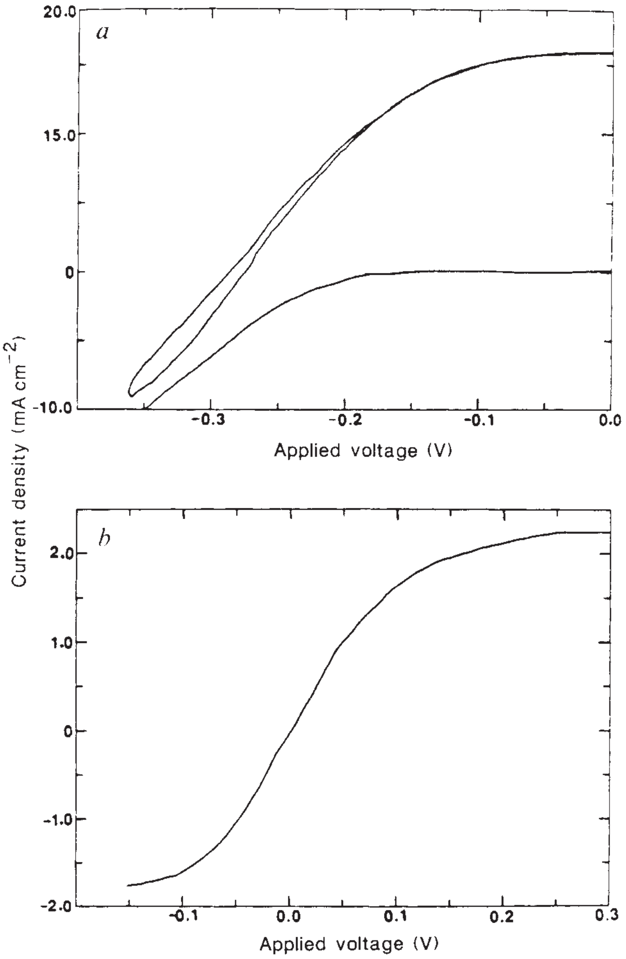

FIG. 3 *a*, I-V properties of the n-InP/CH$_3$OH (75%)-tetrahydrofuran (25% by volume)-0.50M LiClO$_4$-40.0mM Me$_{10}$Fc-0.5 mM Me$_{10}$Fc$^+$ system ($E =$ -0.107 V relative to SCE) in the dark (lower curve) and under illumination. (Note the scale change on the abcissa as compared to Figs 1 and 2.) *b*, I-V properties of the n-InP/CH$_3$OH-1.0M LiClO$_4$-20.0mM CoCp$_2$-1mM CoCp$_2^+$ ($E = -1.10$ relative to SCE) interface in the dark. Compared to the I-V data in *a* and Fig. 1, this system shows much higher dark currents and poorer rectification. I-V curves under Air Mass 2 illumination exhibited very low ($<$10 mV) V_{oc} values.

system, it is necessary to postulate either a large tunnelling barrier at the n-InP/CH_3OH interface, an anomolously low cross section of electron capture for the Me_2Fc^+ ion or a substantially increased barrier height for the liquid junction. The presence of a thick, insulating tunnelling barrier is ruled out by the low series resistance for charge transfer evident in the $I-V$ data of Figs 1 and 2. Also, X-ray photoelectron spectra indicate that n-InP photoelectrode surfaces that have been operated in the CH_3OH-$Me_2Fc^{+/0}$ electrolyte possess $\leq$1-2 Å of oxide overlayers, which is consistent with the low levels of oxide observed by other workers after emersion of InP from other liquids[20]. Postulating a low electronic cross section of carrier capture for the Me_2Fc^+ ion would be in direct conflict with the excellent dark $I-V$ behaviour in Fig. 1 and is also in contradiction to the rapid, reversible electron transfer rates exhibited by ferricenium ions at numerous electrode surfaces[15-17]. For liquids, some suppression of electron injection rates might be expected because of the necessity for solvent reorganization around the acceptor ion and the relatively low concentration of acceptor states[21]. A discrepancy of 10^8 in exchange current is, however, far too large to be explained in this fashion[21]. We thus conclude that the effective barrier height for majority-carrier transport in the n-InP/$Me_2Fc^{+/0}$-CH_3OH semiconductor/liquid system is much larger than that obtainable for n-InP semiconductor/metal Schottky barriers.

Additional information regarding the recombination processes at the n-InP/CH_3OH interface can be obtained[2] from plots of V_{oc} against temperature T. Such plots for the n-InP/CH_3OH-$Me_2Fc^{+/0}$ system (220-300 K) were extremely linear (correlation coefficient >0.995) and yielded an extrapolated intercept ($T = 0$ K) of 1.2 V. This value is much higher than the 0.4-V intercept expected for electron exchange processes over a 0.4-V barrier height[10,19]. Also, at low temperature (234 K) and higher light intensity ($\sim$300 mW cm^{-2} of ELH-type W-halogen illumination), we observed V_{oc} values >0.81 V. These data, combined with the room temperature $I-V$ data of Fig. 1, clearly indicate that restrictions on photovoltaic performance and on junction leakage predicted by Fermi-level pinning at Schottky barriers do not apply to n-InP/CH_3OH liquid interfaces. It is this difference between the interfacial properties of liquid/semiconductor and metal/semiconductor junctions that enables the construction of efficient photoelectrochemical cells from semiconductors such as n-GaAs and n-InP, even though these materials have been shown to yield inefficient Schottky-barrier photovoltaic devices.

The n-InP system provides a key comparison in the III-V family of semiconductors because it is well documented that the surface Fermi level is pinned very near (0.3-0.5 V) the conduction band for a variety of metal contacts[5-9]. This implies that extremely poor InP junction behaviour should be obtained for all such systems. Previous reports have observed inferior $I-V$ properties of n-InP/liquid contacts[22-24] and differential capacitance measurements have been interpreted as indicating a high density of surface states pinning the Fermi level of n-InP/liquid junctions[25]. By contrast, our data on n-InP/liquid systems clearly show that excellent photoelectrochemical-cell systems can be obtained despite the limitations of the solid-state devices, and that the $I-V$ behaviour of the semiconductor/liquid devices can be extremely responsive to the electrochemical potential of the contacting phase. In fact, the $I-V$ properties of the mirror-finished, (100) n-InP/CH_3OH-$Me_2Fc^{+/0}$ semiconductor/liquid junctions in Fig. 2 are comparable to those obtained from mirror-finished, (100) n-GaAs interfaces[26], which have yielded photoelectrochemical-cell efficiencies of >10% after optimization of surface etching and electrochemical-cell configurations[2,26]. In conjunction with the recent studies of passivation of III-V surfaces at interfaces with non-conductors[27-29], the observation that efficient energy conversion systems can be obtained with n-InP/liquid contacts demonstrates that semiconductor/metal barrier-height measurements are not a reliable guide to the $I-V$ behaviour of III-V semiconductor/liquid interfaces and that new options are available for the utilization of semiconductor/liquid systems in energy conversion applications. ☐

Received 21 February; accepted 13 July 1989.

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ACKNOWLEDGEMENTS. We thank Dr N. Newman, Prof. W. Spicer and Dr S. C. Pyke for supplying some InP samples and for discussions. We also thank B. J. Tufts for performing photoemission experiments. This work was supported in part by the Office of Naval Research. N.S.L. also acknowledges support as a Dreyfus Teacher-Scholar and as an A. P. Sloan Foundation Fellow. This is contribution number 7882 from the Division of Chemistry and Chemical Engineering.

Direct measurement of the diffusive sublayer at the deep sea floor using oxygen microelectrodes

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THE diffusive sublayer is the region of fluid next to a solid surface, where turbulence is suppressed and molecular diffusion dominates transport of solutes. Diffusive impedance of solute exchange across the benthic sublayer in the deep sea can limit the rates of some diagenetic reactions in the sediment. We present the first direct *in situ* measurements of the thickness of the diffusive sublayer for dissolved oxygen in the deep sea. The positions of 17 oxygen microelectrode profiles relative to the visible sediment/water interface reveal that the sublayer is 0.5–1.5 mm thick, with measurements ranging to 3.5 mm. The sublayer reduces the diffusive flux of oxygen into the sediments by ~10% in these environments. Also, the diffusive flux of isotopically light carbon through the sublayer should cause the ^{13}C content at the interface of typical deep-sea sediments to be ~0.1‰ lighter than the bottom-water value, setting a limit on the precision of the record of past bottom-water given by the carbon isotope composition of the shells of benthic foraminifera.