The cationization of the molecular species has been shown to stabilize the parent molecule.[2] We found one NiC_6H_6 species in the calculations. The Ni involved was a neighboring atom, not the atom under the benzene. Since some recombination is involved, the experimental observations of the cationized species cannot be used as evidence that the organic molecule is directly bonded to the metal atom. This is completely analogous to the recombination mechanism of cluster formation of atomic adsorbates with metal atoms.[9,10]

The factors leading to the ejection of molecular fragments from ion-bombarded solids are then clear, at least in a mechanistic sense. These include the facts that (i) the energy of the primary ions is rapidly dissipated to energies of the order of chemical bond strengths by multiple collisions in the solid, (ii) the molecular fragments can eject intact since there are many internal vibrational modes which can absorb energy from an energetic collision, and (iii) multiple atoms can be struck by a larger substrate atom, forcing them to move in a concerted fashion. Although the classical dynamics calculations neglect the ionization process and the possible fragmentation of molecules on the way to the detector, the predicted nuclear motion giving rise to the ejection of stable molecules appears physically reasonable. The results provide the basis, then, for interpreting SIMS spectra in terms of the molecular structure of the original sample.

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An Efficient Photocathode for Semiconductor Liquid Junction Cells: 9.4% Solar Conversion Efficiency with p-InP/VCl_3–VCl_2–HCl/C

Sir:

The first efficient semiconductor–liquid junction solar cell based on a p-type semiconductor is reported. At an insolation of 110 mW/cm^2, the output of the photoelectrochemical p-InP/VCl_3–VCl_2–HCl/C cell is 10.4 mW/cm^2 for a solar-to-electrical conversion efficiency of 9.4%. The output power remains stable upon passage of 13 000 C/cm^2 near the maximum power point (0.52 V, 20 mA/cm^2), and there is no measurable weight loss. The results contradict suggestions of a fundamental limitation to the efficiencies of p-type cells from surface states and fermi-level pinning.

Although both n- and p-type regenerative liquid junction solar cells have been investigated, conversion efficiencies above 5% for sunlight have hitherto been obtained only with n-type photoanodes.[1-10] The present benchmarks of 12% and 7.8% for single-crystal and polycrystalline chemically vapor deposited electrodes, respectively, were reached with n-GaAs/selenide–polyselenide/carbon cells.[5,6,10] These achievements required counteracting the effects of surface states and grain boundaries on cell behavior.[5-10] Surface and/or interface states can lead to high electron-hole recombination rates which are manifested as a deficit in maximum power output and may even pin the semiconductor fermi level at the surface, thus limiting the open-circuit voltage. Interface modification by chemisorbed ions such as Ru(III) and Pb(II) was used in the case of n-GaAs, thereby reducing recombination losses so that the theoretical cell output could be more closely approached.[5-10]

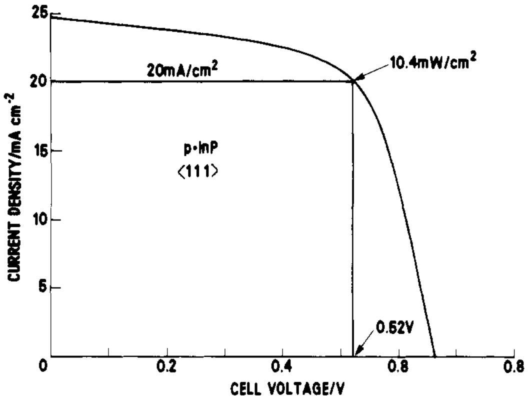

Figure 1. Current voltage characteristics of the cell p-InP/VCl_3–VCl_2–$ZnCl_2$–HCl/C at 110 mW cm^{-2} sunlight.

The use of photocathodes instead of photoanodes is intriguing because illumination tends to cathodically protect the semiconductor against the key obstacle to stability, namely, surface oxidation. The reductive degradation of the semiconductor must, however, be slow, and the rate of electron transport to the redox couple dominant. In this respect, we are not aware of photoelectrochemical cell failures traceable to reductive photocorrosion.

These attractions of p-type materials stimulated investigations on a variety of photocathodes such as p-GaP,[11-18] p-GaAs,[11,19-21] p-Si,[22] p-Ge,[23] p-CdTe,[15,24] and p-InP.[15,25-28] None of the resulting

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cells approached the overall performance achieved with n-type systems, although substantial photovoltages have been noted for strongly reducing solutions such as Eu(III)/Eu(II) in acid.[11]

In some cases, cell voltages have appeared insensitive to redox potentials and have thus been limited in value. This has led to the suggestion that p-type photocathodes made of covalently bound semiconductors, e.g., p-Si, p-GaAs, and p-InP, all exhibit pinning of the fermi level of the semiconductor surface and are subject to a "$^1/_3$ band-gap rule",[21] with the consequence that photovoltages ought not exceed $^1/_3$ of the band gap. Our results contradict these generalizations. We find that by judicious choice of the redox system and electrode pairing, a high-efficiency p-type photoelectrochemical cell is feasible.

The single-crystal p-InP photocathode used was grown by the gradient freeze method[29] and had Zn doping to 2.4×10^{17} cm^{-3}, a mobility of 87 cm^2 V^{-1} s^{-1}, and a bulk resistivity of 0.287 Ω cm. The crystal was sliced to yield (111) faces and then polished with an alumina slurry followed by lens paper impregnated with methanol–2% bromine. The A face of (111) InP, consisting entirely of In atms, was exposed to the solution.

A low-reflectance black surface finish was obtained by modifying the 1:6:6 $HCl-HNO_3-H_2O$ etch[30] to 1:2:2. An ohmic back-contact was produced by successively evaporating 300-Å Zn and 1000-Å Au and heating to 450 °C for 15 s. Details of electrode mounting have been reported previously.[10] The V(II)/V(III) redox couple solution contained 0.35 M total vanadium. The solution was prepared by reacting 3 N purity V_2O_5, a small excess of 6 N Zn over V(V) → V(II) stoichiometry, and sufficient electronic grade HCl to yield 4 M after the reduction. The solution potential was adjusted by access of air or additional Zn to -0.48 ± 0.02 V vs. SCE. At this potential, the solution shows three absorption maxima; 400 nm (ϵ 6.4 cm^{-1} mol^{-1}, half-width, $\Delta = 100$ nm), 600 nm (ϵ 4.5 cm^{-1} mol^{-1}, $\Delta = 150$ nm), and 890 nm (ϵ 0.8 cm^{-1} mol^{-1}, $\Delta = 120$ nm). Carbon counterelectrodes and magnetic stirring were used.

Stability tests under tungsten–halogen illumination of the p-InP/VCl_3-VCl_2-HCl/C cell showed stable maximum power point characteristics at 50 mA cm^{-2} and 0.5 V in extended (3 days) operation. No measurable (±1 mg) weight change was observed upon passage of 13 000 C cm^{-2}. Furthermore, no deterioration in current, voltage, fill factor, or electrode weight was found upon cycling between short-circuit and open-circuit conditions while accumulating 3000 C cm^{-2}.

Figure 1 shows the current–voltage curve for a p-InP/VCl_3-VCl_2-HCl/C cell illuminated by natural sunlight of an incident irradiance of 110 mW/cm^2. The short-circuit current density is 25 mA cm^{-2}, the open-circuit voltage 0.66 V, and the fill factor 0.63. The maximum solar-to-electrical power conversion efficiency is thus 9.4%. The difference between the experimentally observed short-circuit current density and the 39 mA cm^{-2} theoretically predicted[31] for the above irradiance at the band gap of InP (1.35 eV at room temperature) can be accounted for by solution absorbance and reflection losses.

We propose that the exceptional stability and performance of the new cell are due to the fast kinetics of the V(II)/V(III) couple, the suitable placement of the band edges, our nonreflective surface finish, and the unique surface chemistry of InP. The latter is probably the most important factor. It is known that the surface recombination velocity of vacuum-cleaved n-InP decreases upon oxidation by exposure to air from 10^6 cm s^{-1} to 10^3 cm s^{-1}.[32,33] Futhermore, the exceptionally high solar power conversion efficiency of indium oxide and indium tin oxide junctions of InP compared to corresponding junctions of other III–V compounds has been clearly related to the interfacial chemistry.[34] The formation of a very thin oxide layer on the surface of the p-InP electrode is likely upon either exposure to air or reaction with water. The observations on the oxidation of InP and the resultant reduction in the surface recombination velocity have been interpreted in a previous paper[35] as being due to the saturation of reactive surface bonds by oxygen. Such saturation reduces the density of interface states in those semiconductors that are oxidized exclusively to stable oxides with large energy gaps. In view of the large free energy of formation of both indium and phosphorus oxides and of their large band gaps, it is expected that some of the states characteristic of oxidized InP interfaces will be above and below the band edges and thus will not limit the performance of solar cells. For this reason, one would predict well-behaved liquid junctions independent of whether a bulk oxide film seals the InP surface or whether chemisorbed oxygen accounts for the removal of interface states.[35] Note that for GaAs, the thermodynamic instability of the arsenic oxide/GaAs system[36–38] may lead to the formation of free arsenic and gallium oxide at the interface. Arsenic will introduce states between the edges of the valence and conduction bands. It may be responsible for the high recombination velocity and, in some cases, for pinning of the fermi level at the surface of GaAs. As a consequence of this basic difference in the surface chemistry of GaAs and InP, no noticeable reduction is observed in the 10^6 cm s^{-1} free-surface recombination rate after exposure of GaAs to air.[32,39–41] A confirmation of the expectation based on this interpretation is that p-InP photocathode based liquid junction cells exhibit power conversion efficiencies substantially superior to cells with p-GaAs photocathodes.[11,19–21]

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Note Added in Proof: Addition of $RuCl_3 \cdot 3H_2O$ or insertion of a Pt wire cause rapid evolution of hydrogen by the reaction

$$V^{2+} + H^+ \rightarrow V^{3+} + {}^1/_2H_2$$

This suggests the feasibility of photoassisted electrolysis in the cell

$$\text{p-InP}/V^{3+} - H^+(\text{catalyst})\ H^+/Pt$$

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Theoretical Study of a Low-Energy UV Transition in a 2,6-Dithiaadamantane Derivative

Sir:

Recently, we have reported that bis(γ,γ-dimethylallenyl) sulfone (**1**) undergoes a novel and facile base-catalyzed cyclodimerization to the 2,6-dithiaadamantane derivative 4,8,9,10-tetraisopropylidene-2,6-dithiaadamantane tetraoxide (**2**).[1] Surprisingly,

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