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Fermi Level Pinning of p-Type Semiconducting Indium Phosphide Contacting Liquid Electrolyte Solutions: Rationale for Efficient Photoelectrochemical Energy Conversion

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A recent report[1] concerning p-type InP-based photoelectrochemical cells prompts us to give this preliminary account of our work on p-type InP/liquid interfaces. We report data that show that p-type InP gives a photovoltage E_V, of ~0.8 V with respect to solution redox couples where the formal potential of the redox couple, $E°$, can vary over a potential range that significantly exceeds the magnitude of the band gap, E_g, of InP. Indeed, for $E°$'s more negative than ~−0.40 V vs. SCE in CH_3CN/0.1 M n-Bu_4NClO_4, we find essentially a constant value for E_V. When E_V is independent of $E°$ for a semiconductor/liquid interface the semiconductor is said to be "Fermi level pinned".[2-7] One intriguing finding is that the ratio E_V/E_g for p-type InP is the highest reported thus far for a semiconductor/liquid interface.

Single-crystal p-type InP, fabricated into photocathodes,[8] has been studied in CH_3CN/0.1 M n-Bu_4NClO_4 or aqueous electrolyte solutions containing fast, outer sphere, reversible, one-electron transfer reagents whose $E°$'s span a wide potential range. The strategy in using such redox reagents is to explore interface energetics without the complication of poor electrode kinetics.[2-7,9] The use of CH_3CN as a solvent is necessary owing to the fact that H_2O has a rather restricted negative potential window because H_2O can be (photo)reduced at (photo)cathodes. We have performed cyclic voltammetry studies and steady-state current–potential experiments with illuminated ($\geq E_g$ light) p-type InP contacting various solvent/electrolyte/redox couple combinations.

Figure 1 illustrates typical cyclic voltammetry behavior, and Table I summarizes some of the quantitative data that we have collected. Consider first the cyclic voltammetry in Figure 1. The CH_3CN/0.1 M n-Bu_4NClO_4 electrolyte solution contains a number of one-electron reducible materials at ~1 mM concentration where the associated $E°$'s span a wide range of potential. Compared to the cyclic voltammetric peaks at Pt (a reversible electrode), the cathodic peak associated with reduction of the various oxidized species at illuminated p-type InP is shifted to a more positive value (Table I). Three facts are crucial: (1) all of the oxidized species are photoreducible at illuminated p-type InP at an electrode potential more positive than at Pt; (2) the extent to which the photocathodic current peak is more positive is nearly the same for the couples whose $E°$ is more negative than −0.4 V vs. SCE; (3) the potential range of $E°$'s spanned significantly exceeds the magnitude of E_g = 1.35 eV for InP.[1] Taking the difference in position of the cathodic current peak at Pt and at illuminated p-type InP to be a reasonable relative measure of E_V,[4-6] we see that for many $E°$'s the E_V is very large, ~0.8 V.[10]

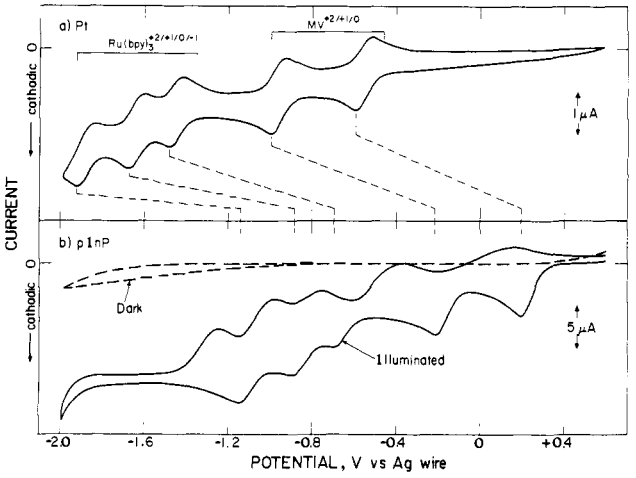

Figure 1. Cyclic voltammetry of a CH_3CN solution containing 0.1 M TBAP, ~1 mM MV^{2+} and ~1 mM $Ru(bpy)_3^{2+}$ at (a) Pt and (b) p-InP in the dark and under irradiation with 632.8-nm light. Scan rate employed is 100 mV/s. Light intensity was ~50 mW/cm^2.

Table I gives the values of E_V for p-type InP contacting various redox couples. In addition to the data from CH_3CN solvent, we include data for CH_3CN containing CH_3COOH and for H_2O at different pH's. For the $MV^{2+}/MV^{+\cdot}$ system we make special note of the fact that the value of E_V is essentially independent of the medium.

From steady-state current–voltage scans for illuminated p-type InP in the presence of various redox couples, we have found high efficiency for the conversion of light to electricity, as was previously reported for the p-InP/VCl_3–VCl_2–HCl/C cell.[1] Short-circuit photocurrents, open-circuit photovoltage, and fill factors are high, and we concur with the conclusion of other workers[1] that the efficiency of p-type InP-based photoelectrochemical energy conversion devices can be quite high. But on the basis of the data presented in Table I, we conclude, in contrast to earlier workers,[1] that p-type InP is indeed "Fermi level pinned". This is most certainly the case in CH_3CN where various redox couples having a very wide range of $E°$'s give essentially the same value of E_V. The similar E_V for the $MV^{2+/+\cdot}$ system in H_2O and CH_3CN and the pH independence of E_V provide support for the contention that p-type InP departs from ideal semiconductor/liquid interface behavior.[2,11]

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(8) Electrodes were constructed by using a Zn-doped p-type InP, ⟨111⟩ or ⟨$\bar{1}\bar{1}\bar{1}$⟩ face exposed, with a carrier concentration ~1 × 10^{18} cm^{-3}. Ohmic contacts were made by ultrasonic soldering of a copper wire to the crystal back with In/Zn (saturated with Zn) solder. The InP surface was etched in 5% Br_2/MeOH for 60 s at 25 °C followed by rinsing with MeOH. The electrochemical equipment has been described previously;[4] solutions were degassed and typically contained 1 mM of electroactive material.
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(10) The value of E_V increases only modestly from the ~0.8 V upon increasing light intensity beyond the ~50 mW/cm^2 used. The highest E_V observed has been 0.86 V at ~10 W/cm^2. The ~50 mW/cm^2 approximates the visible intensity from the AM1 solar spectrum. Other workers have investigated p-InP in nonaqueous media[9d] and found a smaller E_V. This may be due to lower quality InP samples or to a poor ohmic contact. However, even the earlier work[9d] revealed a photovoltage for a range of $E°$'s exceeding E_g of InP.
(11) An earlier study [Van Wezemael, A.-M.; Laflrere, W. H.; Cardon, F.; Gomes, W. P. *J. Electroanal. Chem.* **1978**, *87*, 105] of the p-InP/H_2O interface as a function of pH suggested that the value of E_V would be fixed relative to the H^+/H_2 because the so-called flat-band potential was found to shift 59 mV/pH unit in the same direction as $E°(H_2O/H_2)$. Since the E_V relative to $MV^{2+}/M^{+\cdot}$ is independent of pH, we conclude that the potential determining species in such a case is $MV^{2+}/M^{+\cdot}$. A shift in the flat-band potential with pH is apparently ruled out when the $MV^{2+}/M^{+\cdot}$ system is present. For interpretation of the constant E_V relative to H_2O/H_2 in the absence of deliberately added redox couples, we offer the suggestion that the p-InP is Fermi level pinned by a mechanism not involving acid–base equilibrium of surface functionality.

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Table I. Photovoltage from Illuminated p-Type InP with Respect to Various Redox Couples

electrolyte system	redox couple	Pt $E_{P_{cath}}$ [a]	Pt $E_{P_{anod}}$ [a]	p-InP $E_{P_{cath}}$ [a]	E_V [b] ± 50, mV
CH_3CN, 0.1 M TBAP[c]	anthracene$^{0/-}$	−2.05	−1.96	−1.28	770
	$Ru(bpy)_3^{0/-}$ [d]	−1.81	−1.72	−0.99	820
	$AQ^{-/2-}$ [c]	−1.67	−1.55	−0.88	790
	$Ru(bpy)_3^{+/0}$	−1.62	−1.47	−0.80	820
	$Ru(bpy)_3^{2+/+}$	−1.37	−1.30	−0.55	820
	$AQ^{0/-}$	−1.00	−0.92	−0.28	720
	$MV^{+/0}$ [f]	−0.88	−0.81	−0.06	820
	$MV^{2+/+}$	−0.47	−0.39	+0.33	800
	$[PtS_4C_4(CF_3)_4]^{+/0}$	−0.19	−0.10	+0.45	640
	$[Fe(C_5Me_5)_2]^{+/0}$	−0.16	−0.07	+0.44	600
	$TMPD^{1+/0}$ [g]	−0.05	+0.15	+0.30	350
	$[Fe(C_5H_5)_2]^{1+/0}$ [h]	+0.35	+0.43	+0.70	350
CH_3CN, 0.1 M TBAP	$MV^{2+/+}$	−0.48	−0.41	+0.26	740
CH_3CN, 0.1 M TBAP, 0.1 M HOAc	$MV^{2+/+}$	−0.48	−0.41	+0.26	740
CH_3CN, 0.1 M TBAP, 0.5 M HOAc	$MV^{2+/+}$	−0.48	−0.41	+0.26	740
pH 7.5 phosphate buffer[i]	$MV^{2+/+}$	−0.72	−0.63	+0.05	770
pH 6.0 phosphate buffer[i]	$MV^{2+/+}$	−0.72	−0.63	+0.00	720
pH 4.0 acetate buffer[i]	$MV^{2+/+}$	−0.72	−0.63	+0.06	780
pH 2.0 10^{-2} M $HClO_4$[i]	$MV^{2+/+}$	−0.72	−0.63	+0.08	800

[a] $E_{P_{cath}}$ and $E_{P_{anod}}$ refer to cathodic and anodic current peaks, respectively, in the cyclic voltammetry. The $E_{P_{cath}}$ for p-InP is for an illumination intensity of ~50 mW/cm² at 632.8 nm. Potentials are V vs. SCE. [b] E_V is the photovoltage taken to be the difference in $E_{P_{cath}}$ at Pt and at illuminated p-InP. [c] TBAP = n-Bu_4NClO_4. [d] bpy = 2,2'-bipyridyl. [e] AQ = anthraquinone. [f] MV = N,N'-dimethyl-4,4'-bipyridinium. [g] TMPD = N,N,N',N'-tetramethyl-1,4-benzenediamine. [h] Couples having $E°$ more positive cannot be studied owing to dark anodic decomposition of the p-type InP. [i] Solvent is H_2O.

We take Fermi level pinning to be a situation where the value of E_V depends little or not at all on the value of $E°$. It is a phenomenon that accommodates the observation of photoeffects for redox couples spanning a range of $E°$'s that is greater than band gap. Concluding whether the term "Fermi level pinning" applies cannot be made on the basis of a determination of E_V for a narrow range of $E°$'s, as was done by the earlier workers.[1] Fermi level pinning only means that E_V is fixed and implies nothing about its magnitude relative to E_g. For p-type InP it appears that Fermi level pinning does apply for a wide range of $E°$'s and the fixed value of E_V of 0.8 V is a much larger fraction of E_g than predicted by the so-called "$^1/_3$ band gap rule".[3,12] In fact, our studies of p-type InP were initiated after surveying the solid state (semiconductor/metal Schottky barrier) literature to find the p-type semiconductor having the highest E_V/E_g ratio.[12] It appears that p-type InP/M interfaces exhibit Fermi level pinning also, and the E_V is similar to that which we find for the p-type InP/liquid interfaces. Thus, the solid-state measurements,[12] not the $^1/_3$ band gap rule, were a good predictor of the behavior of the liquid electrolyte based systems.

There are at least two mechanisms for the origin of the $E°$ independent E_V over a large range of $E°$'s. One possibility is that there is a significant density of surface states (including surface oxides) that cause a departure from the expected variation of E_V with change in $E°$.[2] Another possibility is so-called carrier inversion[13,14] that results when there is sufficient band bending to change the relative carrier density, in a p-type material from a "hole"-rich surface layer to an electron-rich layer. There may also be a combination of these physical possibilities. It is difficult to envision a surface state free semiconductor exposed to liquid electrolyte. The question is what is the density and distribution of surface states or surface species. Whatever the explanation for p-type InP, we have shown empirically that p-type InP is Fermi level pinned in the sense that E_V is independent of $E°$ for a wide range of couples, consistent with measurements for solid-state devices.

Deliberate chemical treatments or changes in solvent/electrolyte combinations could effect chemical modifications of surface structure that may lead to increased cell performance.[4] We note that constant E_V is found for n-GaAs (E_g = 1.4 eV) cells for a large number of outer-sphere reagents whose $E°$'s span a range of 2.0 V.[2] Chemisorption of $RuCl_3$ onto n-GaAs has been shown to increase output parameters of the n-GaAs/Se_2^{2-}/Se^{2-}/0.1 M KOH/C cells.[15] Surface modification can thus alter the output performance predicted from the finding that n-Si,[2] n-GaAs,[2] n-CdTe,[6] n-MoS_2,[5] n-$MoSe_2$,[5] p-GaAs,[3] p-Si,[4] and p-InP electrodes exhibit Fermi level pinning for a wide range of solvent/electrolyte/redox couple combinations.

We note that the potential regime over which the Fermi level pinning occurs can vary with different materials. For materials such as n-Si,[2] p-Si,[4], n-MoS_2,[5] and p-InP there is a potential range near the region of "ohmic contact",[2] where E_V will vary with the $E°$.[5] In this regime, the potential drop occurs over both the semiconductor space charge layer and the solution Helmholtz layer. Choice of a redox substrate whose $E°$ lies in this region will yield a lower E_V than is possible at these interfaces. Small variations of $E°$ relative to E_g in this potential regime will yield changes in E_V. As the data in Table I for InP indicate, Fermi level pinning occurs for redox couples outside this potential range ($E°$ more negative than −0.4 V vs. SCE for p-InP) and for excursions of potential greater than E_g of the semiconductor.

With regard to efficiency for p-type InP-based cells, it is encouraging to find a system that gives such a good E_V/E_g ratio for an E_g nearly ideally suited to the conversion of solar energy. We have exploited the large E_V for the $MV^{2+}/MV^{+\cdot}$ couple and the surface chemistry of our new surface derivatizing system[16,17] to improve the efficiency for the generation of H_2 from H_2O that has poor kinetics at naked p-type InP.[18] The details of these

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studies will be reported in the full paper.

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Dianions of 2-Methyl-2-butene: Evidence for the Stability of a "Y-Aromatic" Species

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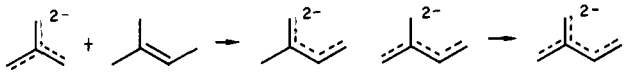
Recently the suggestion was made that certain cross-conjugated species, such as dianion **1**,[1] may possess a novel aromatic character, the so-called "Y aromaticity".[2,3]

We wish to report that metalation of 2-methyl-2-butene with 2 equiv of base gave initial formation of the linearly conjugated dianion **2**, with facile and complete isomerization to the thermodynamically more stable cross-conjugated dianion **3**.

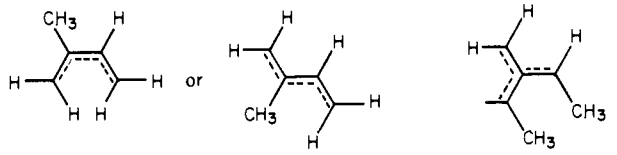


1 **2** **3**

The preparation of dianions in systems in which either a linear or a cross-conjugated dianion could form allows the evaluation of the relative stabilities of each species and an estimation of the aromaticity of the cross-conjugated dianion. As further evidence, the ^{1}H NMR chemical shift of the parent anion (**1**) was measured and is in agreement with its proposed aromatic character.

Metalation was carried out by adding 1 equiv of alkene to 2 equiv of the *n*-butyllithium-tetramethylethylenediamine (TMEDA) complex[4] under argon at 25 °C. The reaction mixture was usually quenched after 4 days. An alternative preparation involved the addition of 1 equiv of alkene to 2 equiv of Schlosser's base mixture (*n*-butyllithium/potassium *tert*-butoxide[5,6]) in pentane under argon at 25 °C with quenching after 2 days. The *n*-butyllithium/TMEDA system resulted in formation of a dark reddish brown solid, while the anion prepared with Schlosser's base system was orange.

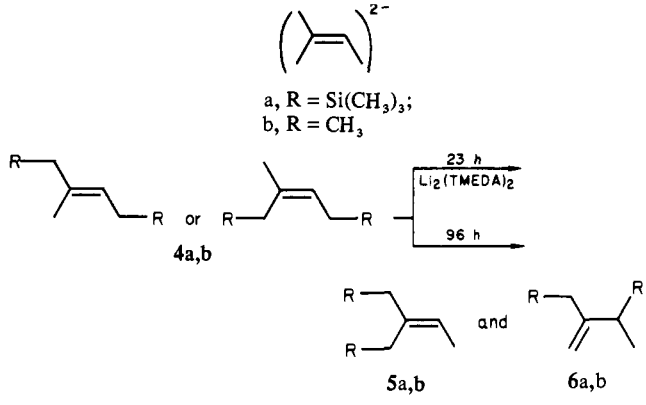
Evidence for dimetalation and the sequential formation of dianions **2** and **3** comes from ^{1}H NMR spectral observations and alkylation and silylation results. Obtaining the spectral parameters was possible only in the *n*-butyllithium/TMEDA metalating system because the dianions were moderately soluble in TMEDA. When Schlosser's base mixture was used, the dianions formed were insoluble in the pentane-based solvent and could not be observed directly. Attempts to dissolve the solid anions in dioxane resulted in immediate decomposition of solvent and anion, presumably by proton abstraction from the solvent by the anion.[7] Although overlap with solvent complicated interpretation of the spectra, the following ^{1}H NMR shifts (δ) and coupling constants (italics) were deduced.



2, δ 4.59; *J* = 10 Hz **3**, δ 3.42; *J* = 6 Hz

Justification of the assignment of the spectral parameters of linear dianion **2** was obtained by comparison with the butadiene dianion whose methine protons resonate at δ 4.8.[1] The most obvious structural feature of the spectrum of the cross-conjugated dianion is the 1:3:3:1 quartet (*J* = 6 Hz) for the vinyl proton at δ 3.42.

The linearly conjugated dianion began to appear after 10 h, reached its maximum concentration after 57 h, and disappeared by 126 h. The cross-conjugated ion appeared at 22.5 h and rapidly grew at the expense of the other dianion. Peaks from dianion **3** were still visible at 241 h, although they were beginning to be obscured by peaks from decomposition of solvent. Dianion **2** was trapped ater 23 h as the bis(trimethylsilyl) derivative by quenching with (chlorotrimethyl)silane. Adducts **4a** were present as 30% of the product mixture, with the remainder due primarily to various products from monoaddition (65%) and to diaddition products from dianion **3** (5%). Trapping of dianion **3** was accomplished



by reaction with (chlorotrimethyl)silane after 96 h to give adducts **5a** and **6a**, in 23% and 17% yield, respectively, with no formation of **4a**. Products from monoaddition comprise the remainder of the product mixture.

Interestingly, when 2-methyl-2-butene was metalated with Schlosser's base mixture and alkylated with either methyl iodide or (chlorotrimethyl)silane, the linear dianion **2** was not observed. In both cases, equal amounts of dialkylated products **5a,b** and **6a,b** formed. In an attempt to trap **2** before it isomerized to **3**, the reaction mixture from metalation with Schlosser's base system was quenched with methyl iodide at times ranging from 20 to 5760 min. There was no product from linear dianion.

For evaluation of the influence of the cation on the reaction of the dianion, we reacted 2-methyl-2-butene with Schlosser's base mixture followed by reaction with LiBr to give the dilithiated dianion.[8] Evidence for the success of the counterion switch comes from the color of the solution of the anion in THF. When the cation was potassium, the solution was reddish brown, while the anion in THF after treatment with LiBr was brownish black, the same color as a solution of the anion from the *n*-butyllithium/TMEDA system in THF. Reaction of the dilithiated dianion (2 days old) with chlorotrimethylsilane gave **5a** and **6a** as the only

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