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## Semiconductor Electrodes

### XVIII. Liquid Junction Photovoltaic Cells Based on n-GaAs Electrodes and Acetonitrile Solutions

Paul A. Kohl\* and Allen J. Bard\*\*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

#### ABSTRACT

Regenerative photoelectrochemical cells (PEC) were constructed utilizing single crystal n-GaAs in acetonitrile solutions. Solution redox couples (anthraquinone, p-benzoquinone, dimethyl ferrocene, ferrocene, hydroxymethyl ferrocene, and tetramethyl-p-phenylenediamine) whose standard redox potential varied by over 1.2V, were photooxidized at the semiconductor electrode and reduced at a Pt counterelectrode converting light directly into electrical energy. A power conversion efficiency of 14% was observed for the n-GaAs electrode in a ferrocene-ferricenium acetonitrile solution at a radiant intensity of 0.52 mW/cm<sup>2</sup> of 720-800 nm light. The efficiency and stability were found to be very dependent upon the residual water concentration, radiant power, and concentration of electroactive species.

The effective utilization of semiconductor electrodes in photoelectrochemical devices for the conversion of light energy to chemical and electrical energy depends upon a knowledge of the mechanism of charge transfer at the interface and hence of the energy level distributions within the semiconductor and solution. These determine the rates of competitive reactions of photogenerated holes or electrons and thus the stability, efficiency, and over-all electrochemical behavior of the semiconductors. The characteristics of a photoelectrochemical cell (PEC) can be predicted from the electrochemical behavior of the individual semiconductors and counterelectrode in regenerative PEC's (or liquid junction photovoltaic

cells) which show no net solution reaction and convert light to electricity, photoelectrosynthetic cells, which cause a net change in the solution composition and creation of chemical free energy (e.g., the decomposition of water to H<sub>2</sub> and O<sub>2</sub>), or in photocatalytic cells in which light is used to catalyze solution reactions at the semiconductor surface. Although a number of aqueous photovoltaic cells have been described, the recent cell by Tsubomura *et al.* (1) utilizing n-CdS and iodide ion in acetonitrile (ACN) is the only reported PEC using an aprotic solvent.

Previous studies of the electrochemical behavior of n- and p-type GaAs in anhydrous ACN solutions have shown that these semiconductors are stable under irradiation and suggested several suitable couples for use in photovoltaic PEC's (2). It was shown that:

\* Electrochemical Society Student Member.  
\*\* Electrochemical Society Active Member.  
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Table I. Output parameters for the cells of the form n-GaAs/Red(xmM), OX(y mM), TBAP(0.2M), ACN/Pt\*

Redox couple*	[Red], x (mM)	[Ox], y (mM)	Light intensity (mW/cm <sup>2</sup> )	$\lambda$ (nm)	Cell voltage (V)	Cell current density (mA/cm <sup>2</sup> )	Maximum power efficiency (%)
TMPD	46	0.12	0.46	720-800	0.31	0.148	10.2
TMPD	46	0.12	10.6	720-800	0.35	2.00	6.6
TMPD	46	0.12	0.1	720-800	0.2	0.020	4
Ferrocene	104	0.82	0.52	720-800	0.375	0.195	14†
Ferrocene	104	0.82	2.4	720-800	0.35	0.925	13.4†
Ferrocene	104	0.82	5.6	720-800	0.35	1.675	9†
	104	0.8	75	Solar spectrum	0.2	9.000	2.4
Dimethyl ferrocene	140	0.7	0.414	720-800	0.33	0.125	10.9†
Hydroxymethyl ferrocene	15.7	0.83	0.24	720-800	0.25	0.080	8.3†
Hydroxymethyl ferrocene	15.7	0.83	0.45	720-800	0.27	0.137	8.2†
Anthraquinone	3	2.5	2	600-1000	0.28	0.600	8.4†
p-Benzoquinone	10	10	0.096	600	0.40	0.028	11.6†

\* Abbreviations used in this table: TBAP, tetra-n-butylammonium perchlorate; TMPD, N,N,N',N'-tetramethyl-p-phenylenediamine.  
† Corrected for solution absorbance.

any dissolution of the GaAs. During such an extended trial the GaAs showed neither an apparent change in weight (<1 mg/cm<sup>2</sup>)<sup>1</sup> nor a change in the surface appearance. During the trial the blue radical cation was observed streaming from the GaAs surface. In reporting the efficiency no corrections were made for

light absorption by TMPD<sup>+</sup> or other solution components or for reflection.

The cell performance can best be understood by considering the current-potential (*i*-*V*) curves of the electrodes and the different current components which contribute to the over-all semiconductor current. A plot of the partial currents in this PEC at two different irradiation intensities are shown in Fig. 2. The partial current for the photooxidation of TMPD via

<sup>1</sup> Since a weight change of 0.1 mg is equivalent to ~4C going to a dissolution reaction of GaAs (assuming  $n = 6$ ), this is not a very sensitive test of semiconductor stability. More extensive tests would be required to demonstrate very long-term stability of the material.

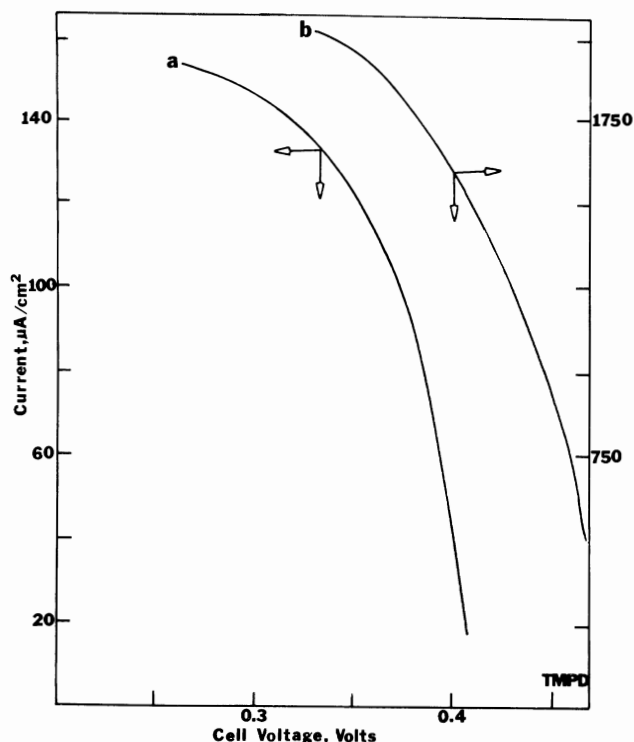
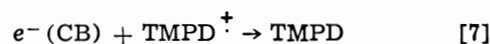


Fig. 1. Current vs. cell voltage for the cell

n-GaAs/TMPD(46 mM), TMPD<sup>+</sup> (0.12 mM), TBAP (0.2M) ACN/Pt illuminated with 720-800 nm light of intensity (a) 0.45 mW/cm<sup>2</sup> and (b) 10.6 mW/cm<sup>2</sup>.

photogenerated holes in the absence of TMPD<sup>+</sup> occurs at potentials just positive of  $V_{fb}$  (-1V) (Fig. 2a).

However, the back reaction, i.e., reduction of TMPD<sup>+</sup> (Eq. [7])



occurred at potentials positive of  $V_{fb}$  (via an intermediate level mechanism (2)) as shown by curves b and c

for two different concentrations of TMPD<sup>+</sup>. The over-all GaAs current results from a combination of these partial currents and leads to no net current at potentials negative of -0.6V vs. SCE. At less negative potentials the rate of reduction of TMPD<sup>+</sup> decreases and

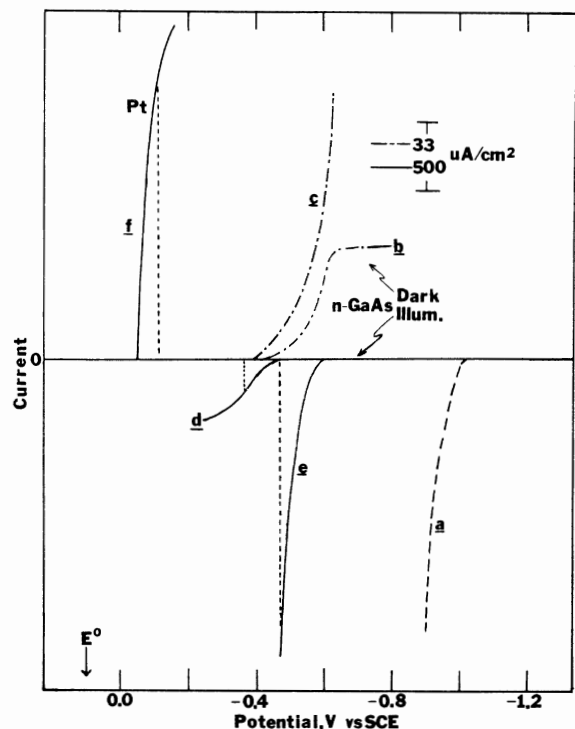


Fig. 2. Current-potential curves for (a) n-GaAs photoanode in absence of back reaction, (b) reduction of 0.12 mM TMPD<sup>+</sup> solution on n-GaAs in the dark, (c) reduction of 0.6 mM TMPD<sup>+</sup> solution, (d) photooxidation of 46 mM TMPD solution with 1.28 mW/cm<sup>2</sup> of 720-800 nm light, (e) same as (d) but with 10.6 mW/cm<sup>2</sup> light, and (f) reduction of 46 mM TMPD, 0.12 mM TMPD<sup>+</sup> solution at a Pt electrode of >20 cm<sup>2</sup>.

a net photoanodic current results; thus combination of curves b or c with curve a yields the net GaAs current given by curves d or e for two different light intensities. The net cell behavior, as shown in Fig. 1 and Table I, is obtained by combining the net GaAs curves (2d or e) with the Pt counterelectrode curve (2f).

Although only a few attempts were made to maximize the power efficiency by varying the concentration of TMPD,  $\text{TMPD}^+$ ,  $\text{H}_2\text{O}$ , and lamp intensity, a few general trends in cell design were noticed. (i) Mass transfer controlled supply of reactant (i.e., concentration polarization) at either electrode limited the current and decreased the efficiency. Concentration polarization at the n-GaAs was avoided by maintaining a sufficiently high TMPD concentration and stirring rate so that the flux of TMPD to the electrode was higher than the flux of holes to the surface. The

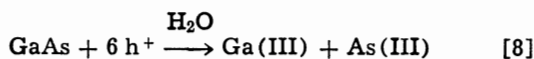
small concentration of  $\text{TMPD}^+$  at the counterelectrode was counterbalanced by using a large area Pt electrode. When the original cell was irradiated with a light intensity of  $10.6 \text{ mW/cm}^2$ , a maximum power of 6.6% was observed at a steady-state current of  $2 \text{ mA/cm}^2$  at 0.35V (Fig. 1b). Although the cell potential was higher at this intensity, the current appeared to be limited by the rate of mass transfer of

$\text{TMPD}^+$  to the Pt electrode. (ii) The back reaction (i.e., reduction of  $\text{TMPD}^+$ ) on n-GaAs limited the output voltage and current. At larger cell voltages the relative current is smaller at higher concentrations of

$\text{TMPD}^+$  because of the back reaction (Fig. 2c vs. 2b). Similarly at lower light intensities the back reaction has a greater effect (Fig. 2d vs. 2e). Thus, lower light

intensities or high concentrations of  $\text{TMPD}^+$  do not produce as high efficiencies, because at larger voltages the photon flux must first compensate for the reduction

current of  $\text{TMPD}^+$  at n-GaAs before a net oxidation is observed. When the light intensity was decreased to  $100 \text{ }\mu\text{W/cm}^2$ , a maximum efficiency of 4% was found ( $20 \text{ }\mu\text{A/cm}^2$  at 0.2V). (iii) The residual water concentration had a large effect on the efficiency and lifetime of the system. In aqueous solutions the GaAs undergoes photodissolution at potentials positive of  $-0.7\text{V}$  (Eq. [8]) so that operation with the GaAs at the potentials used here ( $+0.1$  to  $-0.6\text{V}$  vs.



SCE) would not be possible in aqueous media.

The occurrence of even a small amount of lattice oxidation because of small amounts of water in the ACN appeared to passivate the GaAs and thus destroy the photovoltaic effect. As shown previously in cyclic voltammetric experiments (2), when the flux of holes exceeded the flux of TMPD, the current and underpotential decayed on subsequent potential scans. After injection of 0.5 ml of  $\text{H}_2\text{O}$  into 25 ml of the original cell solution, the current decayed to 25% of its initial value after 0.05C had passed. The lifetime and efficiency of the original cell depended on the radiant intensity relative to the water concentration. When the original cell was operated at  $-0.31\text{V}$  and  $150 \text{ }\mu\text{A/cm}^2$ , a 2% increase in current was observed after 21 hr. However, when the intensity was increased so that the cell current was  $360 \text{ }\mu\text{A/cm}^2$ , the current decayed continuously, as shown in Fig. 3. This was attributed to a more successful competition of the passivation process for holes at higher light intensities and current densities. (iv) The absorption of light by the solution was minimized by keeping the concentration of the colored species,  $\text{TMPD}^+$ , low. (v) Surface pre-

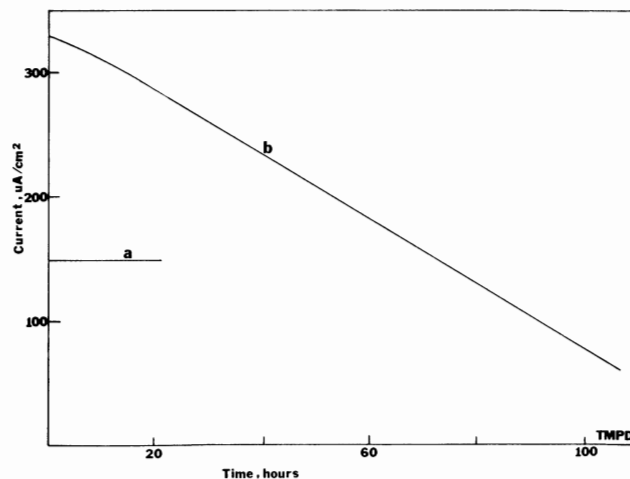


Fig. 3. Cell current vs. time for two different light intensities where that of (b) is 2.2 times that cell as in Fig. 1.

treatments, as discussed previously (2) and as will be illustrated in a later example, greatly affected the magnitude of the photocurrent and efficiency.

**Ferrocene-ferricenium cells.**—Wrighton and co-workers (9) have demonstrated that the ferrocene-ferricenium couple was useful in stabilizing Si photoanodes in PEC's with ethanolic solutions. The characteristics of such a cell with n-GaAs and ACN solutions of this couple are illustrated in Fig. 4a. When the light intensity at the GaAs surface is calculated by correcting that incident on the cell ( $0.52 \text{ mW/cm}^2$ ) using the solution absorptivity of 0.082 (6 mm of solution), a maximum power conversion efficiency of 14 ( $\pm 1$ )% was observed (output current density  $195 \text{ }\mu\text{A/cm}^2$  at 0.375V). With solar radiation ( $75 \text{ mW/cm}^2$ ) this cell produced an open-circuit photopotential of 580 mV and a current of  $9 \text{ mA/cm}^2$  at 0.2V, for a solar power conversion of 2.4%.

The lifetime of the cells again depended upon the residual water concentration. The behavior of the cell described above in which the ACN was triply distilled over  $\text{P}_2\text{O}_5$  is shown in Fig. 4b, curve 1. A more complete removal of water by 30 hr of stirring of the ACN containing the ferrocene and TBAP over alumina greatly improved the stability as shown by curve 2. Injection of 500  $\mu\text{l}$  of  $\text{H}_2\text{O}$  into the solution (25 ml) caused the cell current to decay to almost zero in a relatively short period of time because of the passivation of the n-GaAs. Decomposition of the adhesives and electrode supports prevented experimental trials with durations of longer than several days. During such trials there was no visual deterioration or weight loss ( $< 1 \text{ mg/cm}^2$ ) caused by photodissolution of the n-GaAs.

The electrochemical behavior of the 1,1-dimethylferrocene redox couple was very similar to that observed with TMPD[2] and ferrocene. With cyclic voltammetry at an n-GaAs electrode, as described in (2), the reduction of the dimethylferrocene cation in the dark was observed on n-GaAs at potentials well negative of the  $E^\circ$  of the dimethylferrocene redox couple as determined with a Pt microelectrode, as shown in Fig. 5. When illuminated with light of energy greater than the bandgap, an underpotential of  $\sim 0.6\text{V}$  was observed for the oxidation. Upon scan reversal, after positive going scans in the light, the reduction peak height increased, because the concentration of the cation, which was photogenerated at the electrode surface, was higher. This reduction of the cation represents the back reaction in a PEC which must be minimized for efficient operation while still maintaining an adequate flux of the cation at the counterelectrode. As shown in Table I conversion

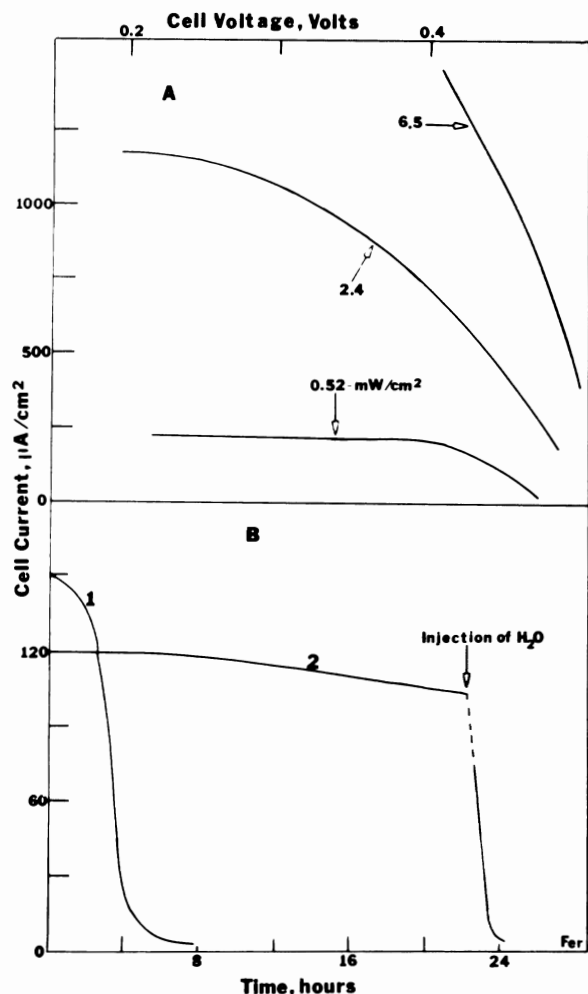


Fig. 4. (a) Cell current vs. potential for three different intensities of 720-800 nm light for the cell

n-GaAs/ferrocene(0.108M), ferricenium(0.87 mM), TBAP(0.2M)ACN/Pt  
 (b) Cell current vs. time (1) cell as in part (a); (2) [ferrocene] = 0.146M and [ferricenium] = 2.4 mM. 500  $\mu$ l of water injected in the cell as indicated.

efficiency greater than 10% was observed with the cell producing the *i*-*V* curves given in Fig. 6.

The *i*-*V* curves for a PEC containing the hydroxymethyl ferrocene couple as described in Table I, are given in Fig. 7. The reported efficiency is based on an incident light intensity corrected for solution absorption. Increasing the cation concentration to about 2 mM decreased the power efficiency to about 6.5%, probably because of the increased rate of the back reaction. The cell current vs. time curves were similar to those for ferrocene (Fig. 4b, curve 2) and again there was no apparent change in weight or appearance of the electrode after about 24 C/cm<sup>2</sup> of charge was passed.

**Quinone cells.**—The limited solubility of AQ allowed only rather dilute solutions to be used as shown in Table I. An open-circuit photovoltage of 700 mV was observed with the AQ cell at higher light intensities. As noted previously (2), the largest and most efficient photocurrents were observed after the GaAs was first biased to potentials more negative than -2V vs. SCE, presumably because of the development of a surface layer. The surface pretreatment also greatly affected the cell output and over-all electrochemical behavior of the n-GaAs. When the electrode was etched in only HCl without the H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O etchant, a much smaller photocurrent was observed under similar conditions. The

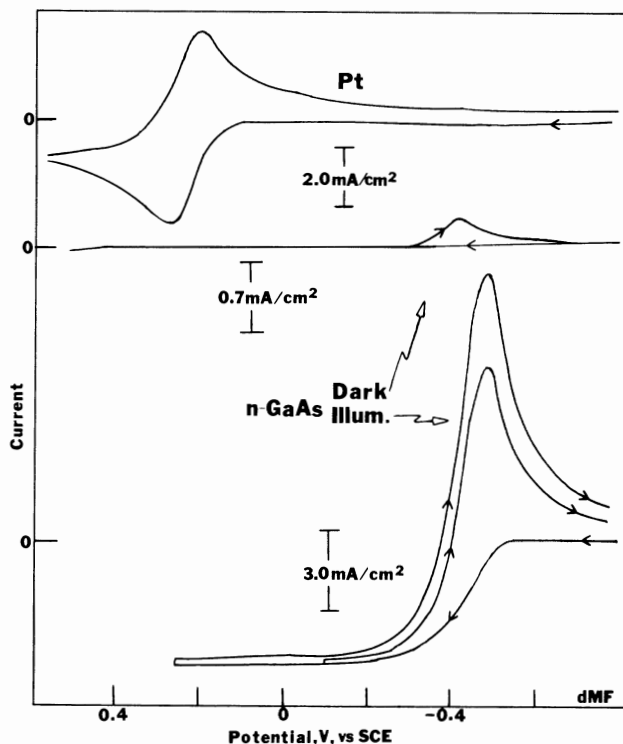


Fig. 5. Cyclic voltammogram of (a) 6.1 mM solution of dimethyl ferrocene at a Pt disk electrode, (b) and (c) 140 mM dimethyl ferrocene, 0.7 mM dimethyl ferricenium at a single crystal n-GaAs electrode in the dark and illuminated with red light. The scan rate was 0.2 V/sec and the supporting electrolyte was 0.2M TBAP.

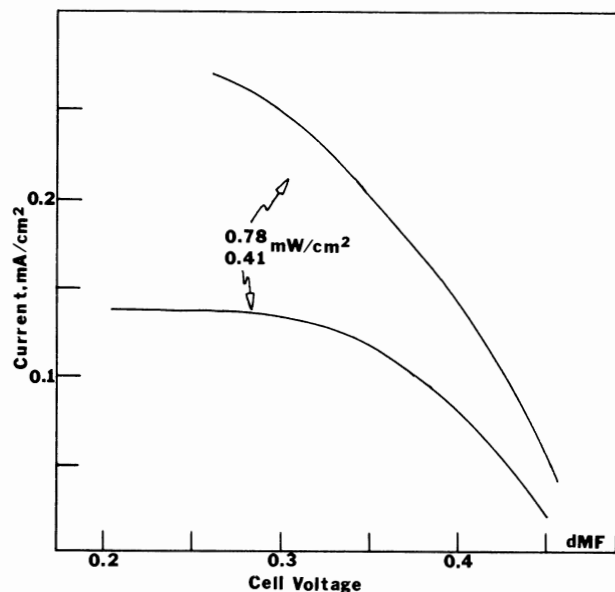


Fig. 6. Cell current vs. voltage for two intensities of 720-800 nm light for the cell

n-GaAs/dimethyl ferrocene (0.14M), dimethyl ferricenium (0.7 mM), TBAP (0.2M) ACN/Pt

p-n cell utilizing both p- and n-GaAs

p-GaAs/AQ (2.5 mM), AQ<sup>-</sup> (3 mM),

TBAP(0.1M)ACN/n-GaAs [9]

produced an open-circuit photovoltage ( $V_{oc}$ ) of 920 mV. This high value for  $V_{oc}$  can be attributed to underpotentials developed at both electrodes when both are irradiated. A high (corrected) efficiency was found with a PEC utilizing BQ and its radical anion (Table

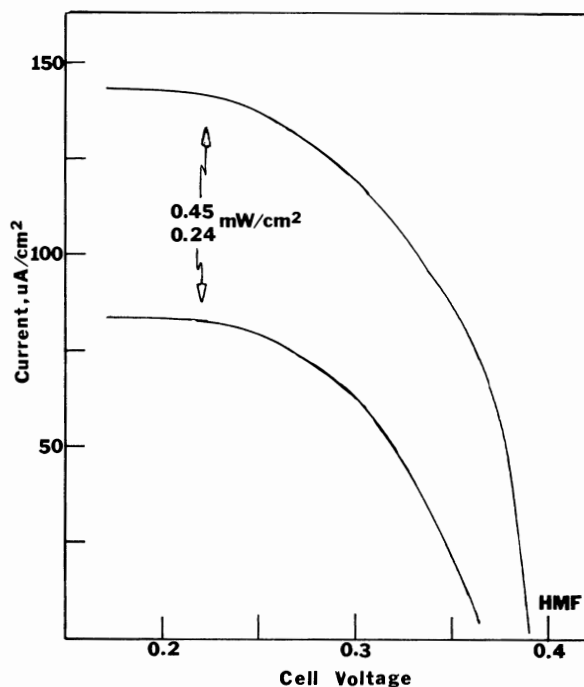


Fig. 7. Cell current vs. voltage for two intensities of 720-800 nm light for the cell  
 n-GaAs/hydroxymethyl ferrocene (15.7 mM), hydroxymethyl ferricenium (0.83 mM), TBAP (0.2M), ACN/Pt

I) when irradiated with 600 nm light through a filter (10 nm band pass).

In general, there was no evidence of photodissolution of the GaAs in any of the cells. The wide potential range of electrochemical stability, and hence the large numbers of redox couples which can be used in the PEC's, is possible only in nonaqueous solvents where the extent of the photodissolution reaction is decreased and surface effects can produce photovoltages over a large potential range. Although reasonable efficiencies are demonstrated, the maximum efficiency appears to be a compromise of several factors hinging on the light intensity, water concentra-

tion, counterelectrode area, and the concentration of the reduced and oxidized species. The cells presented represent only a crude attempt to demonstrate the factors involved in simple regenerative PEC's. Although nonaqueous systems suffer from a number of disadvantages compared to aqueous ones, such as generally lower solubilities of (usually colored) solution redox couples and higher solution resistances, the main advantage of GaAs in ACN appears to be its wide potential range for PEC's of not only the regenerative form but also for photoelectrosynthesis and photocatalysis.

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