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PHOTOELECTROCHEMICAL CELLS BASED ON n-GaAs AND THE
Cu(II)/Cu(I) REDOX COUPLE IN ACETONITRILE

by

M. E. Langmuir, M. A. Parker and R. D. Rauh

Presented at

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EIC Laboratories, Inc.
111 Chapel Street
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M. E. Langmuir, M. A. Parker and R. D. Rauh
EIC Laboratories, Inc., 111 Chapel Street, Newton, MA 02158

ABSTRACT

In acetonitrile, the potential of the Cu(II)/Cu(I) redox couple is very dependent on the coordinating strength of the anion present. In the presence of perchlorate or nitrate, the potential is not within the GaAs band gap, and the redox couple does not stabilize GaAs with respect to photodecomposition. Chloride ion, which coordinates with both cations, shifts the potential within the gap and stabilization of the semiconductor can be obtained. It is important that Cu(II) be present as the tetrachloro complex to prevent loss of Cu(II) from the PEC by a photoreduction to Cu(I). Present conversion efficiency for a poly-GaAs electrode in Cu(II)/Cu(I) tetrabutylammonium chloride, acetonitrile electrode at 80 mW/cm² is 4.8%.

INTRODUCTION

The use of nonaqueous electrolytes in photoelectrochemical cells has some promise for extending the voltage range of stabilizing redox species beyond that possible in water. Numerous examples exist where redox couples incapable of sustaining stable photocurrents at semiconductor/aqueous liquid junctions are capable of stabilizing the semiconductor in acetonitrile (1,2), propylene carbonate (3) or alcoholic electrolytes (4,5).

The strong solvation (or solvent coordination) of the Cu(I) ion renders it much more stable in acetonitrile than in water. The fact that the oxidizing power of Cu(II) salts in CH₃CN decreases with increasing complexing strength of the anion is well known and agrees well with the formal potentials given in Table 1 for the Cu(II)/Cu(I) couple in the presence of ClO₄⁻, NO₃⁻ and Cl⁻. The Cu(II) perchlorate salt is soluble in acetonitrile up to 0.2M, but is virtually undissociated at room temperature while the Cu(I) perchlorate salt is totally dissociated (6). With NO₃⁻, only Cu(II) forms a complex (7) and with Cl⁻ a number of chloro complexes are possible for both oxidation states. The stepwise formation constants and extinction coefficients of the four Cu(II) and two Cu(I) complexes generally found to be stable in acetonitrile are given in Table 2 (8).

In this paper, we present studies of the requirements for stabilization of the n-GaAs photoelectrode by the Cu(II)/Cu(I) redox couple in acetonitrile.

EXPERIMENTAL PROCEDURES

Materials. Semiconductor electrodes were prepared as previously described (1) from large grain polycrystalline GaAs naturally doped n-type with $N_D = 8 \times 10^{16} \text{ cm}^{-3}$, obtained from Laser Diode Corp. The crystal was matte etched in 1:1 $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$ before each use.

Electrolyte solutions were prepared under Ar in a Vacuum-Atmosphere dry box using Burdick and Jackson (UV) acetonitrile ($<0.004\%$ H_2O) without further purification. Solutions of anhydrous nitrate and perchlorate salts of Cu(I) were prepared by quantitative reaction of pure copper metal with the corresponding anhydrous silver salts. Cu(I) chloride solutions were prepared directly from the anhydrous CuCl salt (99.9% pure, Alfa). The Cu(II) salts, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and supporting electrolytes, TMAC, TEAC, TBAC (Southwestern Chemical) and TBAP were vacuum dried at 70°C for several days before storage in the dry box. The total dryness of the chloride salts was confirmed by titration of weighed samples with standard AgNO_3 solution.

Concentrations of the various Cu(II) chloride complexes in the electrolyte solutions were determined spectrophotometrically. Potentials of the redox couples were measured with a Hewlett-Packard high impedance voltmeter on a Pt electrode versus a $0.01\text{M AgNO}_3 (\text{CH}_3\text{CN})/\text{Ag}$ reference electrode (E° vs. $\text{SCE}_{\text{aq}} = +0.273\text{V}$) (11). Photoelectrochemical cell measurements were made in a cell described elsewhere (1) in which the current-voltage characteristics could be measured as a half-cell using a Pt wire pseudoreference electrode, or as a two-electrode "solar cell." Stirring could be provided if desired. All current-voltage curves were recorded at a scan rate of 20 mV/cm^2 unless otherwise stated.

The light source for PEC measurements was a 100W tungsten halogen lamp with a Pyrex collimating lens system and KG-2 infrared filter. This system closely approximates the AM1 spectrum. Intensity was measured with an EG&G Radiometer calibrated with an Optronic Laboratories, Inc. standard tungsten halogen lamp. Intensity was varied by use of neutral density filters. All intensities are reported as intensities at the cell face and are not corrected for cell reflectance or solution absorbance.

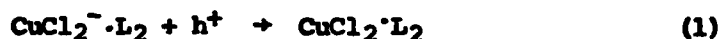
RESULTS AND DISCUSSION

Results of initial experiments with the Cu(II)/Cu(I) redox couple in acetonitrile are shown in Table 3. With no redox couple present, the photocurrent decayed rapidly due to the formation of an insoluble oxidation product on the GaAs surface. Similar behavior was found in the presence of the perchlorate and nitrate electrolytes. However, in the saturated TMAC solution of the copper chlorides, which contained 0.1M Cl^- , the photocurrent remained steady even without stirring at low light intensity and at higher intensity could be maintained with

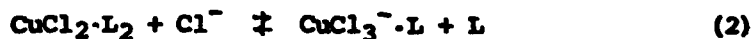
stirring. This indicated that the Cu(I) chloride species was competing effectively for holes at the photoelectrode at low intensity, but that at high intensity the Cu(I) oxidation was mass transfer limited due to its low concentration. The observation of a brown oxidation product (CuCl_2 or CuCl_3^-) streaming from the GaAs surface confirmed this interpretation of the initial observations. To increase the concentration of Cu(I) in solution, it was necessary to find a chloride source which was more soluble in acetonitrile than TMAC. Tetrabutylammonium chloride (TBAC) proved satisfactory, being soluble to more than 2M. The solubility at 25°C of CuCl in 1M TBAC was determined to be 0.43M. Most solutions for the subsequent photoelectrochemical cell (PEC) measurements were prepared as 0.4M CuCl and 1M TBAC with varying concentration of anhydrous CuCl_2 added.

At $\text{Cl}^-:\text{Cu(I)}$ concentration ratios of 2-100, the major Cu(I) species is known to be $[\text{CuCl}_2\text{L}_2]^-$.^{*} Addition of CuCl_2 to make the solutions 5-100 mM in Cu(II), resulted in the mixture of Cu(II) chloro species shown in Figure 1A as determined spectrophotometrically, and the change in redox potential shown in Figure 1B. The shift of the redox potential to more negative values as the concentration ratio of $\text{CuCl}_4^{2-}:\text{CuCl}_3^-$ increased, reached a minimum at +0.07V vs. SCE_{aq} . This equilibrium rest potential is well within the n-GaAs band gap, as shown in Figure 2, and allows stabilization of the photoelectrode.

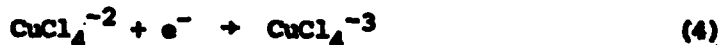
The photoanode reaction in these solutions is presumably reaction (1),



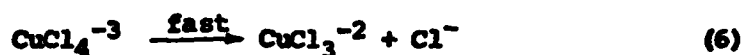
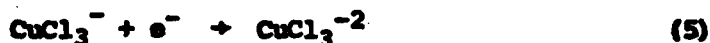
followed by the relatively slow solvent displacement by chloride ion (reactions (2) and (3)) to give the equilibrium Cu(II) chloro species according to the stepwise formation constants given in Table 2.



The counter electrode reactions must be reduction of the CuCl_3^- and/or CuCl_4^{2-} to the corresponding tri- and tetrachloro Cu(I) species, followed by rapid displacement of Cl^- by acetonitrile to give the equilibrium Cu(I) species, i.e., CuCl_2^- :



* $\text{L} = \text{CH}_3\text{CN}$. In all copper complexes in acetonitrile, L coordinates through the nitrile nitrogen to the copper ion in competition with the other ligands. The copper ions are always tetrahedrally coordinated, and L takes up the positions not occupied by Cl^- . For simplicity, we have omitted the L from the ion notation except when absolutely necessary for clarity.



Evidence for reactions (1 through 7) comes from polarographic data (12) and from cyclic voltammograms taken at scan rates as high as 11V/sec (13). At very fast scan rates, it was possible to detect the tri- and tetrachloro Cu(I) species by their reductions to Cu^0 at peak potentials (E_p) = -1.8 and -2.6 volts vs. Ag^+/Ag , respectively, in a solution which initially contained only CuCl_4^{-3} and excess chloride. For the CuCl_2^- species, E_p for reduction to Cu^0 lies at -1.1 volts. At slow scan rates (20 mV/sec), this reduction peak and the corresponding stripping peak are found in the voltammograms. However, at scan rates greater than 5 V/sec and a negative limit of -1.5V, they are no longer detectable, because the equilibria (6) and (7) cannot occur before the reduction to Cu^0 . The stripping peak is found again when the negative limit is set beyond the cathodic peaks for CuCl_3^{-2} and CuCl_4^{-3} .

Because of the equilibria following the electron transfer reactions, for both anodic and cathodic reactions, the electrolyte system may be considered electrochemically "nonreversible"; however, the whole system is chemically reversible and completely regenerative in the dark and in the absence of oxygen.

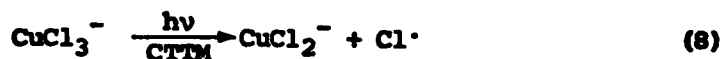
PEC parameters were determined using the solutions of the compositions shown in Figure 1A. Figure 3A shows a typical linear short circuit current versus intensity plot for the n-GaAs/Cu(II/I) chloride half cell. At the concentrations shown, the half cell did not appear to be mass transfer limited. Also typical was the linear increase in open circuit photovoltage with log intensity shown in Figure 3B. At 80 mW/cm² light intensity on the cell face, the flat band potential was not reached (see also Figure 1). If the energy levels are correct, the V_{oc} should reach about 1V at saturation. Figure 4, which illustrates a series of current-voltage curves at different intensities, shows decreasing power conversion efficiencies with increasing light intensity, primarily resulting from decreasing fill factors (0.34 at 80 mW/cm² and 0.55 at 8 mW/cm² irradiation). This decrease is true of many other semiconductor/electrolyte PEC cells and is due to the many interacting factors which affect the fill factor adversely at high light intensities, i.e., diffusion of the electroactive species to the site of the photohole, electron transfer rate, diffusion of the product away from the semiconductor surface to avoid the reverse dark reaction, etc.

We have also compared half cell PEC parameters at 80 mW/cm² for our poly n-GaAs electrode in (0.8M saturated Na_2Se , 0.1M Na_2Se_2 , 1M NaOH) electrolyte and in the 0.4M Cu(I), 0.05M Cu(II), 1M TBAC in acetonitrile and found that the matte-etched electrode gave the same value for power

conversion efficiency ($\eta = 4.8\%$). In the case of the polyselenide, the V_{oc} and short circuit were smaller but the fill factor was greater. Ruthenium ion treatment (14) increased the η to 6.8% for the polyselenide electrolyte but had no effect on the PEC parameters in the acetonitrile electrolyte.* Apparently the rate of electron transfer or mass transfer in the latter case is not fast enough to take advantage of the increased effective lifetime of photoholes caused by ruthenium adsorption at recombination sites (15).

Determination of Stability. The half cell short circuit current as a function of time was studied under a variety of conditions to determine the stability of the GaAs to photodecomposition in the electrolyte. In solutions where $CuCl_4^{2-}$ was the dominant Cu(II) species, the photocurrent at 0 to 80 mW/cm² AM1 insolation was quite stable over a four hour period. However, in solutions where the $CuCl_3^-$ concentration was significant, one of two things occurred: i) the short circuit current increased with time as the solution absorbance due to Cu(II) species decreased. Eventually the Cu(II) concentration was so small that the reduction of Cu(I) to Cu⁰ became the dominant reaction at the platinum counter electrode rather than the reduction reactions (4) and (5). At the same time, brown $CuCl_2$ or $CuCl_3^-$ could be seen streaming from the photoanode; or ii) after a period of steady photocurrent, the short circuit photocurrent decreased while a reddish-brown film grew on the face of the GaAs crystal.

Cu(II) Loss. The disappearance of Cu(II) chloride species in the first case was due to photoreduction of the $CuCl_3^-$ species in acetonitrile solution according to reaction (8) which has recently been investigated



by pulsed laser photolysis (16) and by introduction of chloro radical scavengers into the solution (17). Following absorption of a photon, the charge transfer to metal (CTM) occurs with homolytic cleavage of the metal-chlorine bond.

In the presence of free chloride ion, chloro radical is formed:



Cl_2^- does not react with acetonitrile (18) nor does it undergo its usual bimolecular reaction (10),

* In the polyselenide electrolyte, the following figures of merit were obtained at 80 mW/cm²: No Ru treatment, $V_{oc} = 0.60V$, $j_{sc} = 14.5$ mA/cm², $ff = 0.44$, $\eta = 4.8\%$; with Ru treatment, $V_{oc} = 0.73V$, $j_{sc} = 14.1$ mA/cm², $ff = 0.53$, $\eta = 6.8\%$.



(10)

in acetonitrile since no second order decay process was found for Cl_2^- disappearance (19). Rather, it may (a) reoxidize Cu(I) to Cu(II) in a reverse dark reaction, or (b) oxidize or chlorinate impurities in the electrolyte, or (c) react with GaAs if it reaches the semiconductor surface before being quenched by the other two processes. An important fact for our purpose is that the absolute quantum yield measurements (17) show that only the CuCl_3^- species has a significant CTM quantum yield, $\phi_{\text{Cu(I)}} = \phi_{\text{Cl}_2^-} = 0.28$. For the CuCl_4^{2-} species, on the other hand, $\phi_{\text{Cu(I)}} = \phi_{\text{Cl}_2^-}$ is less than 10^{-3} . Thus, the difficulties encountered because of the photoreduction of the Cu(II) species to Cu(I) can be avoided by working in solutions of high enough chloride concentration to convert all of the Cu(II) to CuCl_4^{2-} .

We have shown this to be true in an experiment in which the electrolyte was prepared 0.2M in CuCl, 0.05M in CuCl_2 and 1M in TBAC, and all of the Cu(II) was present as CuCl_4^{2-} . At both 40 and 80 mW/cm² irradiation intensity for four hours, there was no detectable change in CuCl_4^{2-} concentration. At 40 mW/cm², we also observed no change in short circuit current output of the PEC and no change in the matte-etched surface of the GaAs electrode. At 80 mW/cm², some pitting and polishing of the surface occurred during the four hours of operation. Apparently at 0.2M CuCl_2 , diffusion and electron transfer rates do not keep up with photohole production at high intensity, and some lattice oxidation occurs followed by reaction with Cl^- causing dissolution.

Film Formation. We observed film formation on the photoanode to occur at high light intensities under conditions of quiescent electrolyte and when there was little excess free chloride. Under each of these conditions, there seemed to be an induction period during which the short circuit current was steady, followed by a decrease in current as the reddish-brown layer spread across the crystal surface and grew thicker and finally, a steady state current was reached. The film was not removed by stirring the electrolyte in the presence of light but was eventually removed in the dark. The film was soluble in neat acetonitrile, and in moist air appeared to turn colorless. These observations are consistent with identification of the film as $\text{CuCl}_2(\text{L}_2)$ which forms under high current conditions in the same manner as I_2 films form on MoSe_2 photoelectrodes. The mechanism for the I_2 precipitation in the latter case has been well-documented by Tributsch, Sakata and Kawai (20). The induction period exists until the buildup of CuCl_2 oxidation product at the electrode surface exceeds the solubility of CuCl_2 and nucleation occurs on the crystal face. The film is then quickly propagated across the crystal surface causing a decrease in light intensity at the surface. Lack of access of free chloride to the surface to convert CuCl_2 to CuCl_3^- prevents dissolution of the film. The low steady state current following film formation appears to be due to lattice oxidation, since pitting of the electrode under the film has been observed.

Film formation has been prevented by operating at lower light intensities or at the maximum power voltage (rather than at short circuit) to reduce the current density and in so doing the concentration of photoproduct at the surface and/or by employing those means which encourage rapid removal of CuCl_2 from the photoanode surface, including efficient stirring and high free chloride concentration which increases the overall rates of reactions (2) and (3).

CONCLUSION

We have shown that complexation of Cu(II)/Cu(I) ions with chloride in acetonitrile shifts the redox potential to a position within the band gap of GaAs and stabilizes the n-GaAs photoanode. Furthermore, complexation in solutions of high chloride concentration where Cu(II) is present as CuCl_4^{2-} is favored because of (a) less solution absorbance, (b) reduced probability of anodic film formation, and (c) essentially no photoreduction of CuCl_4^{2-} as opposed to the lower Cu(II) chloride complexes.

Our best PEC figures of merit to date at 80 mW/cm^2 at room temperature with a cell using polycrystalline n-GaAs are: $j_{sc} = 19 \text{ mA/cm}^2$, $V_{oc} = -0.74 \text{ V}$, $P_{max} = 3.78 \text{ mW/cm}^2$, $ff = 0.27$ and $\eta = 4.8\%$. Presumably these values can be improved with use of a better quality single crystal n-GaAs electrode and operation at higher temperatures. Very long term stability has not yet been demonstrated for this cell, but obviously will be influenced by current density, redox concentration, and the catalytic nature of the GaAs surface toward Cu(I) oxidation.

ACKNOWLEDGMENT

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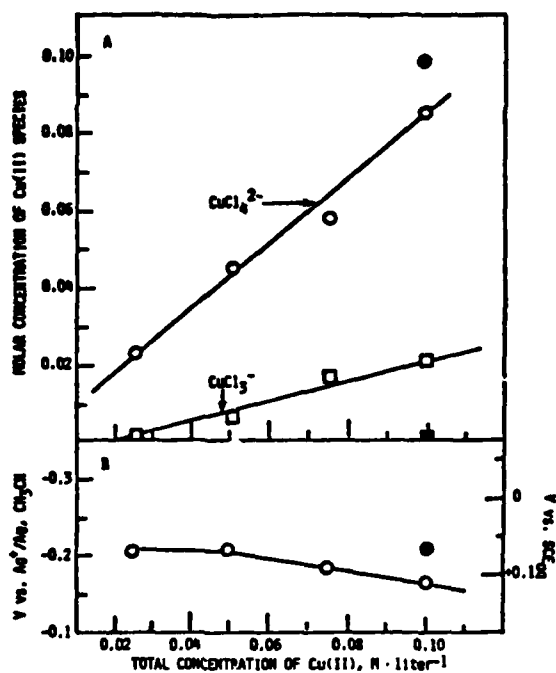


Fig. 1. A: Molar concentrations of major Cu(II) species at constant CuCl (0.4M) in acetonitrile. B: Equilibrium rest potential on Pt. Open symbols in 1M TBAC, filled symbols in 2M TBAC.

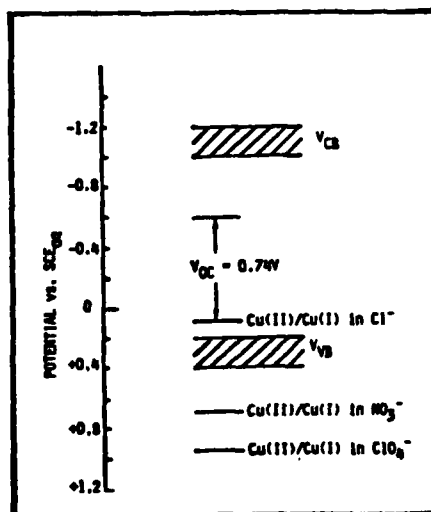


Fig. 2. Potential diagram of n-GaAs in CH_3CN .

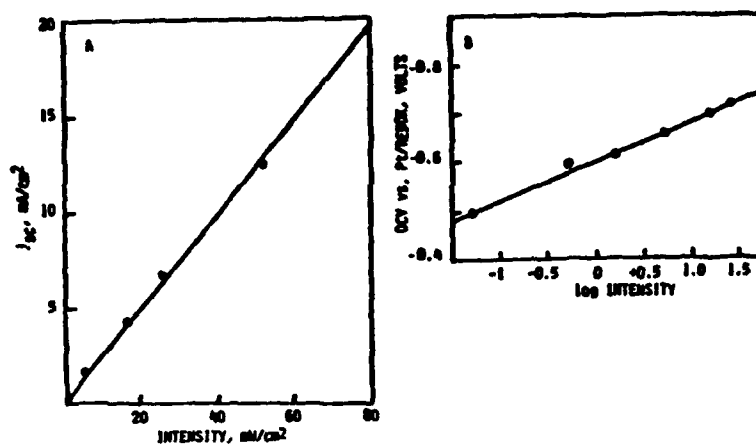


Fig. 3. Half-cell parameters vs. light intensity for the cell:

poly-GaAs | CuCl_2 (0.05M), CuCl (0.32M) | Pt
0.8M TBAC, CH_3CN

W-I lamp, KG-2 filter, stirred electrolyte. A, short circuit photocurrent; B, open circuit photovoltage.

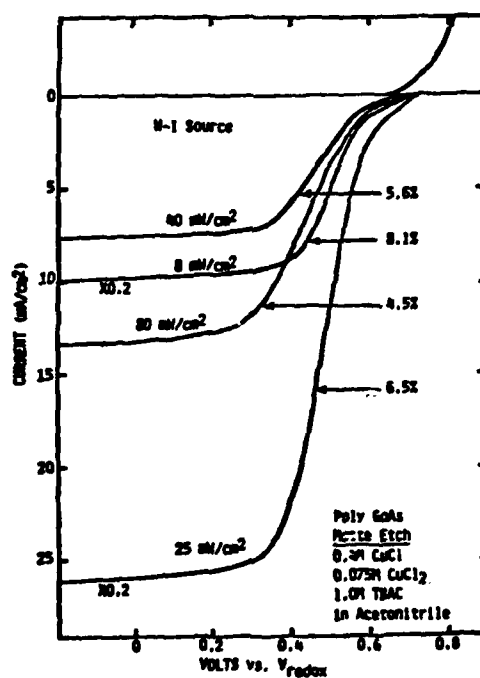


Fig. 4. Half cell current-voltage curves at different intensities.

TABLE 1
FORMAL POTENTIALS OF THE $\text{Cu}^{+2}/\text{Cu}^{+1}$ AND $\text{Cu}^{+1}/\text{Cu}^{+2}$
REDOX COUPLES IN ACETONITRILE

Couple	Anion	E vs. SCE (V)	E vs. Ag^+/Ag (V)	Reference
$\text{Cu}^{+2}/\text{Cu}^{+1}$	ClO_4^-	+0.95	+0.650	(9)
			+0.679*	(10)
	NO_3^-	+0.695	+0.395	(9)
	Cl^-	+0.56**	+0.26	(9)
$\text{Cu}^{+1}/\text{Cu}^0$	ClO_4^-	-0.30	-0.60	(10)
	NO_3^-	-0.30	-0.60	our value
	Cl^-	-0.42**	-0.72	our value

*Corrected for liquid junction potential.
**Refers to the dichloro species.

TABLE 2
STEPWISE FORMATION CONSTANTS OF Cu(I) AND Cu(II) CHLORIDE
COMPLEXES IN ACETONITRILE, AND THEIR LONG
WAVELENGTH EXTINCTION COEFFICIENTS

	Stepwise Formation Constant	Long $\lambda_{\text{max, nm}}$	ϵ
Cu(I)	$K_{\text{CuCl}} = 10^{4.9}$	no absorbance in the visible	
	$K_{\text{CuCl}_2^-} = 10^{5.9}$	no absorbance in the visible	
Cu(II)	$K_{\text{CuCl}^+} = 10^{9.7}$	296	4×10^3
	$K_{\text{CuCl}_2} = 10^{7.9}$	no distinguishing peak	
	$K_{\text{CuCl}_2^-} = 10^{7.1}$	462	1.69×10^3
	$K_{\text{CuCl}_3^-} = 10^{3.7}$		$\sim 2.86 \times 10^3$
	$K_{\text{CuCl}_4^{-2}} = 10^{3.7}$		

Taken from Ref. 8.

TABLE 3
PEC PARAMETERS FOR n-GaAs/Cu²⁺/+1, CH₃CN/Pt HALF CELLS

Electrolyte	E vs. Ag ⁺ /Ag (V)	Light Intensity (mW/cm ²)	V _{oc} (V)	j _{sc} (mA/cm ²)	η (%)	Remarks
0.09M CuClO ₄ 0.01M Cu(ClO ₄) ₂ in 0.09M TBAClO ₄	+0.60	53	-0.75	-	-	Photocurrent decays rapidly with or without stirring.
0.1M CuNO ₃ 10 ⁻⁴ Cu(NO ₃) ₂ in 0.1M TBABF ₄	+0.35	11	-0.42	-	-	Photocurrent decays rapidly with or without stirring.
0.048M CuCl 0.005M CuCl ₂ in saturated TBAC [*] (~0.1M)	-0.2 ^{**}	5.3	-0.708	2.3	15.1	Photocurrent steady without stirring.
Same as above	-0.2 ^{**}	53	-0.79	11.9	3.7	Photocurrent decays unless solution stirred.

* TBAC = tetramethylammonium chloride.

** Approximate potential for oxidation of CuCl₂⁻ species.

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