251. Effect of Doping and Solution Redox Relays on the Efficiency of Photocathodic Processes at the *p*-InP/Water Interface

by **Thomas Geiger, Richard Nottenberg**[1], **Mary-Lou Pélaprat** and **Michael Grätzel**[2])
Institut de Chimie Physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne

(1.X.82)

Summary

Light-induced interfacial electron transfer from two p-InP electrodes differing in the amount of majority carrier doping to a number of electron relays (R) dissolved in aqueous solution was investigated. The material with the lower carrier density (0.71×10^{18} cm^{-3}) exhibited much better wavelength response and quantum yield for electron transfer than the electrode doped with 2.3×10^{18} cm^{-3} charge carriers. Using cobalt(III) sepulcrate, $Co(sep)^{3+}$, as an electron relay a polychromatic light to electrical energy conversion efficiency of 18% was obtained. The potential of this relay for use in a regenerative photoelectrochemical cell is briefly discussed.

Introduction. – Interfacial electron transfer between semiconductor electrodes and electrolytes plays a primordial role in light-energy conversion devices [1]. In the case of p-type semiconductors the transfer involves electrons (e^-_{CB}), promoted by band-gap excitation to the conduction band, which reduce an acceptor (electron relay, R) dissolved in solution *(Eqn. 1)*.

$$e^-_{CB} + R \rightarrow R^- \qquad (1)$$

Competing with *Reaction 1* are surface or bulk recombination with holes, and trapping of e^-_{CB} in surface states. These processes decrease the conversion efficiency, a problem that is particularly notorious for p-type devices [2]. Among a variety of electron acceptors [3] methylviologen (MV^{2+}) has been most widely investigated. Strategies to enhance reduction of MV^{2+} by e^-_{CB} include chemical attachment of the relay to the semiconductor surface (p-type Si [4]) and imcorporation into a polymer layer (p-type GaAs [5]).

---

[1]) Institut de Microélectronique de l'EPFL.

[2]) Author to whom correspondence should be addressed.

0018-019X/82/8/2507-10$01.00/0

We have introduced recently several novel electron relays [6] which, from their absorption and redox properties, are highly suited to be employed in photoelectrochemical devices. The present study explores the characteristics of electron transfer from p-type indium phosphide, InP, to these acceptors. InP has been extensively studied as a semiconducting material for applications in optoelectronics, microwave and photovoltaic devices. Photoelectrochemical experiments with InP have been performed first by *Vervaet et al.* [7] and more recently by *Heller et al.* [8], *Kohl & Bard* [9] and *Dominey et al.* [10]. The 1.34 eV band-gap makes it attractive for solar application. We report here on achievement of 18% polychromatic light to electrical energy conversion efficiency using Co-sepulcrate as an electron relay. Also, a rather pronounced effect on the photoelectrochemical performance brought about by changes in carrier concentration of the p-type InP is demonstrated.

Experimental. – InP single crystals (III plane) obtained from *Cambridge Instruments* and the *Royal Signals and Radar Establishment* were doped with Cd to have 7.1×10^{17} cm^{-3} carrier concentration and with Zn to a carrier concentration of 2.3×10^{18} cm^{-3}, respectively. The crystals were cut into pieces of *ca.* 0.2 cm^2 size and etch-polished with CH_3OH/Br_2-solution. The ohmic back-contact was made by evaporating a Zn/Au-alloy first and heating the crystals briefly to 450° afterwards. Ag-paint was used to mount the electrodes on a Ti-support which was subsequently insulated with wax. No attempt was made to influence the growth of the native oxide layer on the InP [8].

A conventional three-electrode cell with a flat *Pyrex* window for illumination was used for the electrochemical measurements. The solution (*ca.* 15 ml volume) was agitated by a magnetic stirrer. A Ti-wire counter electrode and a commercial aq. Ag/AgCl reference electrode (add 200 mV to convert to NHE.) were separated from the working electrode compartment by sintered glass frits.

Potentiostatic measurements employed a *Bruker E 310 Universal Polargraph* and a *Watanabe* xy-recorder. Scan rate for experiments under chopped illumination was typically 2.5 mV/s. Cyclic voltammetry (scan rate 100 mV/s) was used to determine the redox potentials of the redox couples employed in this study. Working electrodes were a *Metrohm* hanging Hg-drop electrode (HMDE.) and a basal plane pyrolytic graphite electrode.

A 250-W tungsten-halogen lamp *(Osram)* was used as light source and equipped with a 10-cm water filter. The light intensity was measured with a *Yellow Springs Instrument Kettering Model 65A* radiometer. Optical filters were used as indicated for better comparison of measurements with different redox systems and avoided absorption losses by colored solutions. Experiments designed for specific wavelengths employed a *Bausch & Lomb* monochromator with a 500 nm blaze (350 to 750 nm) and a 1000-nm blaze (750 to 1000 nm). H_2 was determined by injecting aliquots of the gas phase above the electrolyte solution into a *Gow-Mac* gas chromatograph.

Solutions were prepared from distilled water and degassed with N_2. MV^{2+}[3]) was from *BDH Chemicals*, $Ru(NH_3)_6\,Cl_3$ from *Johnson-Matthey & Brandenberger* and HCl from *Merck*. $Co(sep)Cl_3$[3]) [11] and *trans*-$[Co([14]aneN_4)Cl$[3]) [12] were synthesized according to literature procedures. Co(cp)(cpCOOH)Cl[3]) was a gift from Dr. *André Braun*, Lausanne.

Results and discussion. – 1. *Electrochemical behavior of p-InP in* MV^{2+}*-solution. Figure 1* shows the current potential curves obtained in a solution of 25 mM/MV^{2+}/ 0.1 M HCl at two p-InP electrodes under illumination with slowly chopped light (10 mW/cm^2). The shape of both photocurrent-potential curves is very similar and they represent typical examples for the photoassisted reduction of an oxidant at the p-type semiconductor/solution interface. The occurrence of reduction is supported, in our case, by the observation of blue clouds of reduced/MV^{2+} that stream

---

[3]) Methylviologen (MV^{2+}) stands for *N,N'*-dimethyl-4,4'-bipyridinium; sep = sepulcrate stands for (*S*)-1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane; [14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane; cp stands for cyclopentadienyl.

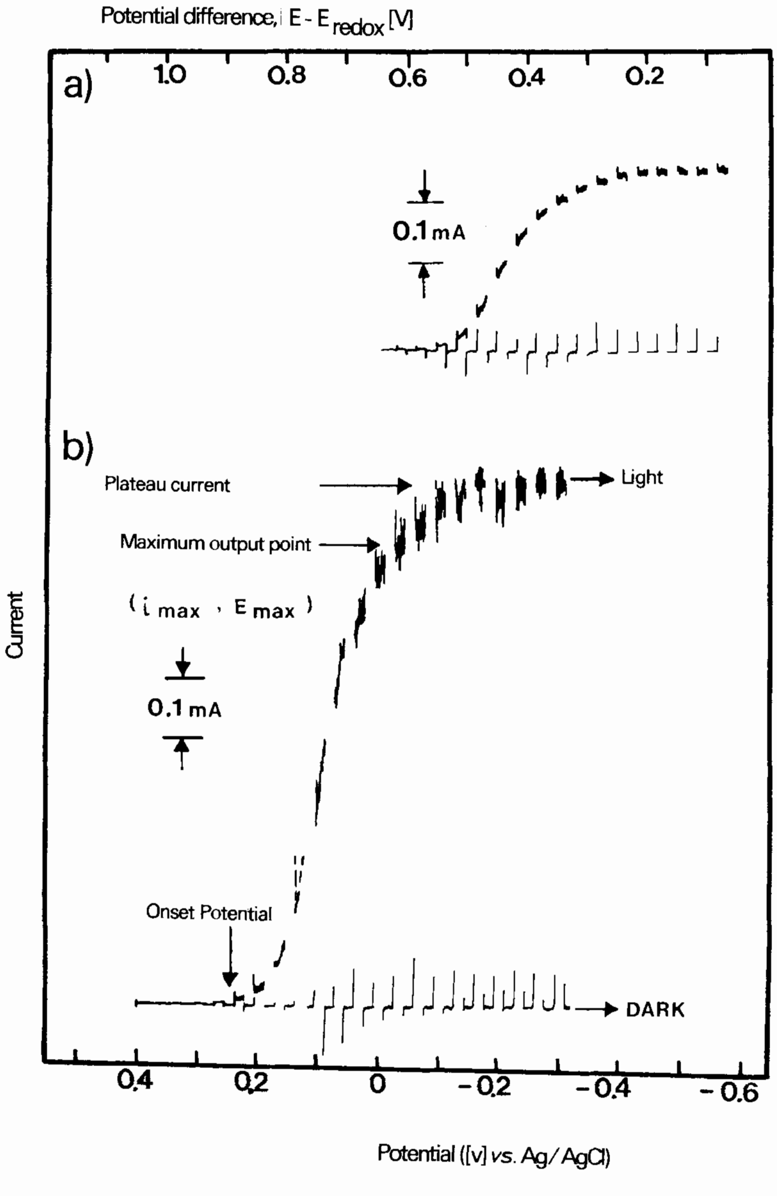

Fig. 1. *Electrochemistry under chopped illumination with 10 mW/cm² light in a 0.1 M HCl-solution of 25 mM MV^{2+}* (E_{redox} = −0.64 V *vs.* Ag/AgCl) *on p-InP single-crystal electrodes* (*electrode a:* carrier concentration 2.3×10^{18} cm^{-3}, electrode size 0.22 cm^2, *electrode b:* carrier concentration 7.1×10^{17} cm^{-3}, electrode size 0.26 cm^2; E_{onset} = onset potential is defined as potential where photocurrent is 1% of plateau current. Maximum output point is defined as point along the photocurrent-potential curve where product of $(E - E_{redox}) \times i_{photo}$ reaches maximum. E_{redox} = solution redox potential for 1:1-mixture of reduced and oxidized form of MV^{2+}).

away from the electrode under illumination. Despite the fact that both experiments in *Figure 1* were performed under identical conditions, there are drastic differences in the results: the magnitude of the plateau-current density observed in *Figure 1b* is over 2.5 times that in curve *1a*, and in addition the latter is shifted *ca.* 300 mV towards more negative potentials. For a better and more quantitative comparison, we define two points along the photocurrent-potential curve. The potential where the photocurrent is 1% of the plateau current is called onset potential (E_{onset}) [13], the point where the product of photocurrent and underpotential ($E - E_{redox}$) is greatest we call maximum output point. This product (especially when normalized by the light intensity) gives an idea of how efficient the device converts the incident light into electrical energy. The electrode used in *Figure 1b* is six times more efficient than the one used for *Figure 1a* (see the *Table* for exact values).

Table. *Summary of electrochemical data in the dark*[a]) *and under illumination*[b])

Redox couple	Redox potential E_{redox}[a]) [V *vs.* Ag/AgCl]	Plateau current density[b]) [mA/cm^2]	Onset potential E_{onset} [V *vs.* Ag/AgCl]	Under-potential $E_{onset} - E_{redox}$ [mV]	Maximum output point	
					E_{max} [V *vs.* Ag/AgCl]	Output[c]) [%]
A) p-InP Carrier concentration 2.3×10^{18} *cm*$^{-3}$						
$[Co([14]aneN_4)Cl_2]^{+/o}$	0	0.77	+0.37	370	+0.08	0.25
$[Ru(NH_3)_6]^{3+/2+}$	−0.13	0.9	+0.45	580	+0.15	1.8
$[Co(sep)]^{3+/2+}$	−0.515	1.44	+0.03	545	−0.27	3
Methylviologen ($MV^{2+/+}$)	−0.64	1.3	−0.07	570	−0.3	3.8
B) p-InP Carrier concentration 7.1×10^{17} *cm*$^{-3}$						
$[Co([14]aneN_4)Cl_2]^{+/o}$	0	3.4	+0.54	520	+0.3	6.9
$[Ru(NH_3)_6]^{3+/2+}$	−0.13	3.6	+0.57	700	+0.25	11
$[Co(sep)]^{3+/2+}$	−0.515	3.5	+0.32	835	+0.07	18
Methylviologen ($MV^{2+/+}$)	−0.64	3.4	+0.25	890	−0.025	18
$[Co(cp)(cpCOOH)]^{+/o}$	−0.8[d])	2.8[d])	+0.17[d])	970[d])	−0.15[d])	16[d])

[a]) Determined by cyclic voltammetry on HMDE. or pyrolytic graphite electrode. Scan rate 0.1 V/s. E_{redox} is the mean of cathodic and anodic peak potentials. 0.1 M HCl was used as electrolyte. [b]) Experiments under illumination were done in 0.1 M HCl containing 25 mM of the redox couple. Irradiation was 10 mW/cm^2. A 550-nm filter was used for measurements employing $Co(sep)Cl_3$ and Co(cp)(cpCOOH)Cl, a 695-nm filter for *trans*-$[Co([14]aneN_4)Cl_2]Cl$. For symbols and definitions, see *Figure 1*. [c]) Output is defined as product of photocurrent density and underpotential (at maximum output point) divided by irradiance. [d]) Data less reliable. The reduced form of this redox couple is only sparingly soluble under experimental conditions, and plates out on the electrode. Numbers given are approximations for an uncoated electrode.

The reason for this difference becomes clearer from *Figure 2*. Here the photoelectrochemical quantum efficiency (number of electrons harvested by the solution redox couple divided by number of incident photons) was determined for the same electrodes as a function of light energy. For the electrode in *Figure 1b* the quantum efficiency approaches unity (assuming a 20-30% loss from reflection) for photons from 350 to 750 nm; with longer wavelength the quantum efficiency drops sharply

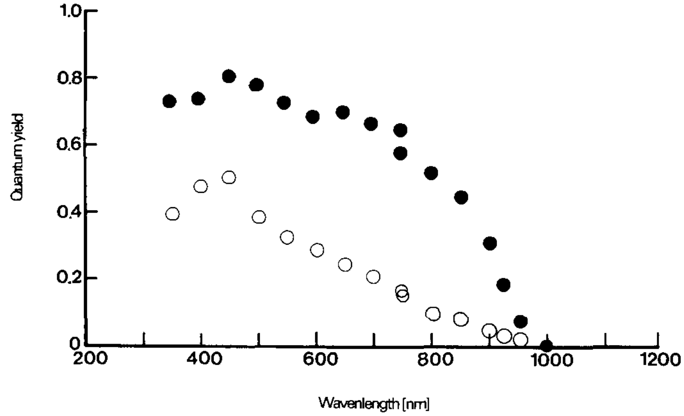

Fig. 2. *Spectral dependence of the photoelectrochemical quantum efficiency* (no. of electrons/no. of photons) *for p-InP* (○ carrier concentration was 2.3×10^{18} cm^{-3}; ● carrier concentration was 7.1×10^{17} cm^{-3}. Electrolyte was as in *Fig. 1*. See *Exper. Sect.* for details)

and photons of less energy than the band-gap do not produce a photocurrent. In contrast, the other p-InP electrode shows a very low quantum yield over the whole visible spectrum and most of the incident photons do not yield a photocurrent.

The key to understanding this behavior lies in the fact that only those photons that are absorbed within a narrow range close to the semiconductor/liquid interface can effect a photocurrent. The depth of this range is determined by the width of the depletion layer W and the minority-carrier diffusion length L_n and has to exceed the length needed for quantitative absorption of the incident light to achieve unity quantum yield [14].

A depth of *ca.* 0.5 μ is required for 90% light absorption if the absorption coefficient a of the material is 2×10^{-4} cm^{-1} (value for InP at 825 nm). This number has to be compared to W and L_n. Using the *Gärtner* equation [14] we calculated for the electrodes used in *Figures 1a* and *1b*, a depletion layer width of only 0.024 and 0.044 μ, respectively, sufficient for not more than 10–20% light absorption[4]. Thus, it is clear that the photocurrent (at 825 nm) is predominantly due to light-generated electrons which can reach the space-charge region by diffusion.

The total light-generated minority carrier current for a n^+/p-junction solar cell (under short circuit conditions) at a given wavelength can be expressed by *Equation 2*,

$$I(\lambda) = \frac{q\,F(\lambda)\,(1-R)\,a L_n}{a L_n + 1}\, e^{-a(x_i + W)} \tag{2}$$

where a is the absorption coefficient, q the electronic charge, $F(\lambda)$ the number of photons incident per sec per cm^2 of wavelength λ, R the reflection coefficient and x_i

---

[4] The following values were used for our calculations: band-bending = 1 V; dielectric constant $\varepsilon = 12.4$; absorption coefficient $a_{750\,nm} = 3.24 \times 10^4$ cm^{-1}; $a_{900} = 10^4$ cm^{-1}. Plateau currents were used instead of short circuit currents.

the width of the n$^+$-region [15]. For the present investigation the exponent in the above equation is close to unity since there is no appreciable light absorption in the electrolyte and W is very small. In this case *Equation 2* can be written as in *Equation 3,* where

$$\alpha^{-1}+L_n=q(1-R)L_n(F(\lambda)/I(\lambda)) \tag{3}$$

$I(\lambda)/F(\lambda)$ is the quantum yield as determined in *Figure 2.* The minority-carrier diffusion length L_n can therefore be obtained from a plot of (quantum yield)$^{-1}$ *vs.* (absorption coefficient)$^{-1}$ *(Fig. 3)* [15]. It is found that L_n is 0.5 μ for electrode *1b*, but less than 0.1 μ for electrode *1a*. The small diffusion length for the electrode in *Figure 1a* is clearly responsible for the reduced long-wavelength photoresponse as observed in *Figure 2.* More than 70% of the incident 825-nm photons are absorbed at a distance greater than one diffusion length from the junction edge and thus suffer recombination in the bulk. The photocurrent increases with photon energy since the absorption coefficient of the semiconductor increases in the same sense. The large difference in L_n for both electrodes is consistent with the reduced minority-carrier transport expected at high doping levels.

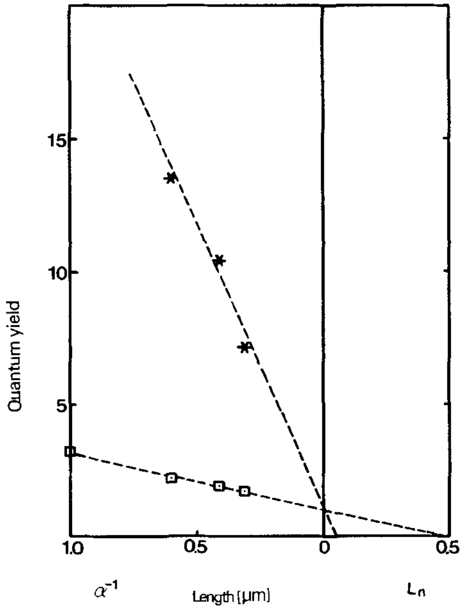

Fig. 3. *Plots of inverse quantum yield* vs. *inverse absorption coefficient for the graphic determination of the minority-carrier diffusion length L_n* (intercept with the abscissa) (* carrier concentration was 2.3×10^{18} cm^{-3}, □carrier concentration was 7.1×10^{17} cm^{-3})

2. *Other redox relays.* Photoinduced electron transfer from the conduction band of p-InP to a number of other electron acceptors was also investigated and results are summarized in the *Table.* It is not surprising to find that the underpotentials,

currents and efficiencies depend on the carrier concentration of the p-InP electrode involved just as discussed above for MV^{2+}. However, another aspect of the data in the *Table* deserves attention. For an ideal semiconductor/liquid junction, *Equation 4* holds [14], where U_{oc} is the open-circuit potential of a photoelectrochemical cell

$$U_{oc} = E_{fb} - E_{redox} \tag{4}$$

and E_{fb} is the flat-band potential. This equation predicts that the open-circuit potential shifts linearly with solution redox potential. In our study open-circuit potentials were not measured, but we can assume that the difference $E_{onset} - E_{redox}$ is a close approximation. Hence, $E_{onset} - E_{redox}$ should vary linearly with E_{redox} or, in other words, E_{onset} should be independent of solution redox potential and fall close to the flat-band potential. It is obvious that this prediction is not fulfilled by the data compiled in the *Table*. Unfortunately, we do not known the exact location of the flat-band potential of p-InP under our experimental conditions. A reported value for $E_{fb} = +0.9$ V *vs.* SHE. at pH 2.1 [16] corresponds to $E_{fb} = +0.77$ V *vs.* Ag/AgCl under our experimental conditions. This would set the cathodic limit for the location of the conduction band at -0.6 V *vs.* Ag/AgCl. A simple model for semiconductor/liquid junctions assumes that only solution redox couples with a potential located within the band gap should show photoeffects. MV^{2+}, however, has a redox potential of -0.64 V *vs.* Ag/AgCl but is nevertheless reduced[5]) by conduction-band electrons of p-InP. Inconsistencies between experiments and simple theory have led *Bard et al.* [17] to introduce the concept of *Fermi*-level pinning at semiconductor/liquid junctions. Briefly, this concept invokes that E_{VB} and E_{CB} are not independent of the solution potential, but shift with it. Open-circuit voltages smaller than those calculated from *Equation 4*, and photoeffects with solution couples having potentials outside the band-gap can thus be explained.

Since there is some uncertainty about the exact location of the flat-band potential of p-InP and from the above argument of more positive solution redox potential, there is the possibility that MV^{2+} falls just within the gap. It was therefore our intention to study this question further by using other redox couples with more negative potentials than MV^{2+}. However, it proved to be extremely difficult to realize this goal without changing the solvent or at least the pH of the electrolyte. (It is known that the InP-bands shift with pH.) Several viologen derivatives exhibiting reversible electrochemistry on Hg or graphite at more negative potentials than MV^{2+} were tested. Whereas this was confirmed for solutions at neutral pH, all of the viologens tested showed only an irreversible reduction wave and no re-oxidation when the cyclic voltammetry was performed in 0.1 M HCl.

We finally settled for a cobaltocene derivative, $[Co(cp)(cpCOOH)]^{+/o}$ with a redox potential of -0.8 V in 0.1 M HCl [18]. This is, however, not as nicely reversible a redox couple as the other systems investigated. The reduced form of the complex (which is neutral at this pH) is only sparingly soluble. A red precipitate is plated out on the electrode. This clearly indicates that even a redox couple with such a negative potential can be reduced in a photoassisted manner.

---

[5]) It should be kept in mind that the solution redox potential is somewhat more positive than -0.64 V due to the less than 50%-conversion of MV^{2+} in the reduced form.

However, it should be ascertained whether the photocathodic effect observed in the presence of $[Co(cp)(cpCOOH)]^+$ arises indeed from *Fermi*-level pinning or alternatively from hot carrier ejection [19].

3. *Light-energy conversion.* There are two conceptually different schemes for solar energy conversion that might be based on a semiconductor/liquid junction [20]. In a photoelectrosynthetic cell, one is interested in producing substances with high chemical potential such as H_2. Alternatively, in a regenerative photoelectrochemical cell, the redox process occurring at the semiconductor electrode is reverted at a suitable counter electrode. No net chemical changes occur in the solution and the solar energy is converted into electricity.

Of the redox couples investigated here, $Co(sep)^{3+/2+}$, $MV^{2+/+}$ and the cobaltocene derivative gave high conversion efficiencies and, therefore, are considered for such regenerative cells. The last two redox relays, however, do not withstand close scrutiny. One criterion which is not fulfilled by $[Co(cp)(cpCOOH)]^{+/o}$ is high solubility in the two oxidation states. In such a case, mass transfer of a redox couple becomes easily a problem at high current densities. This is demonstrated in *Figure 4.*

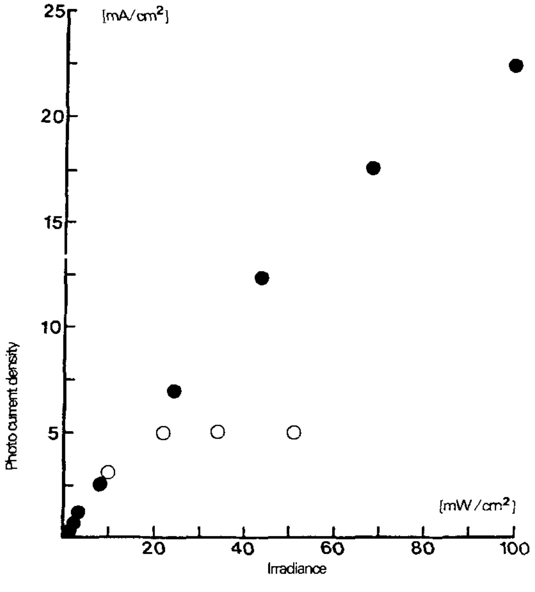

Fig. 4. *Effect of irradiance on the photocurrent for MV^{2+}-reduction* (Electrode used was p-InP with carrier concentration 7.1×10^{17} cm^{-3}; solution contained 25 mM MV^{2+} (○) and 200 mM MV^{2+} (●))

The light intensity was varied for the MV^{2+}/HCl-system described before. Despite vigorous stirring and careful placing of the semiconductor electrode the maximum photocurrent did not exceed 5 mA/cm² at all light intensities for a 25 mM MV^{2+}-solution. Only by increasing the concentration of MV^{2+} drastically, enough oxidized material could be supplied to the electrode to scavenge all of the available conduction-band electrons. In this situation only a minor deviation of the photocurrent at high light intensity is observed from values extrapolated from low irradiance.

Apart from the solubility, it is important that the electron relay is stable and only moderately colored in both oxidation states. These requirements eliminate MV^{2+} from the list of potential relay compounds in a photovoltaic cell. The reduced form of MV^{2+} is very intensely colored and also known to be extremely oxygen-sensitive. The most promising candidate for use in a regenerative cell is $Co(sep)Cl_3$. It is only weakly colored in both oxidation states ($Co(sep)^{3+}$ in H_2O [11]: $\varepsilon_{472}=109$; $\varepsilon_{396}=9.9$; $Co(sep)^{2+}$ in H_2O [11] $\varepsilon \approx 8$ at 465 nm and $\varepsilon \approx 5$ at 915 nm) and, in the reduced state, is surprisingly unreactive towards oxygen [11]. These properties make in much superior to MV^{2+} and V^{3+} [8] as a relay compound. The underpotential of the onset potential is over 800 mV and even at the maximum output point the underpotential is still nearly 600 mV. However, entries in the *Table* are only meaningful with respect to a regenerative cell if the desired reaction (reduction of the redox couple) is the only process that contributes to the photocurrent. Photocorrosion of the semiconductor and reactions of the reduced relay other than being oxidized at the counter electrode are detrimental. With respect to the stability of p-InP, the studies by *Heller et al.* [8] and our own work appear to show no evidence for photocorrosion. As for the relay, a potential side reaction of $Co(sep)^{2+}$ would be the (in 0.1 M HCl thermodynamically downhill) reaction with protons to give H_2. We have, therefore, irradiated p-InP in 25 mM $Co(sep)^{3+}$/0.1 M HCl-solution (conditions similar to those mentioned in the *Table*) for over 7 h and analyzed the gas phase above the electrolyte for H_2. Only traces of H_2 could be found[6]). Thus the high value for light-conversion efficiency of 18% calculated from potentiostatic experiments can be taken as evidence that an efficient regenerative solar cell might be feasible with $Co(sep)Cl_3$ as a relay.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.*

REFERENCES

[1] *H. Gerischer,* J. Electroanal. Chem. *58,* 263 (1975).

[2] *J.J. Kelly & R. Memming,* J. Electrochem. Soc. *124,* 734 (1982).

[3] *K.H. Beckmann & R. Memming,* J. Electrochem. Soc. *116,* 368 (1969).

[4] *R.N. Dominey, N.S. Lewis, J.A. Bruce, D.C. Bookbinder & M.S. Wrighton,* J. Am. Chem. Soc. *104,* 467 (1982).

[5] *F.-R.F. Fan, B. Reichman & A.J. Bard,* J. Am. Chem. Soc. *102,* 1488 (1980).

[6] *V. Houlding, Th. Geiger, U. Kölle & M. Grätzel,* J. Chem. Soc. Chem. Commun. *1982,* 682.

[7] *A.A.K. Vervaet, W.P. Gomes & F. Cardon,* J. Electroanal. Chem. *91,* 133 (1978).

[8] a) *A. Heller, B. Miller & F.A. Thiel,* Appl. Phys. Lett. *38,* 282 (1981); b) *H.J. Lewerenz, D.E. Aspnes, B. Miller, D.L. Malm & A. Heller,* J. Am. Chem. Soc. *104,* 3325 (1982); c) *A. Heller & R.G. Vadimsky,* Phys. Rev. Lett. *46,* 1153 (1981).

[9] *P.A. Kohl & A.J. Bard,* J. Electrochem. Soc. *126,* 598 (1979).

[10] *R.N. Dominey, N.S. Lewis & M.S. Wrighton,* J. Am. Chem. Soc. *103,* 1261 (1981).

---

[6]) Some H_2 is generated when $Co(sep)^{3+}$ is electrolyzed at −0.7 V (SCE.) at a stirred Hg-pool electrode [6]. The fact that virtually no H_2 is found in the present experiment is ascribed to differences in solution composition, electrode material and degree of $Co(sep)^{3+}$-reduction.

[11] a) *I.I. Creaser, J.M. Harrowfield, A.J. Herlt, A.M. Sargeson & J. Springborg,* Inorg. Synthesis, Vol. XX, p. 85 (1980); b) *I.I. Creaser, J.M. Harrowfield, A.J. Herlt, A.M. Sargeson & J. Springborg,* J. Am. Chem. Soc. *99*, 3181 (1977).
[12] *B. Bosnich, C.K. Poon & M.L. Tobe,* Inorg. Chem. *4*, 1102 (1965).
[13] *F.-R.F. Fan & A.J. Bard,* J. Am. Chem. Soc. *102*, 3677 (1980).
[14] *H. Gerischer,* Top. Appl. Phys. *31*, 115 (1979).
[15] *C.-Y. Wu & J.-F. Chen,* Solid-St. Electron. *25*, 679 (1982).
[16] *A.M. Van Wezemael, W.H. Laflère, F. Cardon & W.P. Gomes,* J. Electroanal. Chem. *87*, 105 (1978).
[17] *A.J. Bard, A.B. Bocarsly, F.-R.F. Fan, E.G. Walton & M. Wrighton,* J. Am. Chem. Soc. *102*, 3671 (1980).
[18] *N. ElMurr,* Transition Met. Chem. *6*, 321 (1981).
[19] *R.T. Ross & A.J. Nozik,* J. Appl. Phys. *53*, 3813 (1982).
[20] *A.J. Bard,* J. Phys. Chem. *86*, 172 (1982).