

RECENT PROGRESS AT THE WEIZMANN INSTITUTE IN THE PHOTOELECTROCHEMISTRY OF CADMIUM CHALCOGENIDES AND CuIn CHALCOGENIDES*

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Summary

The effect of the composition of polysulphide electrolytes on cadmium chalcogenide/polysulphide (S_x^{2-}) photoelectrochemical cells is discussed, with emphasis on the effect of the cation in solution, the OH^- concentration and the presence of copper species in solution. It is shown how optimization of the electrolyte composition can lead to dramatic improvements in the efficiency and stability of photoelectrochemical cells. The results of some long-term outdoor stability experiments on $Cd(Se, Te)|S_x^{2-}$ photoelectrochemical cells are also shown and discussed.

The $Cu-In-X|S_x^{2-}$ systems, where $Cu-In-X$ represents $CuInS_2$, $CuIn_5S_8$ and $CuInSe_2$, are treated in terms of their comparison with the $CdX|S_x^{2-}$ systems. The surface chemistries of the two systems are shown to be largely responsible for many of their properties.

Finally, the $CuInSe_2|polyiodide$ system is described briefly, and comparisons between it and the $CuInSe_2|S_x^{2-}$ system are drawn.

1. General introduction

The photoelectrochemistry group at the Weizmann Institute of Science (WIS) has been active in the field since the beginning of 1975. Our main activity during the first years involved the $CdSe|S_x^{2-}$ system, although we were aware then of the possible importance of the $CuInS_2|S_x^{2-}$ system [1]. Our early work concentrated on the preparation of thin layers of CdS and optimization of the $CdSe|S_x^{2-}$ system as well as *in situ* storage systems. This work expanded to cover $Cd(Se, Te)$ photoelectrodes and emphasis was also placed on surface treatments of the semiconductor layer. Also, we began to place increasing emphasis on $CuInS_2$ and related materials as photoelectrodes. Most of the above work is covered up to and including 1982 in two review articles on metal chalcogenide/polychalcogenide photoelectrochemical cell systems [2] and on polycrystalline photoelec-

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trodes [3]. The purpose of the present paper is to report on more recent developments in this field from the WIS group, which are not covered in those reviews.

In our quest for stable efficient photoelectrochemical cells we have, over the last few years, concentrated on two complementary areas of research: (1) analysing, understanding and optimizing the (electro)chemistry of polysulphide solutions and (2) investigating the surface, solid state and (photo)electrochemical properties of CuIn chalcogenides. Both have resulted in photoelectrochemical cells of better than 10% efficiency with fair-to-high stability. These two areas of research will be covered in this paper. Other fields of activity in our group, mainly the preparation of thin layers of CuIn chalcogenides, *in situ* storage, semiconductor particle systems and metal/semiconductor contacts, will not be discussed, both for reasons of space and in order to present a coherent interrelated picture of part of our research.

2. CdX photoelectrodes: effect of solution composition

2.1. Introduction

It is known that the composition of the polysulphide electrolyte is very important in the determination of the performance of CdX|S_x²⁻ photoelectrochemical cells. The stability of these cells can vary considerably with relatively small changes in the electrolyte composition. The efficiency, while it is dependent on the composition to a lesser degree than is the stability, can still show considerable variation with change in composition. It is notable that a composition which gives increased stability also tends to give improved efficiency. This correlation between efficiency and stability is understandable since both are based on the (electro)chemical kinetics of the reaction between photogenerated holes and electrolyte species. Thus, we have presented evidence that the rate-determining step in the overall polysulphide oxidation is the dissolution of photogenerated sulphur in the electrolyte [4] and that the rate of this dissolution is a maximum at a sulphur-to-sulphide ratio of about 1.5 to 1. In addition, we found that the stability of the CdSe|S_x²⁻ system is greatest at a similar sulphur-to-sulphide ratio [5]. We also found the efficiency of CdX|S_x²⁻ photoelectrochemical cells to be greatest at the same sulphur-to-sulphide ratio, mainly as a result of an increase in the open-circuit voltage [6]. For all these reasons we have until recently most often used an electrolyte of approximate composition 2 M KOH[†], 1.6 M Na₂S and 2.8 M S.

Sulphide ions dissociate in water according to the following equilibrium:



The addition of OH⁻ to such a solution should then increase the concentra-

[†]The term molar (M) refers to the concentration of added species. Because of the complicated equilibria involved in polysulphide solutions this need not (and probably will not) be the same as the final concentration of that species.

tion of S^{2-} , which was often tacitly assumed to be the active species at the CdX surface. Recent results which indicate that the S^{2-} ion does not exist to any considerable extent in sulphide solutions, at least at pH values up to about 15 [7, 8], as well as the fact that no HS_x^- species have been reported in the more practically important polysulphide solutions lead us to believe that the addition of OH^- ions to the polysulphide electrolyte will not necessarily increase the concentration of active sulphide species at the CdX surface. In fact, as we shall show below, the addition of OH^- ions has a detrimental effect on the performance of $Cd(Se, Te)|S_x^{2-}$ photoelectrochemical cells. A major factor in choosing a polysulphide composition for CdX photoelectrodes has been recently shown by us to be the choice of alkali metal cation [9], and this will be discussed here. Also, the addition of a copper salt to the polysulphide electrolyte has a beneficial effect on the performance of the photoelectrochemical cell [10], mainly through an increase in the open-circuit voltage. This effect is greater for polycrystalline photoelectrodes than it is for single-crystal photoelectrodes.

These three factors, the cation effect, the OH^- concentration and the addition of copper salts (in generally decreasing order of importance), form the basis of our more recent results in the area of $CdX|S_x^{2-}$ photoelectrochemical cells and will be discussed in this first half of the paper, together with some results on the long-term stability of photoelectrochemical cells.

2.2. Cation effect

Both the efficiency and the stability of $CdX|S_x^{2-}$ photoelectrochemical cells have been shown to increase as the cation size increased from Li^+ to Cs^+ [9, 11]. These effects are shown in Figs. 1 and 2 for single-crystal CdSe. The effect on the stability is particularly striking. While these differences are less for thin film CdX (particularly the stability differences), they are still considerable and reproducible.

This large effect of increasing the cation size seems at first sight to be surprising, since the cation is not normally considered as an "active" species

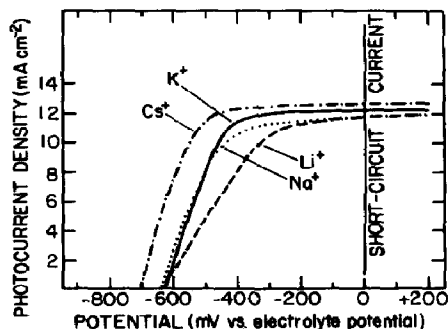


Fig. 1. Photovoltage-photocurrent density curves for a photoetched CdSe single crystal in an electrolyte of composition 1 M MOH, 1 M M_2S and 1 M S where $M \equiv Li^+, Na^+, K^+$ or Cs^+ , as designated on the figure. It should be noted that the rest potential of the polysulphide solution becomes more negative by about 35 mV in going from Li^+ to Cs^+ (most of this change occurs between Na^+ and K^+). The current density-voltage curves are drawn with respect to the rest potential for the respective electrolytes.

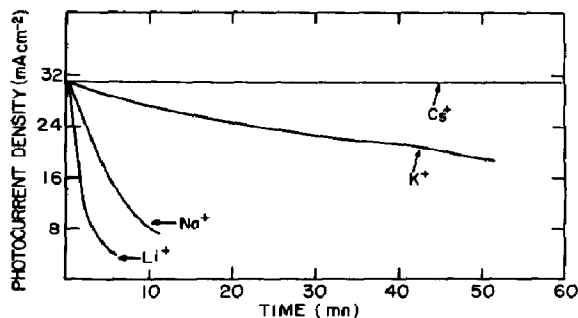
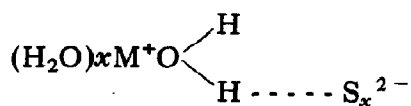


Fig. 2. Stability curves for chemically etched (not photoetched) single-crystal CdSe in an electrolyte of composition 1 M MOH, 1 M M₂S and 1 M S at an electrode potential of 0 V measured with respect to a standard calomel electrode (SCE).

in the polysulphide solution. However, Licht *et al.* [9, 11] have shown that the nature of the cation affects the activity of polysulphide species in these solutions. This effect is based on the decreasing hydration number of the cation as its size increases. Thus, the small Li⁺ ion, with a high charge density, is highly hydrated, while the large Cs⁺ ion, with a much lower charge density, is believed to have no water of hydration attached to it. If we take the hydration sheaths into account, then the large Cs⁺ ion is actually smaller than the "small" Li⁺ ($x\text{H}_2\text{O}$) ion. Licht *et al.* [11] consider that the major effect of this variation in hydration on the (photo)electrochemical properties of (photo)electrodes in polysulphide solutions is a result of increased ion pairing between the more highly hydrated cations and the active (poly)sulphide species. They invoke a model proposed by Robinson and Harned [12] to explain this increase in ion pairing. According to this model the anion (polysulphide) is linked to one of the waters of hydration by a type of hydrogen bonding, *i.e.*



The result of this cation-anion association is a decreased mobility of both ions (the cation mobility is decreased by the hydration sheath even in the absence of ion pairing) and, most important, decreased activity of the active (poly)sulphide species. Thus, by using the less-hydrated larger cations, we can reach activities which are much larger than the nominal concentrations. This results in better electrochemical kinetics of the (poly)sulphide oxidation and thus in improved efficiency and, more importantly, stability of the CdX|S_x²⁻ system. This improvement in electrochemical kinetics has also been shown to occur at metallic electrodes (Cu₂S) in polysulphide solutions [11, 13]. While it can be ascribed partly to increased conductivity of the solutions with larger cations as measured by Licht *et al.* [9, 11], much of the improvement can only be explained by better electrochemical kinetics.

One experimental result which is not directly explained by the ion pairing model is the large negative shift (about 100 mV) in the flat-band potential of CdX in Cs_2S_x solutions compared with polysulphide solutions of the other ions. This has been measured by the capacitance-potential (Mott-Schottky) technique [11], as well as manifesting itself as an increase in the open-circuit voltage in Cs_2S_x solutions. A negative shift of flat-band potential of this magnitude means either a considerable increase in the negative charge on the surface or a decrease in the positive charge. Licht [14] suggests that it is unlikely that the effect of the cation would change the surface concentration of negative (poly)sulphide species by the nearly two orders of magnitude required to give such a shift in flat-band potential. He reasons therefore that the effective surface-adsorbed positive charge, which is presumed to be considerable, is reduced by the replacement of small highly charged cations (possibly H^+ , which have been suggested to be potential-determining in the CdS|sulphide system [15]) by the larger Cs^+ ions, which reduces the effective surface positive charge by locating it further from the surface.

2.3. Hydroxide effect

Limiting the concentration of OH^- in polysulphide solutions has recently been shown to have a number of beneficial effects on photoelectrochemical cells using such solutions [16, 17]. One of these effects, which is easily measured, is a reduction in the absorption of light by the orange solutions. From a comparison of a solution of composition 2 M MOH, 2 M M_2S and 3 M S (where $\text{M} \equiv \text{Li}^+, \text{Na}^+, \text{K}^+ \text{ or } \text{Cs}^+$) (a "typical" polysulphide solution for photoelectrochemical cells), for example, with the same solution without added MOH, the increase in photocurrent density under air mass (AM) 1 illumination due to increased solution transparency will be about 0.7 mA cm^{-2} . Using a computer model to calculate the various species in polysulphide solutions [8], on the basis of experimentally measured characteristics of (poly)sulphide and hydroxide solutions the addition of OH^- to the polysulphide solution has been shown to increase the ratio of S_3^{2-} to S_4^{2-} and thus the visible light absorbance (the absorbance peaks of S_3^{2-} and S_4^{2-} have been measured at 417 nm and 367 nm respectively [18]).

Another advantage of not adding MOH to the electrolyte is that the ionic concentration of M^+ decreases, leading to a decrease in ion pairing and thus to an increase in activity of the polysulphide species with a resulting improvement in photoelectrochemical cell performance, as described previously.

The redox potential E_{redox} of polysulphide solutions becomes more negative with the addition of MOH. This does not seem to be balanced by a shift in the flat-band potential of the CdX and consequently results in a drop in the open-circuit voltage (*i.e.* the counterelectrode potential shifts towards the flat-band potential).

The additive results of all these factors on the photoelectrochemical cell performance are shown in Table 1 for an electroplated $\text{CdSe}_{0.65}\text{Te}_{0.35}$

TABLE 1

Variation in E_{redox} and photoelectrochemical cell output parameters for an electrolyte of composition 2 M K_2S and 3 M S with added KOH^a

[KOH] (M)	Redox potential (V (SCE))	Open-circuit voltage (V)	Short-circuit current density (mA cm ⁻²)	Fill factor	Efficiency (%)
0	-762	0.545	20.5	0.469	5.25
2	-787	0.505	19.8	0.480	4.80
6	-812	0.488	18.6	0.458	4.15
12	-850	0.463	17.8	0.409	3.30

SCE, standard calomel electrode.

^aPhotoelectrode, electroplated $\text{CdSe}_{0.65}\text{Te}_{0.35}$; illumination, W-I₂ lamp (output equivalent to about AM 1 for this semiconductor).

photoelectrode in 2 M K_2S and 3 M S with varying amounts of KOH. With the exception of a modest increase in the fill factor with an increase in [KOH] from 0 to 2 M, an increase in [KOH] leads to a decrease in all the output parameters with very significant efficiency losses.

2.4. Copper effect

For long-term stability tests of CdX|S_x^{2-} photoelectrochemical cells, we originally used either CoS- or Cu_2S -based counterelectrodes [19]. While the Cu_2S (actually sulphided brass) electrodes were physically unstable over long periods of time (of the order of weeks or months), the values of the open-circuit voltage obtained using Cu_2S counterelectrodes were consistently higher than those obtained with CoS counterelectrodes. We initially assumed that the CoS electrodes caused poisoning of the photoelectrodes; however, subsequent comparison with platinum counterelectrodes showed that the lower values of open-circuit voltage obtained using CoS electrodes were not caused by any detrimental action by the CoS, but rather by beneficial action by the Cu_2S electrodes.

In a recent study of this beneficial effect of copper sulphide on CdX|S_x^{2-} photoelectrochemical cells [10] we have shown that the main effect, an increase in the open-circuit voltage, occurs as a result of a reduction in the dark forward current I_f . Although there are several ways of treating the photoelectrode, the end result is the deposition of CuS, probably as islands, on the CdX surface. The fact that the surface copper species is covellite (CuS) rather than one of the Cu_{2-x}S phases has been shown by microprobe analyses and scanning electron microscopy [19] and this was in any case expected, since any Cu_{2-x}S at the surface would be oxidized by the photo-generated holes.

The reason for the reduction in I_f as a result of this treatment is at present unknown, but we have suggested that the CuS species may block some form of defect site at the CdX surface.

The fact that this effect is not merely transient is clear from long-term stability tests of thin film CdSe and Cd(Se, Te) photoelectrodes in S_x^{2-} solutions. The addition of one drop of 0.05 M $CuSO_4$ solution to about 10 - 20 ml of polysulphide (about 0.1 mg of copper to the polysulphide) results in immediate increases in the open-circuit voltage and final stabilized increases of between 25 and 70 mV, with corresponding increases in efficiency. These increases are stable over months of outdoor operation. When degradation does start to occur (see below), comparison with untreated photoelectrochemical cells shows that the copper treatment is not responsible for the degradation.

2.5. Combined solution effects

We now have enough information to choose a polysulphide electrolyte composition close to optimum. Table 2 shows the general effect of the various constituents and their ratios in the polysulphide solution on the photoelectrochemical cell characteristics. The increase in open-circuit voltage with increasing sulphur-to- M_2S ratio is connected with the rapid increase in E_{redox} as this ratio becomes greater than unity. Although the flat-band potential will also shift, it apparently does so less than E_{redox} does. An increase in $[M_2S]$ leads to an increase in both the efficiency (mainly through the short-circuit current) and the stability. However, we do note

TABLE 2

Dependence of photoelectrochemical cell parameters on polysulphide electrolyte composition

Variable	Effect (with reasons) of increase in the variable on the following		
	Short-circuit current	Open-circuit voltage	Stability
$[OH^-]$	Decrease (electrolyte less transparent; more ion pairing)	Decrease (negative shift in E_{redox})	?
Cation size	Increase (less ion pairing)	Increase for Cs (surface adsorption of Cs?)	Increase (less ion pairing)
S: M_2S ratio (for fixed $[M_2S]$)	Decrease (electrolyte less transparent) Increase ^a (better kinetics)	Increase (rapid positive shift in E_{redox})	Increase ^a (faster S dissolution)
$[M_2S]$ (for fixed S: M_2S ratio)	Maximum at 1 - 2 M M_2S : less M_2S , poorer kinetics; more M_2S , ion pairing	Little effect	Maximum at 1 - 2 M M_2S : less M_2S , poorer kinetics; more M_2S , ion pairing

^aUp to S: M_2S \approx 2:1. At higher ratios the stability decreases and the kinetics are poorer.

that in very concentrated K_2S_x solutions (more than about 3 M), both the efficiency and the stability drop [6].

We have recently combined these factors to demonstrate a single-crystal $CdSe_{0.65}Te_{0.35}|S_x^{2-}$ photoelectrochemical cell with a sunlight-to-electrical conversion efficiency of 12.7% in an electrolyte of composition 1.8 M Cs_2S , 3 M S and 0.5 mM $CuSO_4$. For comparison, the same photoelectrode gave 7.7% efficiency in an electrolyte of composition 1 M NaOH, 1 M Na_2S and 1 M S, a commonly used electrolyte in photoelectrochemical cells [17].

2.6. Long-term stability of $Cd(Se, Te)|S_x^{2-}$ photoelectrochemical cells

In this section we present some long-term stability results of slurry painted $Cd(Se, Te)$ photoelectrodes in polysulphide solution. Figure 3 shows the long-term behaviour of seven different photoelectrodes. All the photoelectrodes were of composition $CdSe_{0.75}Te_{0.25}$ (except the 3.5% cell which is $CdSe_{0.8}Te_{0.2}$), were photoetched and were on titanium substrates. The counterelectrodes were all CoS plated on steel. All the electrolytes were of composition 2 M KOH, 1.4 M Na_2S and 2.6 M S and some, as designated by "Cu", had $CuSO_4$ added as described previously. The performance is given in terms of photovoltage over (initially maximum power) load. In some cases the load was changed during the experiment, but usually it was left constant.

Several features can be commented on from this series of experiments.

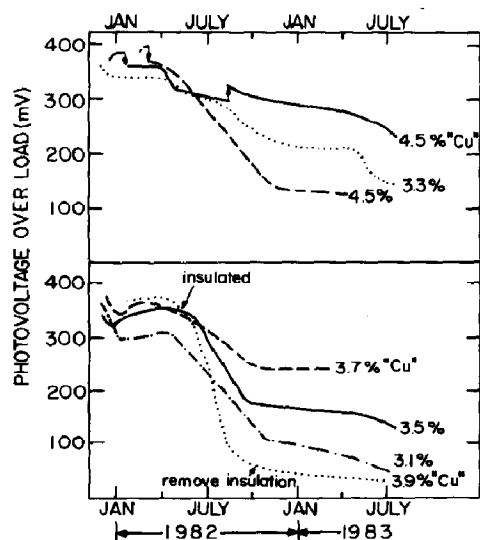


Fig. 3. Long-term stability curves of slurry painted $CdSe_{0.75}Te_{0.25}$ (the 3.5% cell is $CdSe_{0.8}Te_{0.2}$) in an electrolyte of composition 2 M KOH, 1.4 M Na_2S and 2.6 M S in some cases with added $CuSO_4$ (designated "Cu"). The loads are approximately for initial maximum power; arrows indicate a change in load resistance. Cell 1 was insulated and then had the insulation removed, as shown. The efficiencies represent approximate maximum efficiencies, calibrated against an Eppley pyranometer.

(a) There is considerable variation in stability from one cell to another for what are assumed to be very similar cells.

(b) In general, the cells tend to be stable over a period of some months (ignoring initial increases and decreases), after which they gradually degrade.

(c) In view of the observation that the degradation is greatest in summer and tails off in winter, and taking into account the fact that the winter sunlight in Israel is often similar to that in summer in terms of intensity (the sun is lower, but this tends to be balanced by less dust in the air), it appears that the stability is temperature dependent. While it might be expected that an increase in temperature would lead to an increase in stability (better (electro)chemical kinetics), it appears that the opposite is true. This is further supported by the behaviour of cell 1, which was insulated over part of the time (as shown in Fig. 3), reaching temperatures at least 10 °C higher than the other cells; this cell degraded very rapidly over this period.

(d) The cell with the $\text{CdSe}_{0.8}\text{Te}_{0.2}$ photoelectrode showed the highest initial stability (about 6 months). However, in view of the subsequent rapid degradation as well as the fact that this is only one experiment, we should be cautious in reading any meaning into this.

(e) The cells with CuSO_4 added ("Cu") were in no way less stable than the other cells (on the (reasonable) assumption that the instability of cell 1 was due to the higher temperature) and in fact may even be more stable, although again it would be premature to conclude this on the basis of two experiments.

(f) There does not appear to be any correlation between the initial efficiency and the stability. While it might be expected that more efficient cells would degrade faster because the photocurrent density is (presumably) higher, it might also be argued conversely that the surfaces of the more efficient electrodes improve the electrochemical kinetics, thereby improving the efficiency, or else contain fewer defects which could facilitate the photo-decomposition of the semiconductor.

With respect to the apparently negative effect of temperature on the stability, Licht [13, 20] has developed a computer model which calculates the thermodynamically expected spontaneous decomposition of S_x^{2-} to thiosulphate (which presumably is oxidized further to sulphate). From this model he has calculated the temperature dependence of the decomposition to be very strong. For example, a rise in temperature from 20 to 70 °C results in a calculated drop in the stability of the polysulphide solution of about three orders of magnitude. Whether such a decomposition does in fact occur has not yet been checked experimentally by us.

We finish this section by noting that the polysulphide electrolytes used in these long-term experiments are far less stabilizing than those which we now know to be available.

3. CuIn chalcogenide photoelectrochemical cells

3.1. Cu-In-X|polysulphide systems

We have investigated the above systems for n-type CuInS_2 [21], CuInSe_2 [22] and CuIn_5S_8 [23]. In this section, we shall for the main part confine the discussion of these systems to a comparison between them and the $\text{CdX}|\text{S}_x^{2-}$ systems.

The most striking difference between CuInX_2 ($X \equiv \text{S, Se}$) and CdX is in their surface chemistries. The surface of CuInX_2 used as photoelectrodes is essentially In_2O_3 [23, 24]; that of CdX in polysulphide solution is CdS [25]. CuIn_5S_8 is intermediate in so far as copper depletion does occur at the surface, and oxygen is invariably found. However, it is likely that the surface region is predominantly In_2S_3 with chemisorbed oxygen, and possibly some In_2O_3 , at the actual surface [23].

The most important operational difference between CuInX_2 and CdX or CuIn_5S_8 is in their stabilities as photoanodes. Both CuInS_2 and CuInSe_2 are completely stable under conditions where CdX (CdSe , CdS or $\text{Cd}(\text{Se, Te})$) and CuIn_5S_8 , which can themselves be relatively stable, degrade in output. Thermodynamic calculations on the photodecomposition reactions of CuInX_2 [26] and CdX [2] suggest that the former may be more stable in polysulphide solutions because the stability of the " In_2O_3 " layer on CuInX_2 in polysulphide solution is responsible for the apparent stability of the underlying CuInX_2 . Indium tin oxide layers, which are about 92% In_2O_3 , have been used as electrodes in polysulphide solution without any sign of instability [27], supporting such a conclusion. The apparent absence of a coherent In_2O_3 layer on CuIn_5S_8 would then explain why this semiconductor behaves like CdX , rather than like CuInX_2 regarding its stability.

Another difference between the $\text{CuInX}_2|\text{S}_x^{2-}$ and the $\text{CdX}|\text{S}_x^{2-}$ or $\text{CuIn}_5\text{S}_8|\text{S}_x^{2-}$ systems is the pronounced positive temperature dependence of the $\text{CuInX}_2|\text{S}_x^{2-}$ system [21, 22], a behaviour which does not occur in the $\text{CdX}|\text{S}_x^{2-}$ or $\text{CuIn}_5\text{S}_8|\text{S}_x^{2-}$ systems (unless the electrolyte is "poor" in so much as it leads to kinetic limitations which are reduced on heating). While we offer no explanation for this positive temperature dependence other than the very general possibility that the electrochemical kinetics are slow at the In_2O_3 -covered semiconductors, and thus can be improved appreciably by heating, it is not unreasonable to expect that the actual reason is connected with this oxide surface.

One of the manifestations of such slow kinetics may be in the low values of the fill factor obtained with the $\text{CuInX}_2|\text{S}_x^{2-}$ systems. However, contrary to the previous arguments is the observation that the $\text{CuIn}_5\text{S}_8|\text{S}_x^{2-}$ system also shows low values of fill factor.

Some information on the surface oxide on chalcogenide semiconductors should be obtained from a study of the dependence of the flat-band potential on the pH and $[\text{S}_x^{2-}]$ of an electrolyte. Some preliminary results of such a study using the Mott-Schottky technique on CdS ,

TABLE 3

Values of flat-band potential for different semiconductors in polysulphide-free aqueous solutions of various pH and in polysulphide solutions containing equimolar concentrations of added Na_2S and S

Semiconductor	Flat-band potential (V(SCE))						
	Polysulphide-free solution				Polysulphide solution		
	pH 3.5	pH 5.5	pH 12.0	pH 14.0	$10^{-2} M$	$10^{-1} M$	1 M
CdS (single crystal)	-0.59		-0.62				
CuInSe ₂ (single crystal, n-type)	-0.43	-0.53	-0.65	-0.75	-0.78 (\approx pH 12)	-0.88 (\approx pH 13)	-0.96 (\approx pH 14)
In ₂ S ₃ (large-grained boule)	-0.73	-0.89	-0.94	-1.27			

SCE, standard calomel electrode.

CuInSe₂ and In₂S₃ (In₂S₃ shows a surface free of oxygen [23]) are given in Table 3.

As is generally accepted, CdS shows essentially no change in flat-band potential with pH over the range measured. Both CuInSe₂ and In₂S₃ show a distinct variation in flat-band potential with pH, which is irregular in that most of the change occurs at the low and high pH ranges, and the change over the intermediate pH range is relatively small. If an In₂O₃ surface layer determined the flat-band potential, then a regular shift of 59 mV pH⁻¹ would be expected. The average change for In₂S₃ is not much lower than this, while that for CuInSe₂ is about half (as would be expected for a divalent potential-determining ion). However, if anything, we would expect the situation to be reversed since CuInSe₂ has an oxide surface, while In₂S₃ presumably does not (we have not yet analysed the surface of In₂S₃ after operation in S_x^{2-}). To complicate any interpretation of these results the CuInSe₂ flat-band potential is very dependent on the presence of S_x^{2-} (something we might not expect from an oxide) while the In₂S₃ flat-band potential seemed to be almost independent of S_x^{2-} (we do not show these latter results, since the Mott-Schottky plots were not linear in this case, and thus estimation of the flat-band potential was difficult).

We emphasize that, although the role of the surface oxide is very important in the functioning of CuInX₂, enough inconsistencies occur to show that some fundamental questions remain to be answered about this role.

3.2. The CuInSe₂|polyiodide system

The poor fill factor obtained with the CuInX₂| S_x^{2-} system is generally ascribed to poor electrochemical kinetics of the polysulphide solution at

the CuInX_2 surface, although it should be kept in mind that chemisorption of (poly)sulphide species at the surface may cause surface modification leading to a poor fill factor (the shift in flat-band potential of CuInSe_2 with S_x^{2-} discussed previously indicates that chemisorption does occur at the surface). Polyiodide solutions give a much improved fill factor with n- CuInSe_2 [28, 29], which may be ascribed to the better electrochemical kinetics of the I_3^- solution (or, in parallel with the above, to lack of detrimental chemisorption of I_3^- species at the surface).

While n- CuInSe_2 shows good conversion efficiency, both Cahen and Chen [28] and Menezes *et al.* [29] found that it was unstable in I_3^- , but that the addition of Cu^+ ions to the electrolyte led to a considerable increase in stability. The rationale of Cahen and Chen for adding copper ions to the solution was based on the high mobility of Cu^+ ions in CuInSe_2 and on the experiments of Chen *et al.* [30] which show that Cu^+ is one of the photoanodic decomposition products of CuInSe_2 . Figure 4 shows the beneficial effect of adding Cu^+ ions (and In^{3+} ions, although these have a small effect compared with that of Cu^+ ions) to the iodide solution on the stability of n- CuInSe_2 . Cahen and Chen [28] found a further improvement in stability on air oxidizing a thin ($0.3 \mu\text{m}$) electrodeposited indium layer on the CuInSe_2 crystal (which was itself previously surface oxidized), as shown in Fig. 4(c). At a short-circuit current density of 50 mA cm^{-2} such a cell showed complete stability after 20 kC of photocharge had been passed. Although the role of extra indium oxide is not clear, Cahen and Chen [28] suggested that it might result from the passivation of defect sites which act as initiators for decomposition. This extra oxide layer does not reduce the solar-to-electrical conversion efficiency of the cell, which has been reported to reach 11.7%. The high efficiency is largely a result of the air oxidation of the CuInSe_2 crystal, which as Cahen and Chen have shown leads to

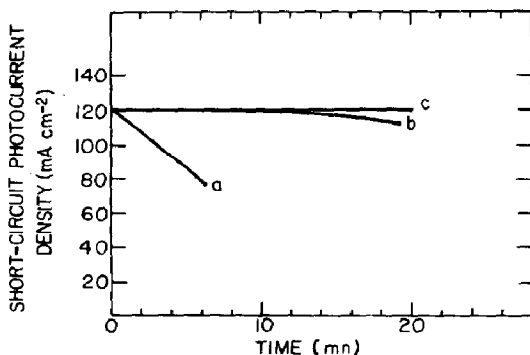


Fig. 4. Stability characteristics of an n- CuInSe_2 single crystal: curve a, in 6 M KI with 20-mM I_2 at pH 7; curve b, as curve a but with 50 mM each of CuI and InCl_3 added to the solution; curve c, as curve b, but CuInSe_2 coated with oxidized indium film. The very accelerated conditions (high SCC) of the experiments should be noted.

formation of an indium oxide (probably In_2O_3) surface highly depleted of copper and selenium. The well-known passivating effect of a native In_2O_3 layer in InP can probably be extended to explain its effect on CuInSe_2 .

In contrast with the $\text{CuInX}_2|\text{S}_x^{2-}$ system, the output of the $\text{CuInSe}_2|\text{I}_3^-$ system has a negative temperature dependence. This shows that the unusual positive dependence of the S_x^{2-} system is not due to the semiconductor itself but is presumably due either to the improvement of sluggish (electro)chemical kinetics or to the aforementioned possibility of detrimental chemisorption of (poly)sulphide species on the surface. It is not so obvious, however, why temperature should have such a large effect in this latter case, since both the strength of chemisorption and the behaviour of surface states formed on the surface as a result of this chemisorption are not expected *a priori* to be so strongly temperature dependent.

Finally, it is worth noting that on indium tin oxide layers the electrochemical kinetics of the S_x^{2-} and I_3^- couples show similar behaviour [27]. Although it is possible that such layers behave differently from In_2O_3 as electrodes, this does raise the question whether the fact that the photocharacteristics of CuInSe_2 are better in I_3^- than in S_x^{2-} is just a result of improved (electro)chemical kinetics. A comparative study of CuInSe_2 (In_xO surface) and In_2O_3 (possibly copper doped) (photo)electrodes in these two electrolytes is important to help to fill in the many gaps in our knowledge of the CuInX_2 -native-oxide-coated photoelectrodes.

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