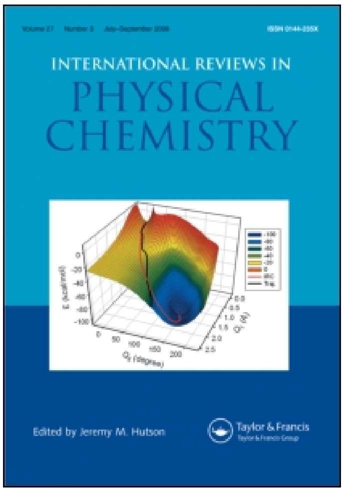

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On the built-in potential in the photoelectrochemical cell n-CdTe|selenide in aq. KOH

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On the built-in potential in the photoelectrochemical cell n-CdTe|selenide in aq. KOH

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In photoelectrochemical cells which convert radiant energy to electrical energy the size of the built-in potential U_b is a key quantity. U_b and the flat-band potential, E_{fb}, change with a variation in the redox potential of the electrolyte. Such changes as have been reported in the literature are reviewed. In addition for the cell n-CdTe|selenide solution the changes in U_b and E_{fb} with redox potential are reported. As E_{redox} went more negative, U_b increased to a maximum and then decreased. The changes are attributed to changing adsorption of selenide species.

1. Introduction

Photoelectrochemical cells to convert radiant into electrical energy have been studied much in recent years because the junction region, in which charge carriers are formed by light, is made simply by immersing a semiconductor crystal in a solution containing a redox couple. General treatments of this subject are found, for example, in Morrison (1980), Wallace *et al.* (1982), Nozik (1981), Haneman (1979), Heller (1977), Cardon *et al.* (1981), Gerischer (1970) and Geiger *et al.* (1982).

The efficiency of converting solar radiation into electrical power has approached or exceeded 10% in several photoelectrochemical cells (Chang *et al.* 1977, Heller 1981, Bachmann *et al.* 1983). With an n-type semiconductor, photogenerated holes are swept, by the electric field built in to the semiconductor in the cell, to the semiconductor surface and these oxidize a component of the redox couple. Under steady conditions, however, the reverse reaction occurs at the other, inert, electrode and so there is no nett change in the composition of the electrolyte.

Current–voltage curves are illustrated in figure 1 (*a*). Important parameters are U_{oc}, the open-circuit voltage; I_{sc}, the short-circuit current; F, the fill factor; and η, the energy conversion efficiency. The electrical power obtained from a cell is given by

$$P_{out} = U_{oc} I_{sc} F = U_M I_M$$

and η equals P_{out}/P_{in}, where P_{in} is the radiant power incident on the cell. U_M and I_M are the voltage and current at M, the maximum power point (figure 1 (*a*)).

Theoretical estimates of attainable solar energy conversion efficiency show that CdTe and GaAs, each with an energy band gap of *c.* 1·5 eV, give the highest results, *c.* 25% (Gerischer 1977), but such values are much higher than any yet measured in photoelectrochemical cells.

Figure 1 (*b*) shows an energy-level diagram for a photoelectrochemical cell n-CdTe|selenide both in the dark and when irradiated and passing a current through a load resistor.

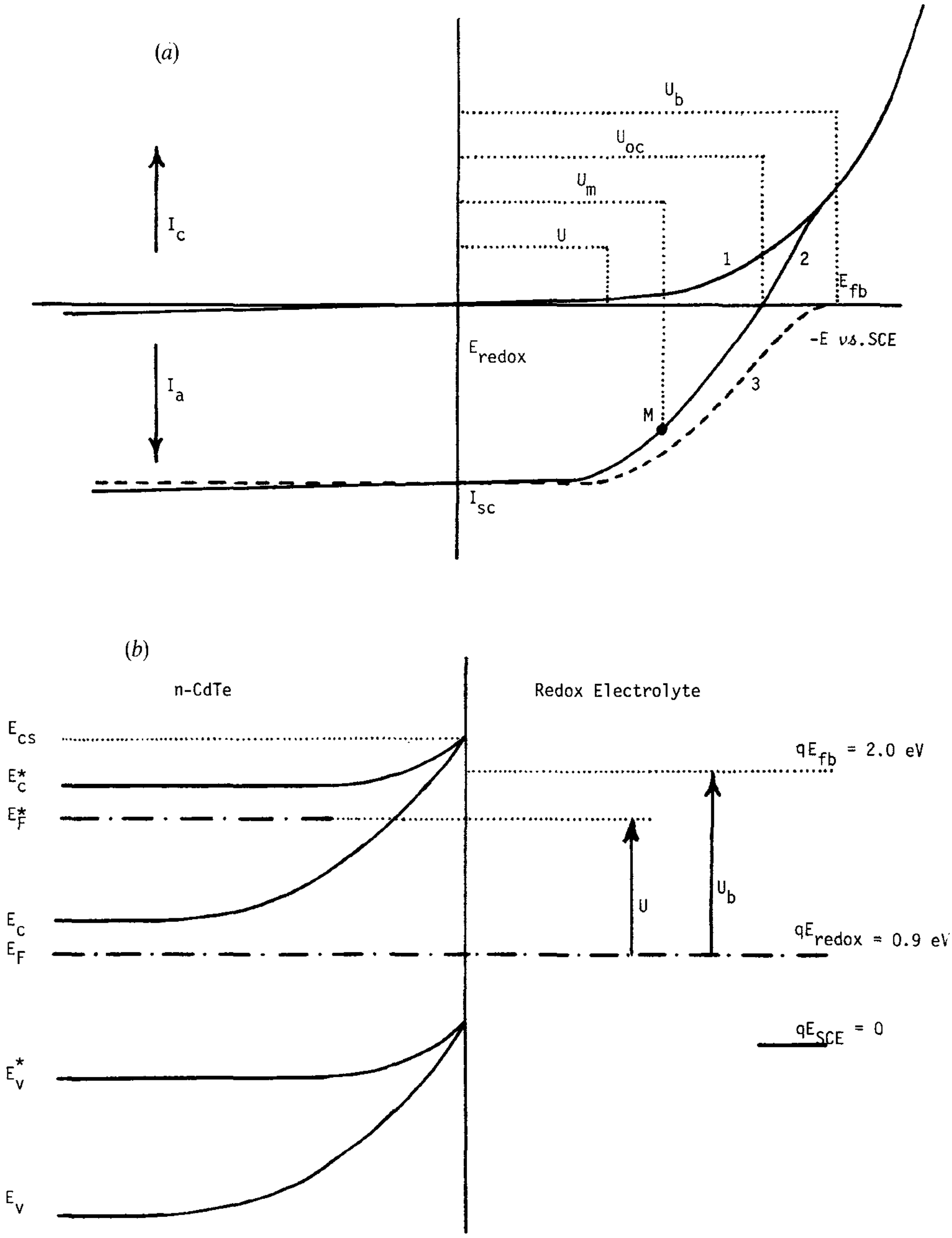

Figure 1. (a) Current–voltage curves for a photoelectrochemical cell, 1, in the dark; 2, with steady light; 3 with chopped light. $I_{c(a)}$, cathodic (anodic) current; E, potential of semiconductor electrode; U, voltage (variable); U_M, voltage at maximum power point M; U_{oc}, open-circuit voltage in steady light; U_b, built-in potential; $U_b = E_{redox} - E_{fb}$; E_{fb}, flat-band potential of semiconductor; E_{redox}, potential of redox couple. (b) Energy level diagram for the cell n-CdTe|selenide, $E_{redox} = -0{\cdot}9$ V versus SCE; $q = -1{\cdot}6 \times 10^{-19}$ C; $E_{c(v)}$, energy of edge of conduction (valence) band in the dark; E_F, Fermi level of semiconductor. Asterisk denotes value in the presence of light. E_{cs}, energy E_c at the surface of the semiconductor.

2. Flat-band potentials, E_{fb}, built-in potentials, U_{b}, and photovoltages as a function of E_{redox}

2.1. *Introduction*

The flat-band potential is the potential of the semiconductor when there is no band-bending. The value of E_{fb} is important for energy conversion studies because (see figure 1 (*a*)) an upper limit for the open-circuit voltage is given by $E_{\mathrm{redox}} - E_{\mathrm{fb}}$.

E_{fb} can be determined from differential capacity measurements as a function of voltage. In the reverse bias region $1/C^2$ is linear with voltage and extrapolation of this (Mott–Schottky) plot to $1/C^2 = 0$ yields the flat-band potential. If the capacity varies with frequency, the complications must be adequately explained and the values of the space-charge capacitance extracted. Various theories have been advanced to explain frequency dispersion of capacity which has often been observed in various cells e.g. Morrison (1980), Madou *et al.* (1977) and Wallace *et al.* (1982).

Flat-band potentials can be determined also by electro-reflectance techniques (e.g. Pollak 1982) or by plotting the square of the photocurrent against reverse bias voltage (Mirovsky *et al.* 1982). Only a lower limit for E_{fb} is given by the potential of onset of the photocurrent at high light intensity.

Values of flat-band potentials of some semiconductors have been listed, e.g. by Morrison (1980).

2.2. *Adsorption and* E_{fb}

E_{fb} is not an invariable property of the semiconductor, being affected by the amount of the charge on the surface of the semiconductor in a given electrolyte, which in turn depends on the presence or absence of surface states or adsorbed charges. For example, anion adsorption shifts the entire band system of the semiconductor, so that E_{fb} becomes more negative, and U_{oc} is increased.

Minoura *et al.* (1977) indeed reported that for CdS, when S^{2-} ions were adsorbed on the Cd surface of the (0001) face, E_{fb} became more negative as the bulk concentration of S^{2-} increased, so that $E_{\mathrm{fb}} = \text{constant} - 0{\cdot}059 \log [S^{2-}]$. (Ginley and Butler (1978), referring to this equation, said that (i) the value 0·059 of the coefficient of $\log [S^{2-}]$ was inconsistent with adsorption of a doubly charged ion, (ii) that E_{fb} varied also with $\log [H^+]$, and (iii) HS^- was the potential determining ion which was adsorbed. Conclusion (iii) is quite consistent, we note, with Minoura's equation, given an equilibrium $H^+ + S^{2-} \rightleftarrows HS^-$.)

Similar logarithmic relationships have been found in other cases involving cadmium chalcogenides, e.g. Cd^{2+} on CdS, (0001)S face (Minoura *et al.* 1977), or those semiconductors and metal oxides quoted by Morrison (1980).

2.3. *Surface states, Fermi-level pinning and* E_{fb}

In addition to adsorbed charge, it is necessary to consider the effects of those surface states which result in changes in the applied voltage appearing largely as alterations in the potential drop across the Helmholtz layer rather than across the space-charge layer—similarly to what happens at a contact between a metal and an electrolyte. In this case, the Fermi level of the semiconductor is 'pinned' at a certain value relative to the edge of the conduction or valence band so that changes in E_{redox} of the electrolyte do not alter the observed photovoltage (Bard *et al.* 1980). Fermi level pinning is analogous to a well known effect in semiconductor–metal junctions (e.g. Bardeen 1947, Mead 1966). It was discussed theoretically for semiconductor–electrolyte junctions by Green

(1959). Plots of E_{fb} or of U_b versus E_{redox} show whether or not Fermi-level pinning occurs: if there is no pinning—the 'ideal' behaviour—then E_{fb} is constant, as E_{redox} varies over a range within the band gap of the semiconductor. Consequently the plot versus E_{redox} of the built-in potential U_b (defined by $U_b = E_{redox} - E_{fb}$) shows $U_b \propto E_{redox}$, for an n-type semiconductor. In the presence of Fermi-level pinning, as E_{redox} varies, the opposite results obtain: $E_{fb} \propto E_{redox}$, U_b=constant, and also (possibly) the photovoltage is constant.

Sometimes cases are observed which are intermediate between no pinning and pinning. These are referred to as cases of partial pinning. Analogous results are found with metal–semiconductor junctions.

When E_{redox} lies outside the band-gap of the semiconductor, no photovoltage is obtained for a clean n-type semiconductor where E_{redox} is above (at more negative potential than) the edge of the conduction band (e.g. for n-CdS and n-CdSe (Aruchamy and Wrighton 1980); for n-WS_2 (Baglio *et al.* 1982)). Photovoltages can occur at very negative E_{redox} values, however, where there is a layer on the semiconductor surface chemically different from the bulk (e.g. the oxidized layer on n-CdTe studied by Aruchamy and Wrighton (1980) and by Tanaka *et al.* (1981)).

When E_{redox} lies below the edge of the valence band of a p-type semiconductor, similarly to the results mentioned in the previous paragraph, no photovoltage is obtained, e.g. p-WSe_2 (Baglio *et al.* 1983).

When E_{redox} lies below the edge of the valence band of an n-type semiconductor, or above the edge of the conduction band of a p-type semiconductor, photovoltages are obtained which are constant as E_{redox} varies, e.g. p-GaAs (Di Quarto and Bard 1981); p-WS_2 (Nagasubramanian and Bard 1981); p-InP (Dominey *et al.* 1981). The results have been attributed to Fermi-level pinning or to inversion.

In the following, the variation of E_{redox} is considered only in the band gap region, i.e. E_{redox} lies between the edges of the valence and conduction bands. In this band-gap region, pinning has been observed in cells containing CdTe (e.g. by Aruchamy and Wrighton 1980; Rakhshani and Lyons 1982, White *et al.* 1983). It occurred also in cells with GaAs, Si and TiO_2 (Malpas *et al.* 1981); with InP (Dominey *et al.* 1981) and with Si (Brondeel *et al.* 1982, Nagasubramanian *et al.* 1982). Fermi-level pinning has been observed with electrolytes dissolved in water, acetonitrile, tetrahydrofuran, methanol or liquid ammonia.

The chemical nature of the semiconductor surface sometimes determines whether Fermi-level pinning occurs, and the surface in turn can differ with the nature of the etchant which has been used to prepare it. With n-CdTe, pinning occurs after an oxidizing etch but not after a reducing etch of $Na_2S_2O_4$ in alkali (Tanaka *et al.* 1980, White *et al.* 1983). The oxidizing etch left a surface rich in Te and TeO_2, both of which were removed by $Na_2S_2O_4$. n-CdSe did not behave, however, in the same way as n-CdTe (Aruchamy *et al.* 1983). With p-InP, Heller *et al.* (1981) found that oxidizing the surface removed Fermi-level pinning (in a cell which showed the high solar energy conversion efficiency of 11·5%). With TiO_2, if the surface was specially prepared and if also the electrolyte concentration was sufficiently high, no Fermi-level pinning occurred and the photovoltage followed E_{redox} (Cooper *et al.* 1982).

Fermi-level pinning then is by no means an invariable occurrence. Its non-occurrence was evidenced in the linear dependence of photovoltage on E_{redox} (together with a similar variation of U_b with E_{redox}) observed for n-CdS in an aqueous electrolyte containing $Fe^{2+,3+}$, $Fe(CN)_6^{3-,4-}$, $IrCl_6^{2-,3-}$ or a quinone couple by Gobrecht and Gerischer (1979), who, whilst they reported ideal behaviour, noted that in a particular case, the observed behaviour depends on the nature of the surface pre-treatment. Indeed, a change in the surface during cell operation can replace ideal behaviour with Fermi-level pinning, as was observed with n-Si in acetonitrile electrolyte (Chazalviel and Truong 1981). Ideal behaviour in p-Si|$V^{3+,2+}$, HCl was observed over a 0·5 V range of E_{redox} (Heller *et al.* 1980) and in p-WSe_2, n-WSe_2 and n-$MoSe_2$ (Nagasubramanian *et al.* 1983).

Di Quarto and Bard (1981) found for n- and p-GaAs that the photovoltage was linear with E_{redox} for redox couples within the band gap. Similarly, Nagasubramanian and Bard (1981) and Baglio *et al.* (1982) with n-WS_2 in either aqueous or non-aqueous electrolytes found ideal behaviour when E_{redox} was between $-0{\cdot}2$ and $+0{\cdot}8$ V versus SCE.

In ideal behaviour, not only does the photovoltage, or (better) U_b, follow E_{redox}, but also E_{fb} is constant as E_{redox} changes. Direct measurements of E_{fb} are much less frequent than measurements of photovoltages, as a function of E_{redox}, but some have been made. In particular, Nagasubramanian *et al.* (1983) studied E_{fb} versus E_{redox} for TiO_2, n-CdS, p-Si, p-GaAs and p-InP. Their results for n-CdS showed that E_{fb} varied with E_{redox}, but never more than linearly, for $E_{\text{redox}} > 0{\cdot}3$ V versus SCE, a result which is in partial disagreement with the results of Gobrecht and Gerischer (1979) already cited. (The differences might arise from experimental error; otherwise, differently treated crystals may be involved.) For CdS, and for the similarly behaving TiO_2, Nagasubramanian *et al.* concluded ideal behaviour occurred if E_{redox} was above the mid-point of the energy band gap of the semiconductor, and attributed the non-ideal behaviour for E_{redox} below the mid-point to surface states filled from the reduced form of the redox couple. For p-GaAs, p-Si and n-InP, E_{fb} became less negative as E_{redox} was made more positive, but the variation in all cases was less than linear. For n-WSe_2, n-$MoSe_2$ and p-WSe_2, E_{fb} was independent of E_{redox} outside the band-gap region.

With n-CdSe, Aruchamy *et al.* (1983) found the behaviour was roughly ideal, whereas with intrinsic α-Si : H, Harrison *et al.* (1983) found evidence of a surface state density of $10^{13}\,\text{cm}^{-2}\,(\text{eV})^{-1}$.

The literature therefore reveals variety in the plots of E_{fb} versus E_{redox}, and there is at present no way of predicting in a given case which type of plot will be observed. For the cell discussed in Section 3 the matter was examined experimentally.

3. The photoelectrochemical cell In|n-CdTe| selenide in aq. KOH|Pt

3.1. *Introduction*

The cell was of interest for several reasons:

(i) CdTe has a band gap close to that for the most efficient conversion of solar energy and in fact the cell had been shown to be a relatively efficient energy converter (Heller *et al.* 1978).
(ii) The cell is stable for long periods of operation (Wrighton *et al.* 1977).
(iii) CdTe thin films can be prepared by the simple process of electrodeposition (Danaher and Lyons 1978, Panicker *et al.* 1978) thus encouraging the hope that a future thin-film device could be both efficient and stable.

It therefore was considered desirable to study the cell more closely than had been done previously. In particular, it was desired to know the variation of the built-in potential (and also of the flat-band potential) with E_{redox}. Was the Fermi level pinned or not?

One question immediately presented itself, which arose out of our estimates of the positions in CdTe crystals of E_c and E_v which were based on the known properties of the solid. Such an estimate led to the conclusion that E_{fb} for CdTe should be $-0{\cdot}68$ V versus SCE, so that the photovoltages observed were not explicable without the additional assumption, that in the photoelectrochemical cell, adsorption raised the entire band system and made E_{fb} more negative. Such an assumption is supported by studies of adsorption of $HS^-(S^{2-})$ on CdS, e.g. by Minoura *et al.* (1977).

Adsorption being accepted, it still remained a question as to whether or not the Fermi level is pinned in this system, or, more generally, as to what is the dependence of U_b and of E_{fb} on redox potential.

In order to avoid complicating matters further by changing the nature of the redox couple, E_{redox} was changed by altering the concentrations by oxidizing or reducing the selenide electrochemically *in situ*. In this way, E_{redox} was varied over a range of 350 mV. Such a range however was not very great in view of the errors in determining E_{fb} by means of Mott–Schottky plots. Errors of ±100 mV are commonly reported in the literature.

Accuracy in determining Mott–Schottky plots was therefore essential. Furthermore, it became necessary to elucidate the nature of the concentrations of the various selenide species present in aqueous KOH (1 mol dm^{-3}) at various E_{redox} values, because information in the literature was lacking. These problems were overcome and the results are summarized below.

3.2. *The selenide solutions*

Selenide solutions were made in aqueous KOH (1 mol dm^{-3}) by electroreducing solid Se at a Pt electrode. A fully reduced solution was colourless, but became coloured upon adding selenium. A saturated solution by solubility measurements averaged 3·8 atoms of Se for each selenide ion initially present. By adding Se to a reduced solution ($8{\cdot}0 \times 10^{-3}$ mol dm^{-3}), the redox potential was changed from $-1{\cdot}00$ V to $-0{\cdot}66$ V versus SCE. The titration curve could be fitted by a model in which there were four oxidation levels S_1, S_2, S_3 and S_4 of Se present, all in equilibrium. Activity coefficients in the concentrated KOH were assumed independent of concentration. Absorption spectra showed that S_1 was present, partly as the protonated form HSe^-. $S_{2,3,4}$ can be thought of as derived from S_1 by adding successive Se atoms.

There was no unpaired spin detected by electron spin resonance. Nuclear magnetic resonance for ^{77}Se showed only a broad band, indicating exchange broadening, and so the technique was not able to identify the various species present. Optical absorption spectra were taken of solutions of different redox levels. Computer analysis showed that four oxidation states were needed to explain the results (Lyons and Young 1986).

Assuming Nernst equations for the various equilibria, e.g. for the equilibrium between S_1 and S_2, characterized by $E^o_{1,2}$,

$$E_{redox} = E^o_{1,2} - (RT/F)\ln [S_1]/[S_2]^{1/2}$$

it was possible to deduce not only the titration curve mentioned above but also the values (versus SCE)

$$E^o_{1,2} = -935\,\mathrm{mV}$$

$$E^o_{2,3} = -919\,\mathrm{mV}; \quad E^o_{1,3} = -931\,\mathrm{mV}$$

$$E^o_{3,4} = -778\,\mathrm{mV}; \quad E^o_{1,4} = -914\,\mathrm{mV}$$

It followed that for a given concentration of total Se, the concentrations $[S_i]$ for $i=1,2,3,4$ were known at all values of E_{redox}. The results enabled also an accurate interpretation of the various absorption spectra and the extraction from them of the spectra characteristic of S_1, S_2, S_3 and S_4. Only the spectrum of S_1 was observable directly. Figure 2 shows the composition of solutions with different values of E_{redox}. It is clear that as E_{redox} changed over the range of interest the composition of the electrolyte changed markedly and so changes in adsorption might well be expected.

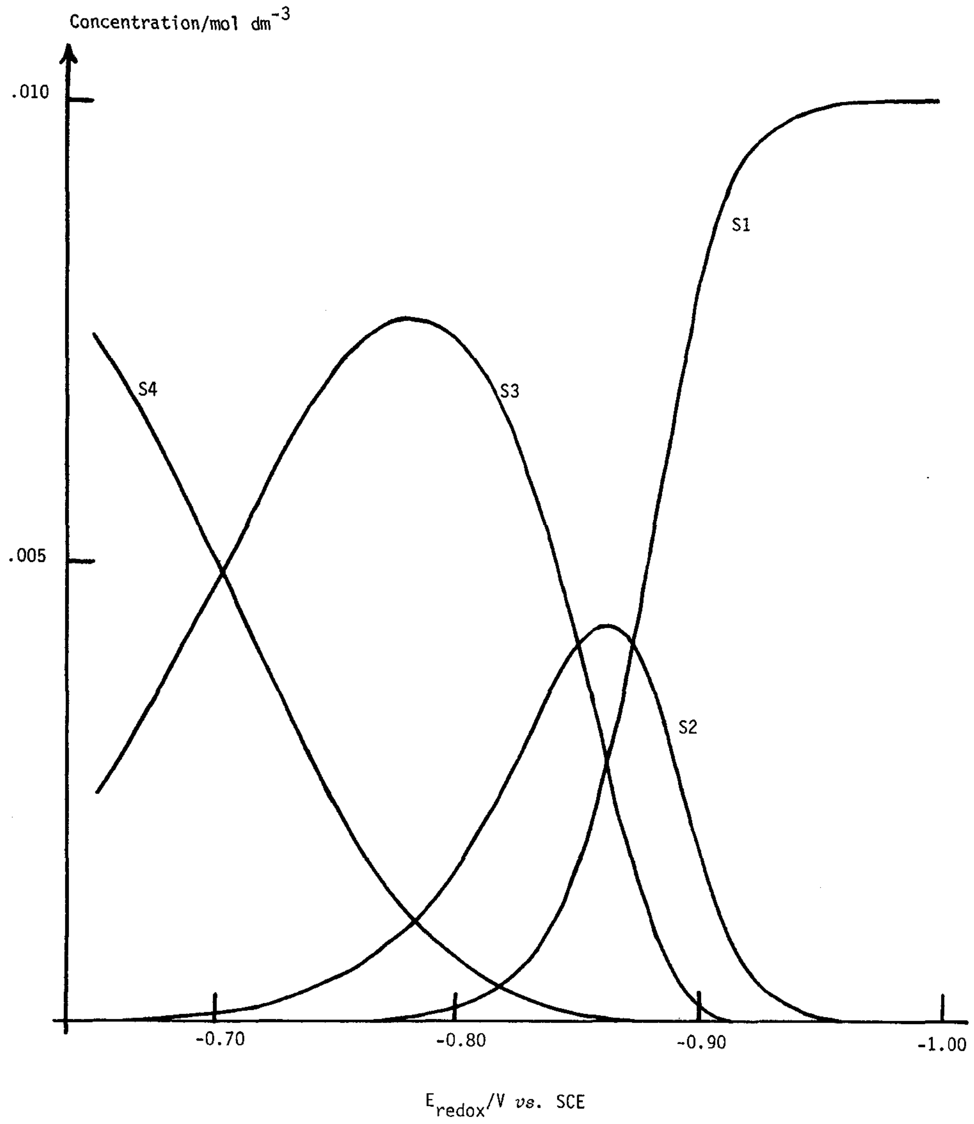

Figure 2. Composition of selenide solution versus E_{redox}. S_i ($i=1,2,3,4$) represent the four oxidation states of selenide ions. $[Se_{total}]=0{\cdot}010\,mol\,dm^{-3}$.

3.3. *The flat-band potential*, E_{fb}

Before immersion in the selenide solution, a crystal was polished with 0·05 μm alumina, etched at 25°C for about 30 seconds with 5% bromine in methanol, and rinsed with methanol and then water.

In the first experiments in which the edges of the CdTe crystal were not sealed with epoxy resin or with Torrseal before immersion in the electrolyte, there was considerable frequency dispersion of the observed capacitance and a consequent variation in E_{fb} as obtained by extrapolation. It proved possible, however, to remove the frequency dispersion by repeated sealing. Mott–Schottky plots were then good straight lines and in any one plot the error in E_{fb} was estimated as 10 mV.

The (111) face of CdTe is not a cleavage plane but can be either Cd rich or Te rich. For a given electrolyte, E_{fb} was 0·2 V more negative for the Cd-rich face than for the other. Figure 3 shows E_{fb} versus E_{redox} for various crystal faces. For E_{redox} more negative than $-0{\cdot}88$ V versus SCE, E_{fb} was constant (± 25 mV) and so Fermi-level pinning was absent. In these experiments the selenide solution, initially fully reduced, was partly oxidized *in situ*, and, consequently, other selenide species were present in addition to S_1. To obtain the results shown in figure 3, the system was allowed to equilibrate for an hour or longer after each change of the redox potential, although the bottom curve was taken more quickly. In further experiments, when S_1 was the only selenide species present, E_{fb} was constant at its most negative value when $[S_1]$ was changed by dilution from 10^{-1} to 10^{-4} mol dm^{-3}, indicating that even at $[S_1]=10^{-4}$ mol dm^{-3} there was maximum adsorption of negative species on the CdTe surface.

3.4. *The built-in potential* U_b

The variation in flat-band potential with E_{redox} corresponds with a variation observed in the built-in potential U_b with E_{redox}, which is shown in figure 4. The top curves of figure 4 were taken in anodic scan on the (110) face of the crystal. Long times were needed to reach equilibrium. The four curves shown in figure 4 illustrate the effect of variations in the crystal surface, even the two curves on the (110) face showing differences of up to 100 mV. Two trends, however, were general: U_b rose as E_{redox} changed from $-1{\cdot}0$ to $-0{\cdot}85$ V, and U_b decreased as E_{redox} became less negative than $-0{\cdot}85$ V. In the range $-0{\cdot}86 > E_{redox} > -1{\cdot}0$ V, in a separate experiment, the redox potential was cycled by electrolytically oxidizing and reducing the solution, and the slope of U_b versus E_{redox} in both halves of the cycle was $0{\cdot}8 \pm 0{\cdot}1$. This was taken as confirmation of the absence of Fermi-level pinning in this range of E_{redox}.

The drop in U_b as E_{redox} was made less negative than $-0{\cdot}86$ V, was unusual. If the Fermi level were pinned, U_b would be constant as E_{redox} changed. Furthermore, the change in E_{redox} to less negative values (on the ideal model) would tend to make U_b larger. The drop in U_b clearly was associated with the drop in E_{fb} to less negative values (figure 3). We attribute the deviation from ideality of both U_b and E_{fb} to a decrease in the adsorbed charge as E_{redox} became more negative.

Although there is evidence in the literature (Nagasubramanian *et al.* 1983; see Section 2) that in some cases E_{fb} became somewhat less negative as E_{redox} went to less negative values, the extent of the change in E_{fb} was not great enough to produce a drop in U_b with less negative E_{redox}. We therefore do not introduce the concept of surface states filled from the reduced form of the redox couple in an attempt to explain our results. Instead, the idea of decreased adsorption is adopted. Furthermore, as E_{redox} became more positive, U_b fell off more rapidly than was expected simply from a change

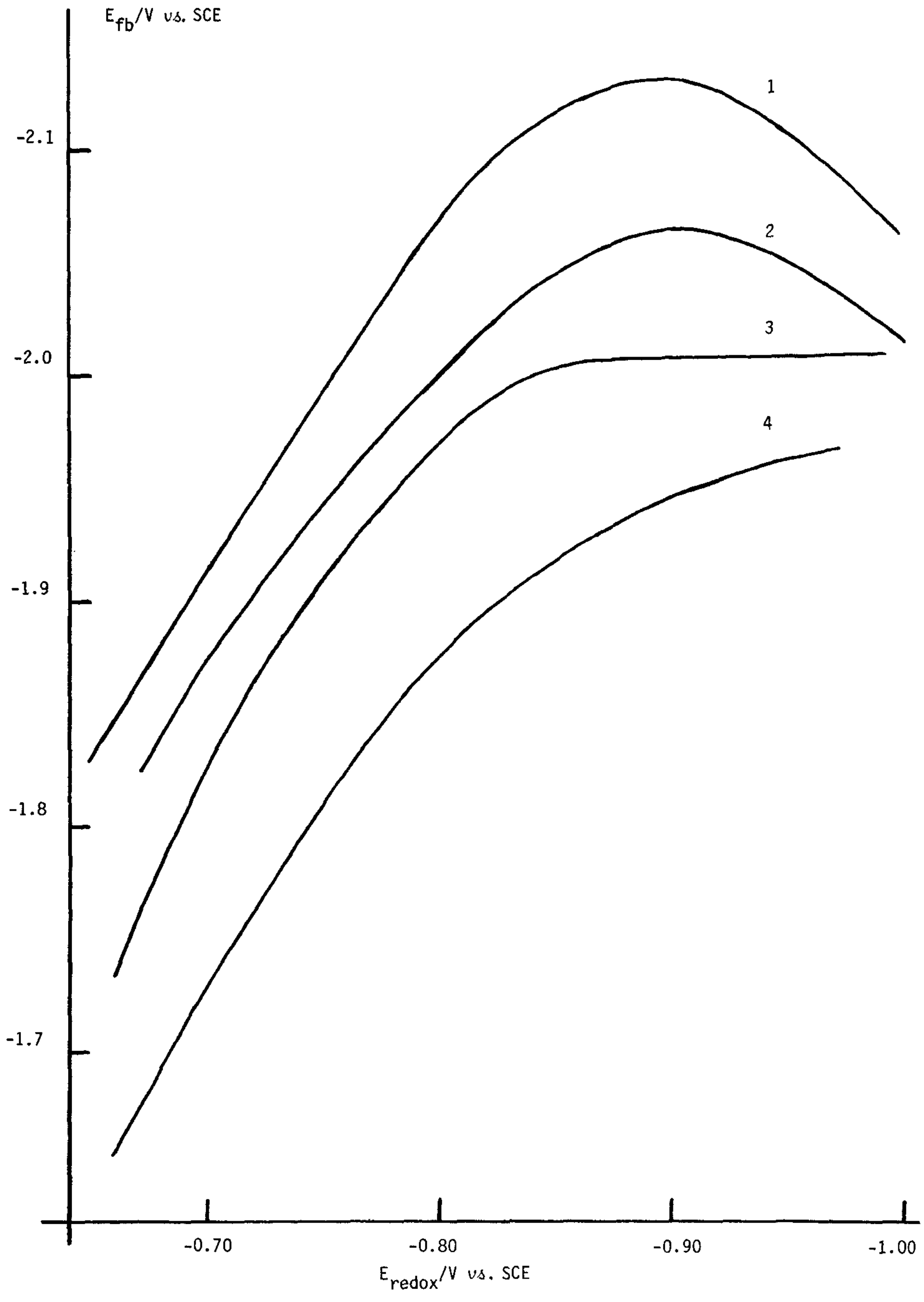

Figure 3. The flat-band potential of n-CdTe in selenide solutions in aq. KOH (1 mol dm^{-3}) versus E_{redox}. 1 and 2 (110 face) total Se concentration (0·010 mol dm^{-3}; 3 and 4 (unidentified face) total Se concentration 0·04 mol dm^{-3}.

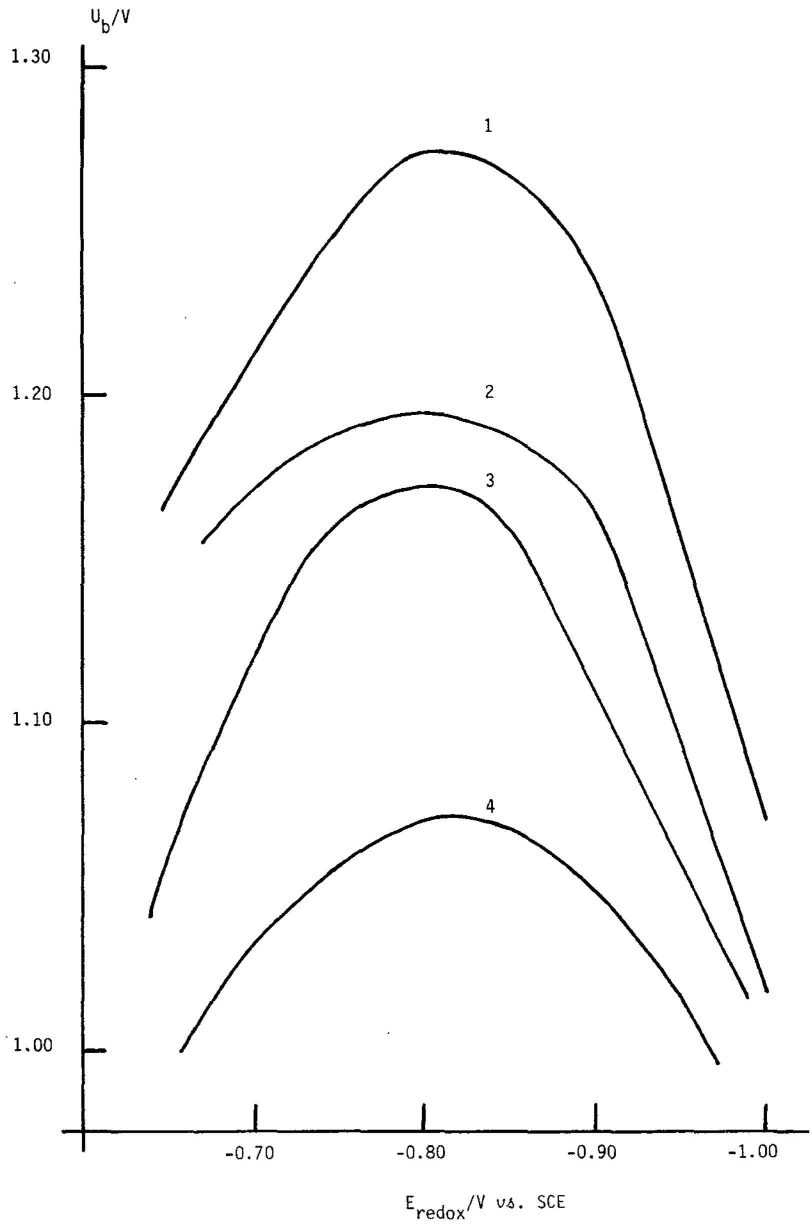

Figure 4. The built-in potential of n-CdTe in selenide solutions in aq. KOH ($1\ \mathrm{mol\,dm^{-3}}$) versus E_{redox}. 1, 2, 3 and 4 as in figure 3.

in $[S_1]$. It appears that competitive adsorption, e.g. of S_2 species, reduced the surface concentration of adsorbed charge below the value expected if S_1 were the only selenide species contributing to the adsorption. Taking the theoretical value of E_{fb} for zero adsorption as $-0{\cdot}7$ V versus SCE and noting that the experimental change in E_{fb} from its most negative value was only 0·3 V, it is clear that a relatively small drop in the maximum value of the adsorbed charge density was sufficient to account for the results. Direct identification of the adsorbed species has not been possible, but is desirable to confirm the present hypothesis.

Various models which allow for adsorption of different species changing with E_{redox} have been considered, with a view to fitting the experimental results for U_{b} versus E_{redox}, but because of the number of variables involved, conclusive proof that any one model is correct has not yet been obtained.

On the (110) face, the maximum value of U_{b} obtained in the present work was 1·3 V and this is expected to exceed the observed U_{oc}. Experimental values for U_{oc} have been up to 0·8 V.

4. Conclusions

(*a*) Adsorption of selenide anions occurred on the CdTe.

(*b*) At negative values of E_{redox}, the built-in potential followed E_{redox} and Fermi-level pinning was absent, as is consistent with the use of an electrolyte which was both strongly alkaline (and so would dissolve any TeO_2 and Te on the crystal surface) and also strongly reducing (and so would reduce oxidized species).

(*c*) The maximum value of U_{b} was 1·25 V, and the most negative value of E_{fb}, −2·1 V versus SCE. U_{b} decreased as E_{redox} became more positive than −0·8 V versus SCE, and this is consistent with a progressive decrease in the amount of negative charge adsorbed on the surface. There was no need to introduce surface states other than adsorbed ions to explain the results.

(*d*) Dispersion of the capacitance with frequency in this system was removed by extremely thorough sealing.

(*e*) Selenide solutions in 1 M KOH consist of species in four oxidation states, and the formal potentials for the three couples involved have been determined, as have the variations in the composition as a function of E_{redox}.

Acknowledgment

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