SHORT COMMUNICATION

Dual electrolyte–semiconductor contact CdSe electrochemical photocell

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1. Introduction

Numerous electrochemical photocells have been investigated for the purpose of converting solar energy into electricity [1–4]. Although as yet, no commercially viable photoelectrochemical cells (PEC) have been developed, several appear to be promising [5–7]. CdSe-based cells have been studied extensively due to their suitable bandgap (1.7 eV) and the possibility of deposition in the form of a thin film on various electrode materials [8]. When this film is dipped into an electrolyte, a depletion layer is formed that leads to charge separation due to photo-excitation. The work done by Tien *et al.* [9] on pigmented lipid membranes suggests that energy transduction is possible even if semiconductor electrolyte contacts are made on both sides of the semiconductor. In the present communication we report such a study on CdSe pellets.

2. Experimental details

Pellets of CdSe, obtained from Alfa Division, USA (lot 012479, 99.999% pure) were made under a pressure of $1.7 \times 10^4 \mathrm{N m^{-2}}$. The thickness of these pellets was about $400\,\mu$m. The pellets were sintered in air at 540° C for 4 h and were later etched in 3 : 1 $HC1/HNO_3$ for 45 s. After washing, the samples were dipped in 1 M Na_2S + 1 M sulphur solution for 1 min. It was observed that these treatments give a non-lustrous finish to the pellets. The pellets were again washed in doubly distilled water and were mounted on a Plexiglass partition in a simple cell with silicon resin. The resin was allowed to cure for 24 h at room temperature. The chambers of the cell were filled with 1 M (Na_2S + S + KOH) + 0.07 M selenium solution (photoexposed side) and 1 M $CuSO_4$ solutions. Platinum and copper were used as electrodes. A Keithley Electrometer (610C) and a Lazar digital meter were used, in conjunction with x–y and x–y/t recorders (Houston Instruments) to measure and record current and voltage, respectively. A halogen lamp (250 W) was used for photoexcitation. The measurements were carried out after keeping the cell short-circuited for 1 h in dark for equilibrium to be established. Light intensity incident on the pellet was $80\,\mathrm{mW\,cm^{-2}}$, which was measured by a Solar Meter (Dodge Products, Inc., Houston Texas).

3. Results and discussion

Figs 1 and 2 show the variation of open circuit voltage (V_{oc}) and short-circuit current (I_{sc}) with time. It can be seen that the cell potential, as well as current, changed polarity during photoexposure. The cell potential in dark is about −600 mV with copper as positive electrode. The short circuit current in dark is between 6 to $7\,\mathrm{mA\,cm^{-2}}$. In light the I_{sc} is around $25\,\mathrm{mA\,cm^{-2}}$, and the open circuit potential is around 600–700 mV with copper as the negative electrode. From dark to photo value the change in V_{oc} is almost instantaneous and returns to the dark value gradually when the light is switched off. The net change in open circuit voltage under illumination is thus more than 1 V.

Some copper deposition was observed on the CdSe surface facing the copper electrode and $CuSO_4$ solution and it was found that the copper electrode had turned slightly greyish, indicating that a copper oxide film had formed. These cells were tested over a period of 5 days and did not show any decrease in the open circuit voltage or short circuit current. No change in V_{oc} or I_{sc}

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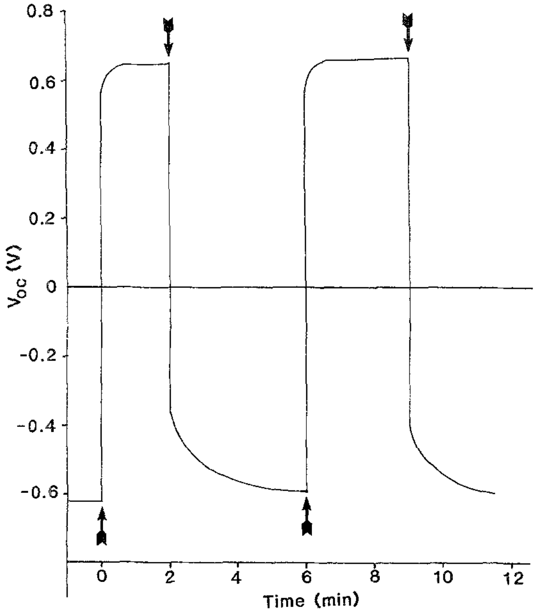

Fig. 1. Photoresponse of open circuit voltage with time. ↑ Light on, ↓ light off.

values was observed on continuous photo-exposure of 2 h; however, the copper sulphate solution turned slightly greenish in colour, indicating the reduction of Cu^{2+} to Cu^{+} ions. This was also confirmed by spectrophotometric studies. A little sedimentation of cuprous sulphate was observed in some cells, on the bottom of the chamber containing $CuSO_4$. Addition of a small amount of KCl in $CuSO_4$ reduced this sedimentation considerably [10]. After storage of the cell in the dark, the greenish solution of cuprous sulphate changed back to its original colour, suggesting the oxidation of Cu^{+} to Cu^{2+} ions in dark.

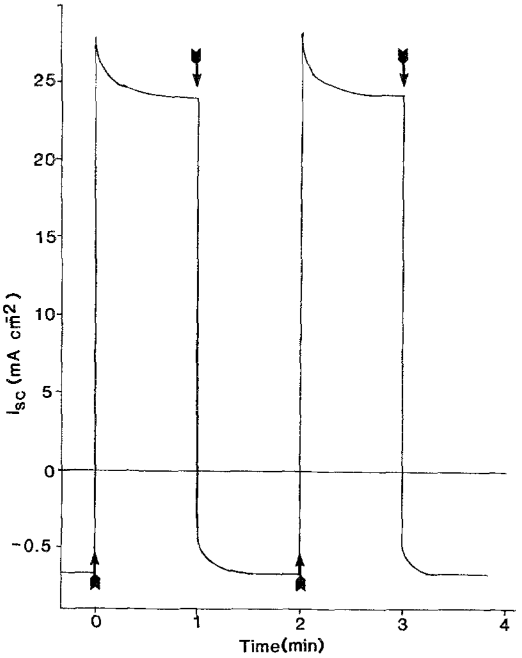

Fig. 2. Photoresponse of short circuit current with time. ↑ Light on, ↓ light off.

These observations suggest that copper sulphate solution plays a crucial role in this cell. It seems that cadmium in the top surface of the pellet is replaced by copper and a very thin layer of copper is deposited on the pellet surface. The standard redox potential of the electrode reactions are 0.339 and -0.402 V, respectively, so this could be possible [11]. The presence of copper on the pellet surface has also been confirmed experimentally.

Some pellets were removed from the cell and washed in distilled water repeatedly. These were later dipped in dilute HNO_3 to dissolve any copper on the pellet surface. When ammonium hydroxide was added to this dilute HNO_3 an intense blue colour was observed, indicating the presence of copper in the solution. This suggests the possibility of the following mechanism taking place in the present cell.

(a) In light. Electrons and holes are generated in the depletion layer, forming at the S^{2-}/S_2^{2-} and CdSe interface, in CdSe, as well as in the bulk of the semiconductor. The holes migrate to the photo-exposed interface, while electrons travel in the bulk of the semiconductor to the other electrolyte semiconductor ($CuSO_4$/CdSe) interface due to the electric field. Holes oxidize sulphide ions to polysulphide ions at the interface, which in turn reduce to sulphide ions at the counter electrode:

$$2S^{2-} + 2h = S_2^{2-}$$

at CdSe–electrolyte interface (1)

$$S_2^{2-} + 2e = 2S^{2-}$$

at the counter electrode (2)

As the counter electrode is losing electrons, it becomes positive upon photo-exposure. At the CdSe/$CuSO_4$ interface the following changes may take place:

(i) Possible deposition of copper on the pellet, and

(ii) Possible reduction of Cu^{2+} ions to Cu^+ ions.

This leads to the following changes at the counter copper electrode:

(i) Dissolution of the copper electrode

$$Cu = Cu^{2+} + 2e \qquad (3)$$

making it negative.

(ii) Oxidation of copper to copper oxide. This seems more probable, as the SO_4^{2-} ion has greater affinity for electrons, compared to hydroxide ions (this being an aqueous solution) [12]. This causes the discharge of hydroxide ions at the copper electrode and reduction of copper oxide.

$$2OH^- + Cu = CuO + H_2O + 2e \qquad (4)$$

All these mechanisms suggest that, while there is no net change in the $2S^{2-}/S_2^{2-}$ electrolyte, on photo-exposure some changes do take place in the other electrolyte and electrode, namely deposition of copper on the pellet, conversion of copper into copper oxide and conversion of Cu^{2+} to Cu^+. In fact, similar values of V_{oc} in dark and light were observed when a copper oxide electrode was used in place of a copper electrode.

(b) In dark. As has been mentioned earlier, the platinum electrode has negative polarity while copper has positive polarity. The potential difference observed here may be due to the redox potentials of the various redox couples, Se_2^{2-}/Se^{2-}, S_2^{2-}/S^{2-}, Cu/Cu^{2+} and Cu^{2+}/Cu^+.

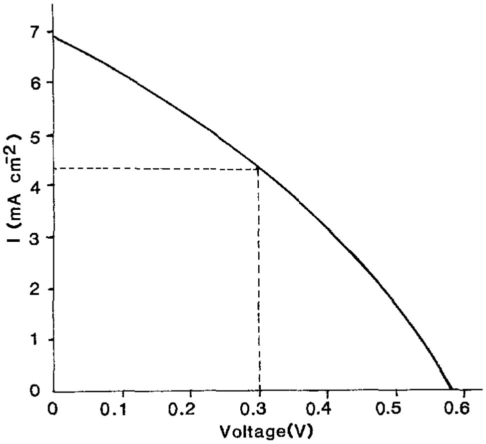

Fig. 3. Load characteristics of the cell in dark.

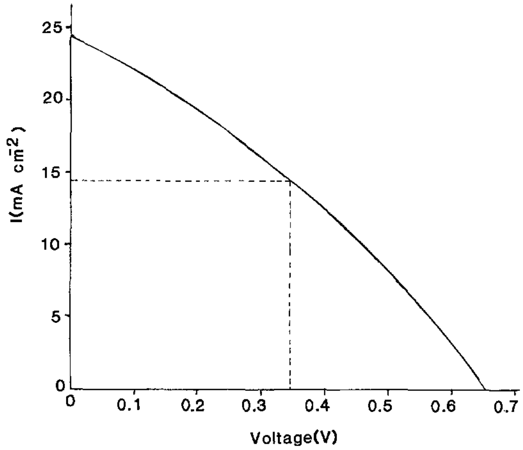

Fig. 4. Load characteristics of the cell in light.

In summary, the copper that has been deposited on the pellet in dark may dissolve in light, and the copper oxide may reduce to copper. The changes that take place in light are reversed in dark, and in some respects, the cell works as a solar rechargeable electrochemical battery.

The load characteristics of the cell in light, as well as in dark, are shown in Figs 3 and 4, respectively. The values of maximum power output $(IV)_{max}$ in dark and light are 1.2 and 4.5 mW cm^{-2}, respectively. These cells give 6% efficiency at 80 mW cm^{-2}. The fill factor is about 0.32. The results indicate that a rechargeable photo-electrochemical cell may be fabricated using this technique.

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