

ELECTROCHEMICAL SOLAR CELLS WITH LAYER-TYPE SEMICONDUCTOR ANODES. PERFORMANCE OF $n\text{-MoSe}_2$ CELLS

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Summary

The output characteristics and the long-term performances of $n\text{-MoSe}_2$ (Γ^- , I_2) electrochemical solar cells have been investigated. It has been confirmed that, by analogy with other layer-type, d-band transition metal dichalcogenide systems, the surface state of the semiconductor plays a key role in the behaviour of the cell. With 'smooth' crystal samples, fill factor and efficiency values of the order of 0.6 and 6%, respectively, have been obtained under AM1 illumination. Such performances are, however, drastically reduced if 'irregular' crystal samples are used.

Control of these undesirable surface state effects has been attempted by chemical treatments specific to the unsaturated transition metal atoms exposed to the electrolyte at the edge sites. Finally, the stability of $n\text{-MoSe}_2$ (Γ^- , I_2) cells under long time operation, has also been evaluated.

Introduction

In recent years considerable attention has been given to regenerative electrochemical solar cells. Among the various types of cells considered, those based on layered d-band semiconductors as photoanodes have recently attracted increasing attention. As originally proposed by Tributsch and co-workers [1 - 5], group VI layered transition metal dichalcogenides are

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characterized by energy gaps of between 1 and 2 eV and by d-d transitions which do not affect the bonding situation at the surface; consequently, cells using these compounds as photoanodes should offer reasonably high solar conversion efficiency and be quite stable against photocorrosion.

This has stimulated a series of studies on layer transition metal dichalcogenide photoanodes. However, the results reported in this area show substantial discrepancies. For example, in the case of the $\text{WSe}_2(\text{I}^-, \text{I}_2)$ aqueous cell, Bard and co-workers reported an efficiency of 14% under illumination with $\lambda > 590 \text{ nm}$ [6], Heller *et al.* [7] obtained solar conversion efficiencies ranging from 3.7% to 5.2%, while Parkinson *et al.* [8] reported values of the order of 1 - 2%*.

It is now well recognized [7, 9] that these discrepancies may be accounted for by differences in the procedure for growing the semiconductor crystal and in the morphology of its surface. Various authors [10, 7, 8] have shown that the semiconductor morphology plays a key role in the performances of the transition metal dichalcogenide photoelectrochemical cells. Surface steps act as recombination centres and, hence, a striking difference in output characteristics has been noticed passing from smooth to irregular photoanodes [7]. Steps, or more generally faults, on the semiconductor surface, exposing unsaturated transition metal atoms to the electrolyte, might also result in active sites for corrosion. Therefore, the semiconductor morphology should not only affect the output characteristics but also the performance of the cell under long-term operation [9].

To fully evaluate these important aspects, we decided to carry out a systematic investigation of the general behaviour of layered semiconductor/liquid electrolyte cells. In this work we report results related to cells based on MoSe_2 photoanodes.

Experimental

Molybdenum diselenide single crystals were grown by chemical transport reactions using either iodine or bromine as the transport agent. The growth temperatures were chosen between 950 and 1050 °C, depending on the transport agent. In a few cases, MoSe_2 crystals could also be grown at a lower temperature, *i.e.*, 850 °C.

As starting materials, commercial dichalcogenides could be used with acceptable results. However, the best samples were obtained starting from the elements. In this case the formation reaction took place in the same silica glass crucible as that in which the transport process was subsequently carried out.

*In the course of the revision of this paper, we became aware that Parkinson and co-workers [11], using selected semiconductor crystals, have obtained efficiencies of the order of 10% with the $\text{WSe}_2(\text{I}^-, \text{I}_2)$ cell.

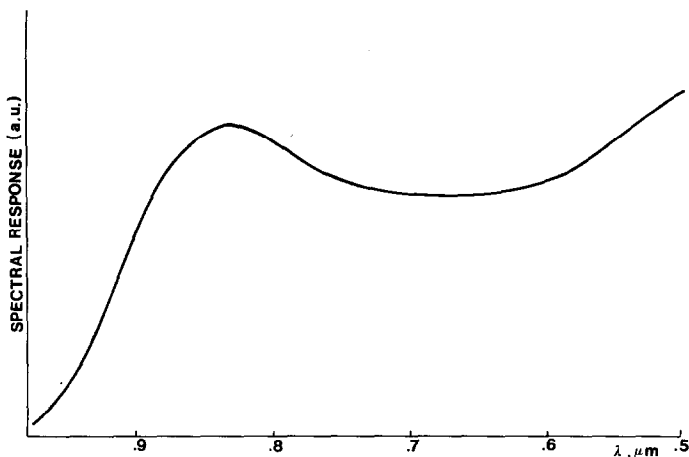


Fig. 1. Spectral response of $n\text{-MoSe}_2$ in 0.1M KI aqueous solution.

Crystals grown without intentional doping were always n -type. Values of charge carrier density ($n \cong 10^{17} - 10^{18} \text{ cm}^{-3}$) and of mobility within the layers ($\mu_l \cong 10 - 30 \text{ cm}^2/\text{V s}$) were similar to those reported in the literature. Structures could be observed on all the surfaces. Even those samples with a smooth appearance were microscopically characterized by growth steps. Moreover, the transport agent cannot be totally eliminated from the grown crystals.

A conventional glass cell with an optical window was used for the spectral response and electrochemical tests. The MoSe_2 crystals were contacted to a copper wire with a silver paste and then embedded into a Teflon holder with epoxy cement. The surface exposed to the electrolyte ($1c$) was evaluated by weighing microscopic photographs of the crystal. A ring-shaped platinum wire was used as the counter electrode.

All the chemical products were reagent grade and the electrolyte solutions were prepared using distilled water. The solutions were not stirred during the measurements.

The spectral response was measured with the following experimental apparatus. Light from the lamp (250 W halogen or high pressure xenon lamp) was chopped at low frequency, dispersed by a high-luminosity grating monochromator (Spex Minimate), and spatially divided into two portions which, through equivalent optical paths, fell on the photoelectrochemical cell and on a flat-response pyroelectric detector (Laser Precision RK-5100). Photoelectric signals were amplified by two PAR-HR-8 lock-in amplifiers and their ratio was then recorded. In this way, corrected photovoltage spectral responses from 0.4 to 2 μm , with a resolution up to 20 \AA and a sensitivity better than 1 μV , could be directly measured.

As the light source for the I - V curve determination, a 100 W halogen (filtered) lamp was used. The I - V curves were determined, both in the

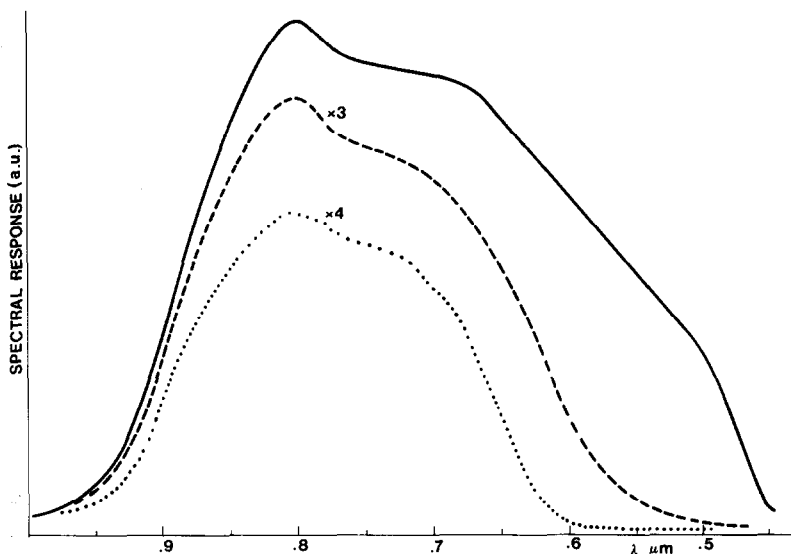


Fig. 2. Spectral response of $n\text{-MoSe}_2$ in KI (0.1M), I_2 aqueous solutions at various iodine concentrations. —, 0.001M; ---, 0.01M; . . . , 0.05M. Optical path: 5 cm.

absence and presence of light, using a potentiostat to control the cell voltage and recording the cell characteristics with an X-Y recorder.

The efficiencies quoted are not corrected for solution adsorption or for reflection from the cell glass window and the crystal surface.

Results and discussion

(i) Spectral response

The spectral response of a semiconductor provides important information on both the optical and transport properties of materials and can aid in the identification of loss mechanisms in a photovoltaic conversion process.

Two kinds of spectral response are generally used: photocurrent and photovoltage responses. Both methods, however, are expected to give identical results. Figure 1 shows the photoresponse of $n\text{-MoSe}_2$ in an indifferent electrolyte, *i.e.*, a 0.1M KI aqueous solution. The spectral line shape reflects essentially the optical absorption spectrum of the dichalcogenide: the photoelectric signal rises at about $0.95\ \mu\text{m}$ and reaches a peak at about $0.83\ \mu\text{m}$, in correspondence with the d-d interband transition, while in the visible-u.v. range a continuously increasing signal is observed, corresponding to the contribution of strong p(chalcogenide) \rightarrow d(metal) transitions.

Owing to the indirect character of the optical transition and the possible presence of impurity absorption tails, photoelectrochemical spectral responses do not allow an unambiguous estimate of the gap value and therefore only upper limits can be indicated. In this respect, we have found for our MoSe_2 samples values of $E_g \leq 1.30\ \text{eV}$.

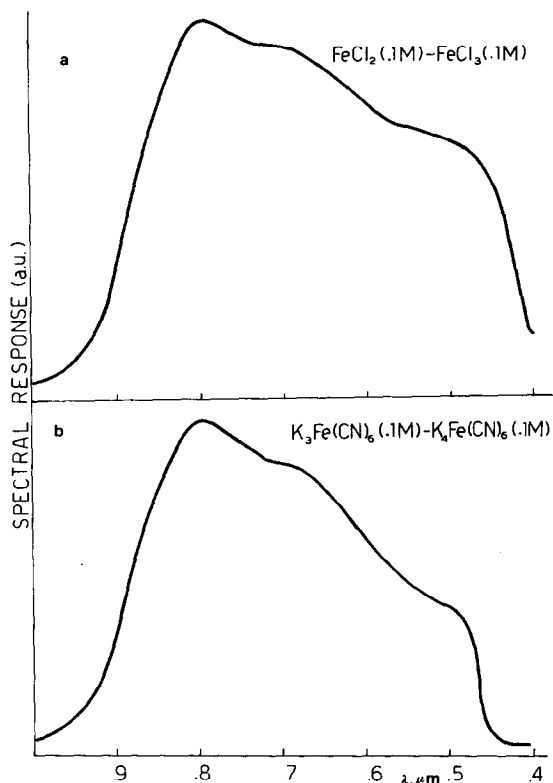


Fig. 3. Spectral response of n -MoSe₂ in FeCl₂(0.1M), FeCl₃(0.1M) (curve a) and in K₃Fe(CN)₆(0.1 M), K₄Fe(CN)₆(0.1M) (curve b), aqueous solutions.

On immersion in electrolyte redox couples, such as I⁻, I₂; Fe²⁺, Fe³⁺; Fe(CN)₆³⁺, Fe(CN)₆⁴⁺, spectral responses of n -MoSe₂ exhibit a continuous and clear decrease in the visible–near u.v. spectral range, as illustrated in Figs. 2 and 3.

A major fact influencing such a decrease is, of course, the optical absorption of the electrolytes, which causes the short wavelength cut-off of photovoltaic signals and, in general, acts as a filter of semiconductor responses. Yet, the effect of electrolyte absorption alone cannot completely explain spectral shapes at short wavelengths when the solution is only slightly absorbent. In these cases, even after correction for the spectral absorption of the solution, photovoltaic response decreases continuously at high energy, where the absorption coefficient of the semiconductor begins to be determinant. The magnitude of this effect depends strongly on the semiconductor sample and on the electrolyte and is not explained by simple theories of the spectral dependence of the photocurrent.

On the other hand, it has been suggested [4] that in transition metal dichalcogenides, active carriers could be generated, essentially from d–d op-

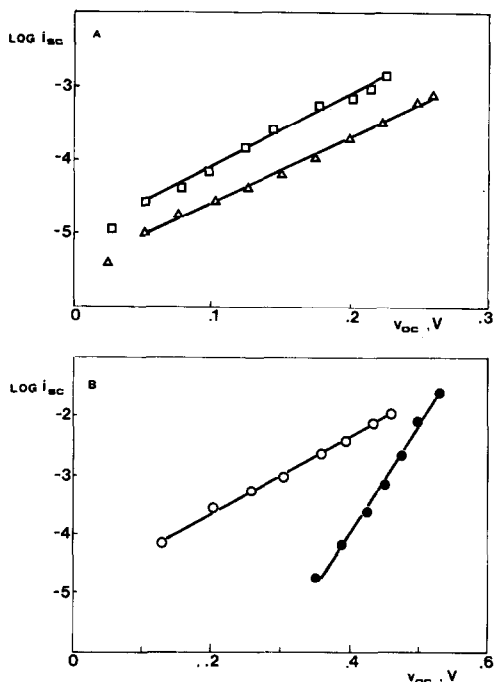


Fig. 4. Short circuit current (A cm^{-2})–open circuit voltage (V) relationship for the n - MoSe_2 /electrolyte junctions. (A), Fe(CN)_6^{3+} , Fe(CN)_6^{4+} (□) and Fe^{2+} , Fe^{3+} (△) electrolyte couples. (B) for $[\text{I}^-/\text{I}_2]$ electrolyte couple with irregular (○) and smooth (●) surface semiconductor samples.

tical transition and not from higher transitions involving both metal and chalcogen orbitals. Such a suggestion accounts qualitatively for photo-response line shapes but not for quantitative differences between various semiconductor samples and electrolytes.

An alternative interpretation could involve the role of the semiconductor interface, with the presence of a 'dead layer' not contributing to photo-carrier generation and possessing a high concentration of impurities and/or recombination centres. When light penetration depth is large by comparison with the thickness of this layer, photocurrent yield can be decreased by interfacial recombination; on the other hand, when penetration length is comparable with this thickness, photogenerated electron–hole pairs immediately recombine and photoresponses fall to zero.

Such an approach is obviously purely phenomenological and much less desirable than a theoretical microscopic description. However, it emphasizes the fundamental role of the interfacial region in layered semiconductor/electrolyte junctions and indicates that spectral response analysis may be a useful tool to gain information on these processes.

(ii) *Photovoltaic characteristics*

Measurements of short-circuit current i_{sc} , and of open circuit voltage, V_{oc} , at various illumination levels, may give indications of the behaviour of the semiconductor/electrolyte junction. In the case of a diode, the relation between i_{sc} and V_{oc} is generally

$$i_{sc} = i_0 \exp \left(\frac{qV_{oc}}{nK_B T} \right) \quad (1)$$

where i_0 (saturation current) and n (diode quality factor) are characteristic parameters of the junction, K_B is the Boltzmann constant, T the absolute temperature and q the electronic charge.

Even if the direct utilization of the p - n diode current-voltage relationship in the case of semiconductor/liquid junctions may not be generally an accurate procedure, an equation such as (1) may be used to describe qualitatively the experimental data obtained for the n -MoSe₂/electrolyte junctions, at least at medium-high levels of irradiation (*i.e.*, for V_{oc} higher than 50 - 100 mV).

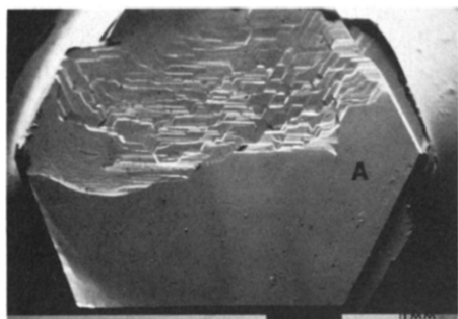
In fact, as shown in Fig. 4, plots of $\log i_{sc}$ vs. V_{oc} are linear for all the electrolytes considered. However, quite remarkable differences in behaviour are obtained, depending on the morphology of the semiconductor surface. Electrodes with 'irregular' surfaces show relatively high saturation currents and diode quality factors in all electrolytes tested, with $i_0 \geq 10^{-6}$ A cm⁻² and $n \geq 2$, which are typical of 'bad' photodiodes with low fill factors. By contrast, 'smooth' semiconductor surfaces give values such as $i_0 \cong 10^{-11}$ - 10^{-12} A cm⁻² and $n \cong 1$ - 1.5, which correspond to nearly ideal diode behaviour. This marked dependence of the diode quality factor on the surface state of the semiconductor is particularly evident in Fig. 4(B), where i_{sc} - V_{oc} characteristics of irregular and smooth MoSe₂ samples in the Γ^- , I₂ electrolyte are compared.

Indeed, the morphology of the semiconductor surface largely influences the performance of photoelectrochemical cells based on layer-type, transition metal photoanodes. This is clearly demonstrated by the shape of the output characteristics of the cell

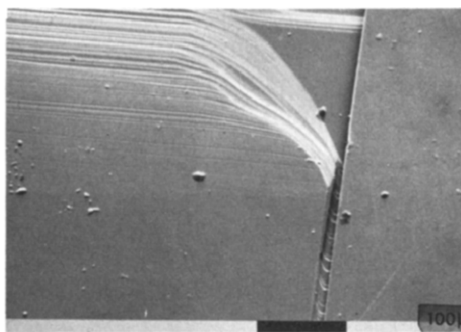


obtained with an irregular semiconductor crystal, *i.e.*, of the type illustrated in Fig. 5(A). The I - V curve reported in Fig. 6(A) shows very poor values of efficiency and fill factor. However, if a smooth portion of the crystal (such as that illustrated in Fig. 5(b)) is isolated, by masking the region of irregularity (such as that illustrated in Fig. 5(C)), with epoxy cement under the microscope, the I - V curve shown in Fig. 6(B) is obtained. A tremendous improvement in efficiency and in fill factor is indeed obtained. Effectively, when smooth crystals are selected, very good performances are furnished by cells of type (II), as illustrated in Fig. 7 and summarized in Table 1.

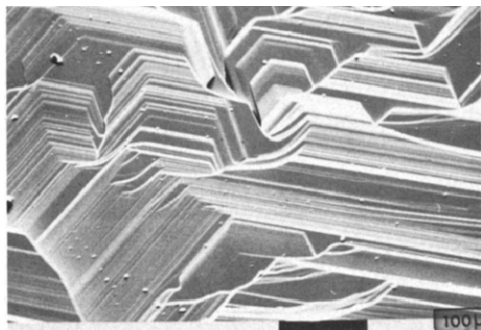
Therefore, electrochemical solar cells based on MoSe₂, and generally on layered transition metal dichalcogenides, are, indeed, potentially capable of



(A)



(B)



(C)

Fig. 5. Morphological aspect of MoSe₂ crystal samples. (A) Irregular MoSe₂ crystal, (B) smooth portion, and (C) highly stepped portion.

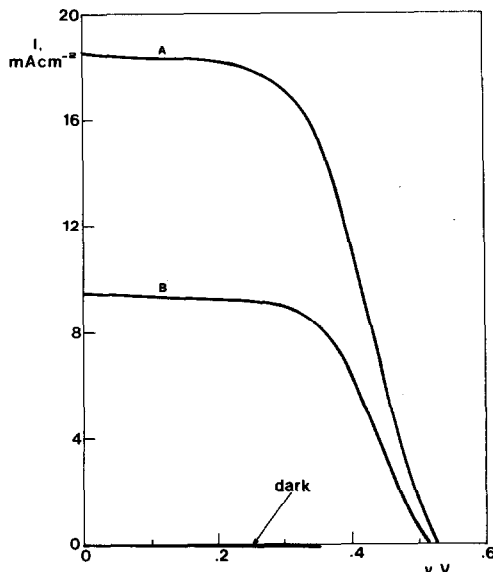
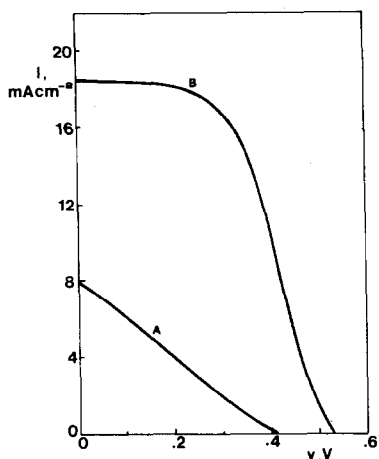


Fig. 6. Output power characteristics of the MoSe₂(I⁻, I₂) photoelectrochemical cell with irregular (curve A) and smooth (curve B) semiconductor samples at 100 mW cm⁻².

Fig. 7. Output power characteristics of the MoSe₂(I⁻, I₂) photoelectrochemical cell with smooth surface semiconductor anodes under illumination of 50 mW cm⁻² (curve B) and 100 mW cm⁻² (curve A).

TABLE 1

Output characteristics of the $n\text{-MoSe}_2/\text{I}^-$, $\text{I}_2(2\text{M}, 0.05\text{M})/\text{Pt}$ solar electrochemical cell, obtained with various semiconductor crystal samples

Sample	V_{oc} (mV)	i_{sc} (mA cm ⁻²)	Fill factor	η (%)	Illumination (mW cm ⁻²)	Surface morphology
BS1	511	20	0.55	5.6	100	smooth
GR1	500	17	0.66	6.2	90	very smooth
BS2	503	13	0.44	3.6	80	partially irregular
BS3*	514	14	0.44	4	80	partially irregular
BS4	430	11	0.36	2.4	70	very irregular

*Obtained from BS2 after cleavage with adhesive tape [5].

delivering high output power values, but their performances are, in practice, strongly affected by irregularities of the semiconductor surface. This is certainly a severe limitation to the applicability of these cells, since, at the moment it excludes the utilization of polycrystalline semiconductor anodes.

It therefore appears important at this stage of the research on layered semiconductor cells, to concentrate attention on this basic problem related to the semiconductor surface states. The poor performances of irregular crystals are likely to be connected with the unsaturated transition metal atoms exposed to the electrolyte solution at the edges of the steps. A possible solution to the problem could then be sought in action designed for the specific inhibition of these atoms in order to prevent their interaction with the electrolyte.

This type of approach has been recently attempted in the case of $n\text{-WSe}_2$ anodes by Parkinson *et al.* [8], who have examined the effect of chemical treatments selective to the W atoms responsible for the surface state. In particular, treatment of the semiconductor crystal with long-tailed molecules, such as 4-tert-butyl pyridine, had a beneficial effect in terms of immediate improvements of cell output performances. The interpretation was that the organic molecules were semi-intercalated at the edge sites of the tungsten diselenide crystal surface, thus blocking interactions with the solution [8]. This beneficial effect, however, decayed quite rapidly during cell operation, probably because of degradation of the organic molecule.

Applying this type of strategy, we have examined a somewhat different approach by exploring the possibility of blocking the transition metal atoms exposed at the edge sites with specific complexing agents, such as ethylenediaminetetraacetic acid disodium salt (EDTA). The results are shown in Fig. 8 in terms of output power characteristics and dark currents for an $n\text{-MoSe}_2$ (I^- , I_2) cell. Curve a refers to the response of a largely 'structured' MoSe_2 crystal (*i.e.*, of the type illustrated in Fig. 5(C)). Curve b shows the response of the same crystal after immersion for 1 h in a saturated EDTA aqueous solution at room temperature. Curve c is the response after 20 h of cell

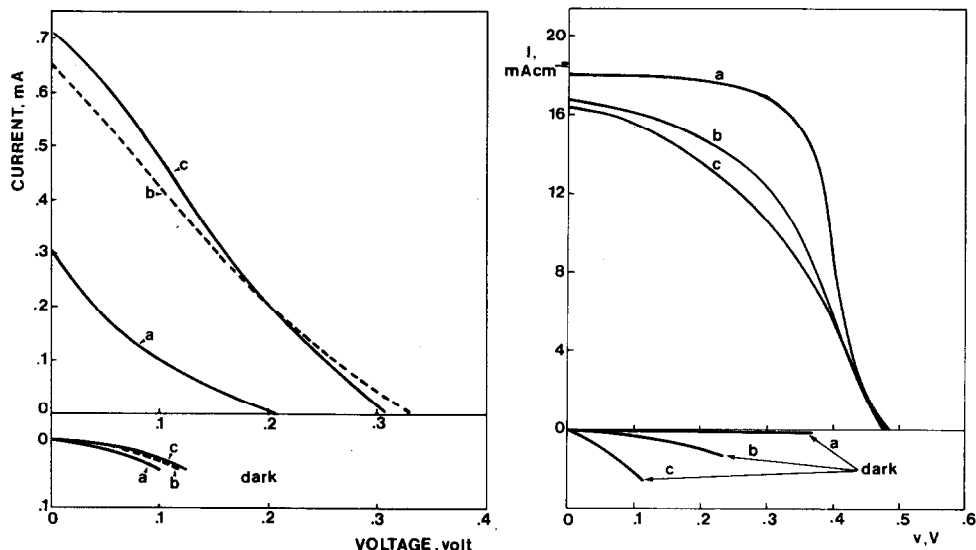


Fig. 8. Output power characteristics of the $\text{MoSe}_2(\text{I}^-, \text{I}_2)$ photoelectrochemical cell under illumination of 100 mW cm^{-2} . Curve a: untreated MoSe_2 crystal, curve b: after treatment with EDTA solution, curve c: after 20 h operation at 0.3 mA (maximum power point). Apparent crystal surface area: 0.15 cm^2 .

Fig. 9. Output power characteristics of the $\text{MoSe}_2(\text{I}^-, \text{I}_2)$ photoelectrochemical cell. Curve a: freshly made cell, curve b: after 105 h of operation with a $2 \text{ k}\Omega$ external load, curve c: after 242 h operation with a $2 \text{ k}\Omega$ external load. Illumination: 100 mW cm^{-2} .

operation at 0.3 mA (*i.e.*, at the maximum power point). In the same Figure the respective dark currents are also shown.

The results indicate that EDTA treatments effectively produce substantial improvements in output values. Furthermore, the EDTA effect does not seem to decay in short periods. This is certainly encouraging, and studies are in progress in our laboratories to fully evaluate the EDTA action under long-term performances, and to systematically investigate other complexing and/or ligand agents of the unsaturated atoms in the layered semiconductor surface.

(iii) Cell stability

Stability under continuous operation is another important parameter in the evaluation of practical cell utilization. To investigate this aspect, a cell of type (2), having a smooth anodic surface, was prepared. Its typical I - V characteristic is shown in Fig. 9a. After illumination for 105 h under a $2 \text{ k}\Omega$ external load, the characteristic changed to assume the shape illustrated in Fig. 9b. The cell was then kept in operation for a further 137 h, after which the characteristic reported in curve 9c was obtained.

During this period of operation, the cell performance appeared to be modified, with fill factor and efficiency decreasing from 0.6 to 0.4 and from

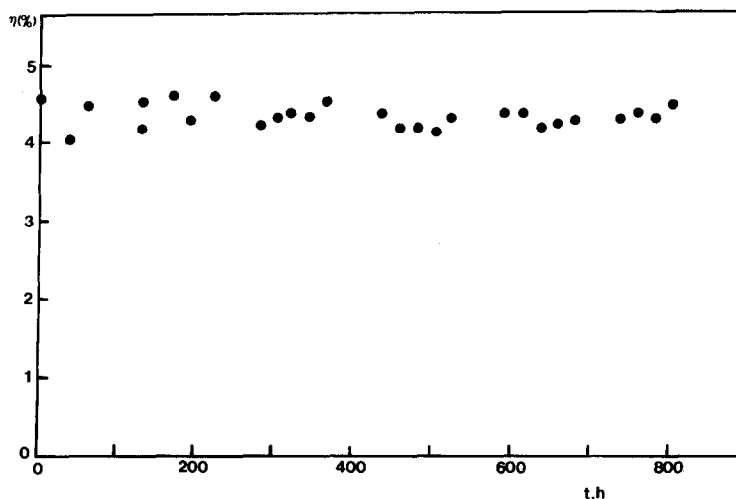


Fig. 10. Efficiency as a function of the operation time of the $\text{MoSe}_2(\text{I}^-, \text{I}_2)$ photoelectrochemical cell. The efficiency values have been determined from output power characteristics obtained after progressive periods of operation under 100Ω external load ($\sim 17.5 \text{ mA cm}^{-2}$) and with an illumination of 100 mW cm^{-2} .

6% to 4%, respectively. However, after this initial decay, the output characteristic recovered, and then practically stabilized, around average values. This is typically indicated in Fig. 10, which shows the efficiency of a $\text{MoSe}_2(\text{I}^-, \text{I}_2)$ cell, determined after progressive periods of operation up to a total time exceeding 800 h. It will be noticed that the efficiency effectively oscillates around an average value of 4.3%.

Conclusion

There is undoubtedly a deterioration of the semiconductor surface during initial periods of operation of the cell, as indicated by the progressively increasing values of the dark current (see Fig. 9). However this process stops upon prolonged operation by a mechanism which is difficult to interpret. The practical result is that the $\text{MoSe}_2(\text{I}^-, \text{I}_2)$ cell indeed shows good long term stability, as originally predicted and experimentally verified by Tributsch, who, in fact, reported that an $\text{MoSe}_2(\text{I}^-, \text{I}_2)$ cell could deliver a continuous output of 10 mA cm^{-2} , without showing appreciable degradation [5].

Such a behaviour, confirmed by the study reported here, is a further indication of the potential advantages offered by the layered, d-band semiconductor electrochemical solar cells, and is certainly another encouraging incentive to continue the systematic study of their properties.

Acknowledgments

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