Semiconductor Electrodes

XXIX. High Efficiency Photoelectrochemical Solar Cells with n-WSe₂ Electrodes in an Aqueous Iodide Medium

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A number of photoelectrochemical (PEC) photovoltaic (or regenerative) cells based on semiconductor electrodes in aqueous and nonaqueous media have been described; see (1-7) and references therein. High solar energy conversion efficiencies in such cells require a semiconductor band gap energy (E_g) which matches well with the solar spectrum, a semiconductor flat-band potential (V_{fb}) and solution redox couple potential (V_{redox}) which maximizes the output voltage, and conditions which minimize recombination processes in the semiconductor and solution and at the interface. The solution redox couple and solvent are selected to stabilize the semiconductor from photoinduced corrosion processes (8,9). The highest published power efficiency for such cells is the 12% reported for a single crystal n-GaAs electrode in a selenide medium (10). We describe here a PEC cell based on single crystal n-WSe₂ which shows comparable efficiencies.

The applicability of the layer-type compounds based on molybdenum and tungsten di-chalcogenides (e.g. MoS₂ and MoSe₂) as semiconductor electrodes was first described and investigated by Tributsch and co-workers (11-15). In more recent work cells based on p-WSe₂ (16,17) and the dependence of the photopotential on the solution redox couple for n-WSe₂ has been described. These materials appear promising as candidates for practical PEC solar cells because their excitation involves d-d transitions which may provide good stability (12) and because they are relatively cheap and abundant materials. However the performance of cells reported to date have been rather modest. We report here an n-type WSe₂ with a high efficiency.

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The n-WSe₂ crystals, grown by chemical vapor transport, were generously donated by Drs. Barry Miller and Frank DiSalvo of Bell Laboratories. They were connected to a copper wire with silver epoxy cement (Allied Products Corp., New Haven, Conn.). Before mounting the crystal, a clean, new crystal surface ($\perp$ c-axis or van-der-Waals surface) was prepared by sticking adhesive tape on the surface, and then pulling it, along with the surface layer of the crystal, off. The crystal was mounted in 7 mm-diameter glass tubing with all sides insulated with silicone rubber sealant (Dow Corning Corp., Midland, Mich.) leaving exposed the van-der-Waals surface with an area of about 0.017 cm². Before use, the electrode surface was etched with 12 M HCl for 5-10 seconds followed by a thorough rinsing with water. The electrochemical measurements followed previous practice (7). The PEC cell consisted of the n-WSe₂ electrode and a Pt foil counter electrode (40 cm²) immersed in a solution of 0.5 M H₂SO₄, 0.5 M Na₂SO₄, 1.0 M NaI and 0.025 M I₂. The path length from the Pyrex window of the cell to the n-WSe₂ electrode was about 1 cm. The n-WSe₂ electrode was irradiated with light from a 450 W xenon lamp which was passed through a 590-nm cut-on and an infrared (water) filter (i.e., only light of wave length longer than 590 nm irradiated the cell). The intensity at the cell window was 150 mW/cm² (which is somewhat higher than the maximum terrestrial solar intensity). Under these conditions I⁻ is photo-oxidized to I_3^- at the WSe₂ and I_3^- is reduced to I⁻ at the Pt counter electrode with the passage of an external current. The short circuit photocurrent was about 65 mA/cm² and the open-circuit photovoltage was about 0.71 V. The i-V curve for this cell, shown in Figure 1, yields a fill factor of 0.46. The maximum power conversion efficiency under these conditions, without corrections

for solution absorbance and electrode and window reflectivities, is about 14%. The short circuit photocurrent was linear with light intensity up to at least 150 mW/cm^2 (Figure 2). Moreover the open circuit photovoltage closely approached its saturation value of 0.7 V at light intensities $\geq$ 10 mW/cm^2. This latter finding and the high fill factor suggests that recombination processes are relatively unimportant for this material. The cell was operated under roughly maximum power conditions for 8 hours. At this time the current and cell voltage were essentially the same as the initial values and the electrode surface showed no apparent change or signs of degradation. (The total amount of electricity passed in this 8-hour trial, about 32 coulombs, would represent on the order of 113 mg of WSe$_2$ lost, assuming a one-electron process, if a photodissolution process occurred.)

While the results here are of a preliminary nature and we have found some sample-to-sample variability with WSe$_2$, they appear to confirm the earlier predictions of Tributsch, et. al. on the potential usefulness of layer-type semiconductors in PEC cells. The nature of the semiconductor surface is also probably of major importance in the attainment of high efficiencies. The investigation of surface pretreatment effects and the application of oriented polycrystalline materials or epitaxial layers of n-WSe$_2$ in iodide media is currently under investigation.
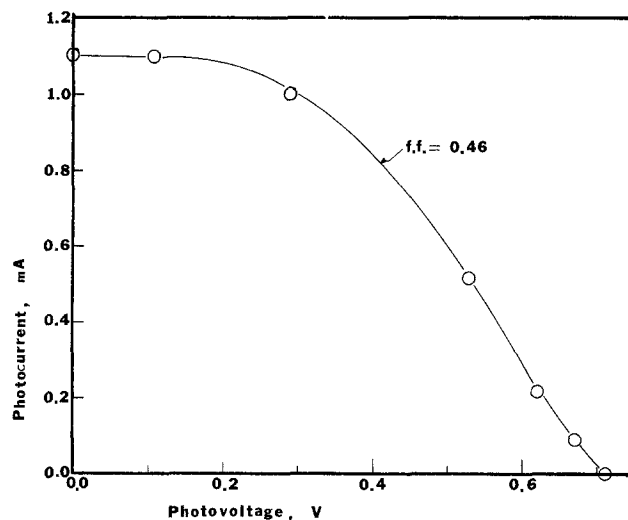
Fig. 1. Photocurrent-photovoltage characteristic of an n-WSe$_2$/0.50 $\underline{M}$ Na$_2$SO$_4$, 0.50 $\underline{M}$ H$_2$SO$_4$, 1.0 $\underline{M}$ NaI, 0.025 $\underline{M}$ I$_2$/Pt PEC cell. Irradiation was with the output (longer than 590 nm and IR filtered) from a 450 W Xe lamp focused onto the photoelectrode. The optical path through the solution is about 1 cm. (f.f. = fill factor).
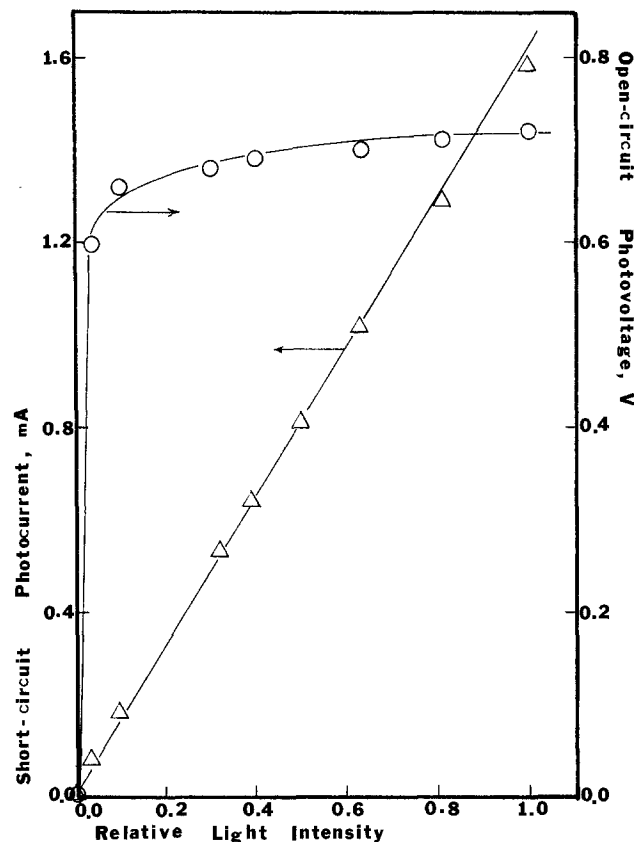

Fig. 2. Open circuit photovoltage and short-circuit photocurrent as functions of light intensity. Conditions as in Fig. 1.

REFERENCES

1. A. J. Nozik, Ann. Rev. Phys. Chem., 29, 189 (1978).
2. D. Laser and A. J. Bard, This Journal, 123, 1027 (1976).
3. A. B. Ellis, S. W. Kaiser, and M. S. Wrighton, J. Am. Chem. Soc., 98, 1635 (1976).
4. T. Inoue, T. Watanabe, A. Fujishima, K. Honda, and K. Kohayaka, This Journal, 124, 719 (1977).
5. B. Miller, A. Heller, M. Robbins, S. Menezes, K. C. Chang, and J. Thompson, This Journal, 124, 1019 (1977).
6. A. B. Ellis, J. M. Bolts, and M.S. Wrighton, This Journal, 124, 1603 (1977).
7. P. A. Kohl and A. J. Bard, This Journal, 126, 603 (1979).
8. H. Gerischer, J. Electroanal. Chem., 82, 133 (1977).
9. A. J. Bard and M. S. Wrighton, This Journal, 124, 1706 (1977).
10. B. A. Parkinson, A. Heller, and B. Miller, This Journal, 126, 954 (1979).
11. H. Tributsch and J. C. Bennett, J. Electroanal. Chem., 81, 97 (1977).
12. H. Tributsch, Ber. Bunsenges. Phys. Chem., 81, 361 (1977).
13. H. Tributsch, ibid., 82, 169 (1978).
14. H. Tributsch, This Journal, 125, 1086 (1978).
15. J. Gobrecht, H. Gerischer, and H. Tributsch, This Journal, 125, 2085 (1978).
16. J. Gobrecht, H. Gerischer, and H. Tributsch, Ber. Bunsenges. Phys. Chem., 82, 1331 (1978).
17. H. Tributsch, H. Gerischer, C. Clemen, and E. Bucher, ibid., 83, 655 (1979).