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ELECTROCHEMICAL PHOTOVOLTAIC CELLS

Final Technical Progress Report for April 15, 1979—April 17, 1980

By
Peter G. P. Ang
Anthony F. Sammells

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Institute of Gas Technology
IIT Center
Chicago, Illinois

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Solar Energy

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ELECTROCHEMICAL PHOTOVOLTAIC CELLS

Project 65021 Final Technical Progress Report
For the Period April 15, 1979, Through April 17, 1980

Peter G. P. Ang
Anthony F. Sammells

Prepared by
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Chicago, Illinois 60616

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INTRODUCTION

The direct conversion of solar energy to electricity can be effectively accomplished via solid-state photovoltaic cells^{1,2} for specific applications where fabrication costs are of minor importance. The technical viability and reliability of such systems (mainly using silicon solar arrays) have been amply demonstrated in the U.S. space program over the last 15 years. If this technology is to find widespread terrestrial application,³ however, and if the cost goals of 50¢/Wp for single-crystal silicon and an installation cost of around \$1500/kWp (in 1975 dollars) are to be achieved by 1986,⁴ dramatic cost reductions will have to be made. Even if such cost goals are met, reliable and economic methods must be found to store the electricity generated from the solid-state cells. At the present time, such electricity storage may be performed by the use of large storage batteries, in the near term by lead acid, where capital storage costs of \$50/kWhr can be predicted, and in the longer term by advanced battery systems such as lithium/metal sulfide,⁵ sodium-sulfur,⁶ zinc chlorine,⁷ or redox systems,⁸ where potentials for lower overall costs have been indicated. Photovoltaic cells used in conjunction with large storage batteries could, therefore, be considered an indirect electrochemical photovoltaic device. Technical and economic viability of both the solid-state photovoltaic cell and large storage batteries have yet to be demonstrated in a practical terrestrial application.

An alternative approach for the collection and storage of solar energy for electric power generation is by use of an electrochemical photovoltaic cell where oxidation and reduction reactions can be effected with species dissolved in an electrolyte at an illuminated semiconductor/electrolyte interface. The basic difference between electrochemical photovoltaic and all solid-state photovoltaic devices is that the oxidation or reduction reactions induced at the semiconductor/electrolyte interface of the electrochemical photovoltaic device are driven by minority carriers generated near the semiconductor surface, whereas direct power generation occurs in all solid-state photovoltaic cells by majority carriers generated within the bulk of the semiconductor.

The objective of this program has been to experimentally identify semiconductor/redox combinations that show promise of achieving solar power conversion efficiencies of 10%, using polycrystalline materials. Such materials will also be used in conjunction with a low-overpotential cathode, where another redox species would be reduced.

Photoelectrochemical cells (PEC) possess several potentially significant advantages over their solid-state photovoltaic counterparts that may give us the opportunity for more convenient storage of the incident photon energy as chemical species. Such chemical species could then be electrochemically discharged for the production of electricity. The formation of the Schottky-like barrier at a semiconductor-liquid junction in these cells is produced simply by immersion of a semiconductor electrode into a redox electrolyte. This is in comparison to a sequence of highly controlled steps necessary for the formation of, for example, a p-n junction in a solid-state cell. To minimize electron-electron hole recombination reactions in solid-state devices, the use of high-purity materials is required to reduce the number of trap sites. For silicon-based solid-state cells, solar conversion efficiencies have been increased by the use of narrower junction depths together with lower surface doping concentrations and antireflection treatments. Power conversion efficiencies achievable with photoelectrochemical cells are beginning to approach those values realized for solid-state photovoltaic devices. Efficiencies for polycrystalline and single-crystal gallium arsenide liquid junction devices have been reported at 7.8%⁹ and 19%¹⁰, respectively.

Regenerative photoelectrochemical cells, where no overall change in the redox electrolyte composition occurs, can be used for the direct generation of electricity. Cells of this type usually consist of an illuminated n-type photoanode and a counterelectrode. Photopotentials and corrosion stabilities for p-type photocathodes have, in general, been lower than for n-type materials.

Liquid-junction devices can be used not only for the direct generation of electrical energy but also for the production of either oxidized or reduced chemical species. As a consequence, the photogeneration of such redox species gives us the opportunity of designing and operating photoelectrochemical cells with a built-in storage capacity. Redox battery technology is compatible with some of the photoelectrochemical systems evaluated in this program.

The origin of photopotentials (and corresponding photocurrents) that develop upon illumination of a photoelectrochemical cell has been adequately documented by others,^{11,12} and requires no detailed explanation here. Empirically the process involves a bending of the semiconductor valence and conduction bands at the interface, which occurs because of an equilibration of Fermi-level differences between the semiconductor and the redox electrolyte. This forms a space-charge layer near the surface of the semiconductor which, because of its inherent electric field, can effect a separation of photoproduced electrons and electron holes. The power conversion efficiency is partly dependent upon the useful light absorbed within the space-charge region.^{13,14} The width of the space-charge region, which is influenced by doping concentration and the voltage drop in the space-charge region, should ideally be equal to, or larger than, the mean reciprocal absorption coefficient. Illumination of photoanodes generates a negative photovoltage by the creation of a net negative charge on the semiconductor. Hence, redox species present at the interface can be oxidized at potentials negative of their equilibrium value. The photopotential, which is the difference between the potential of the illuminated photoanode and the redox equilibrium potential of the counter-electrode, allows electrical power to be extracted from the device upon application of an external load. To a first approximation, the optimum cell potential is determined by the difference between the flat-band potential¹⁵ and the redox potential of the electrolyte. Since the flat-band potential is the most cathodic value the illuminated photoanode can attain, this parameter should ideally be as negative as possible for optimization of the cell voltage. The flat-band potential can be quantitatively related to the electron affinity of the semiconductor,¹⁶ which can be calculated from the atomic electronegativities of the constituent atoms. In practice, because of losses caused by thermal and entropy effects within the space-charge layer upon photon absorption, the initial energy available to drive the photoelectrochemical oxidation or reduction reactions is dictated by the difference between the electron and electron hole quasi-Fermi levels.¹⁷ Several excellent reviews covering the field of photoelectrochemistry have appeared.^{12,18,19,20}

By the substitution of a single-electrolyte photoelectrochemical cell for one containing two redox or electroactive materials separated by an ion-selective membrane, the energy of the incident photon at the photoelectrode can be stored as chemical energy. The design of such cells requires both a

stable low-resistance separator, which minimizes direct chemical reaction of the electroactive species, and the proper selection of redox couples that are able to stabilize the semiconductor. As is well known, photoelectrode stability is dependent upon the relative energy-level positions of electrons, electron holes, and the decomposition potential of the photoelectrode itself. For an illuminated n-type semiconductor, photoanodic corrosion can occur if the quasi-Fermi level for holes is positive of the semiconductor decomposition potential.^{17,21} For a two-electrolyte photoelectrochemical cell to achieve optimum stability, the relative energy levels of the donor redox species ($E_{\text{redox 1}}$) at the photoanode and that of the acceptor species or electroactive material at the counter-electrode ($E_{\text{redox 2}}$), will be required to lie, respectively, negative of the semiconductor decomposition potential and below the lower edge of the conduction band, as shown in Figure 1.

If surface states^{22,23} for the capture of electron holes are present within the semiconductor band gap, reaction of the holes with a redox species may become pinned at a potential more negative than expected and therefore will protect the semiconductor from photoanodic corrosion. The stability of TiO_2 as a photoanode for oxygen evolution has been attributed to this effect. Increased stability for narrow-band-gap photoanodes has been demonstrated also by derivatization of their surface. Most work has been with n-silicon, with surface-attached ferrocene derivatives.²⁴ The objective here is to achieve oxidation of the surface-derivatized group that is faster compared to the kinetics of semiconductor oxidation. Illumination of such photoanodes results in the transient oxidation of the surface-attached group, followed by oxidation of the redox species of interest.

For many semiconductors, their vulnerability to photoanodic corrosion effects can, in part, be attributed to the photoexcitation of electrons from their valence band to their conduction band, which involves bonding orbitals. This can lead to transient bond rupture. Recently²⁵ a new class of semiconductors has been suggested for photoelectrochemical cells that is based upon the transition-metal dichalcogenide-layer compounds. The promise of increased stability against photoanodic corrosion by these materials over other narrow-band-gap candidates comes from the orbitals involved in the electron excitation process. Here photon-induced electron transitions from valence to conduction bands occur predominantly via nonbonding d-d orbitals²⁶⁻³²;

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Figure 1. ENERGY LEVEL DIAGRAM OF AN ILLUMINATED n-TYPE SEMICONDUCTOR/REDOX 1/REDOX 2/COUNTERELECTRODE SYSTEM
(A Diode in the Circuit Prevents Self-Discharge Through the Photoanode in the Dark.)

consequently, phototransitions do not involve bond rupture. N-type MoSe_2 appears as an attractive material for the efficient photoelectrochemical oxidation of halide redox couples. Having a band gap of 1.4 eV, it makes a good match to the solar spectrum. By the introduction of reversible redox couples cathodic of the oxygen potential, long lifetimes have been demonstrated.²⁶

Several photoelectrochemical cells that might facilitate storage have been suggested. Use of third storage electrodes in cells has been proposed,³³⁻³⁵ and two general configurations have been reported. In the first, a storage electrode ($\text{Ag}/\text{Ag}_2\text{S}$) separated from the photoanode and counterelectrode by a cation-specific separator was charged by an illuminated polycrystalline CdSe photoanode, increasing the cathodic activity of the metal sulfide for later electrochemical discharge via a counterelectrode. In a second cell configuration reported by the same workers, two illuminated photoelectrochemical cells were connected electrically in series to achieve sufficient potential for the cathodic deposition of either tin or zinc onto a third electrode. This approach to energy storage has problems that are inherent to many electrochemical devices, whereupon chemical phase changes occur on cycling, resulting in electrode shape change and the inception of dendritic growth, which can possibly lead to cell shorting.

For the PEC systems evaluated in the course of this program the oxidized species produced at the photoanode interface and the corresponding reduced species at the counterelectrode are stored for later electrochemical discharge. The electroactive material at the counterelectrode was either a soluble or an insoluble species. Of the insoluble materials, cadmium is a good candidate because it has demonstrated good electrochemical cycle performance in alkaline-electrolyte cells.

Selection of redox couples for photoelectrochemical cells in this work was based partly upon their previous demonstration of fast electrode kinetics. The redox species also should have high solubilities and ionic conductivities in the electrolyte. Photon absorption by the electrolyte in the wavelength region of interest should be low.

PROGRAM SUMMARY

The overall goals of this program have been to experimentally identify semiconductor photoanode/redox couple systems that a) show promise of meeting acceptable solar efficiencies using polycrystalline materials, and b) have the potential for use in conjunction with a suitable cathode in which another redox species is available for reduction. Such an overall system allows for the convenient removal, storage, and later discharge of reaction products through the use of porous, flow-through redox electrodes.

Increasing solar energy conversion efficiencies and identifying potentially long-life systems were emphasized. Semiconductor/redox couple systems were selected on the basis of the apparent positions of their conduction and valence band energy levels at the interface, together with the semiconductor decomposition potential. Selected redox couples should possess equilibrium potentials that lie negative of the semiconductor decomposition potential and positive of the semiconductor conduction band. Liquid-junction solar cells were characterized using n-MoSe₂, n-MoS₂, n-WSe₂, n-CdSe, and n-GaAs as photoanodes.

Single-crystal n-MoSe₂ was evaluated in a variety of redox electrolytes. Large photocurrents associated with electrode corrosion were observed in HCl bubbled with chlorine. The best photoresponse and stability was found in the electrolyte 1M HBr + 1M Br₂. Under 200 mW/cm² xenon light illumination, photopotentials of about -500 mV, short-circuit currents of 50 mA/cm², power conversion efficiencies of 6.2%, and a 0.55 fill factor were obtained. The crystal has been tested for more than 70 days with no change in its photoelectrochemical properties. The long-term test was limited by the chemical stability of the insulating wax layer. Photocharge and electrochemical discharge of the storage system n-MoSe₂/1M HBr + 0.01M Br₂/Nafion 315/1M HI + 0.18M I₂/Pt have been demonstrated. The bromine-iodine redox-storage system with platinum electrodes demonstrated a polarization resistance of 20Ω-cm² and an electrochemical charge-discharge cycling efficiency of 75%.

Single-crystal as well as natural-crystal MoS₂ showed good photoresponses in 1M HBr + 1M Br₂. The single crystal demonstrated photopotentials up to -555 mV and a short-circuit current of 42 mA/cm² under 200 mW/cm² xenon light. The natural crystal showed a photopotential up to -425 mV and a short-circuit

current of 17 mA/cm^2 . This natural crystal has demonstrated long-term stability for more than 12 days.

An n-type WSe_2 semiconductor was also tested. This electrode developed a photopotential of -590 mV and generated a short-circuit current up to 32 mA/cm^2 under 200 mW/cm^2 xenon light. A power conversion efficiency of about 4.1% and a fill factor of 0.43 were calculated. The long-term performance of this single crystal was studied at a constant-current load of 5 mA/cm^2 under 100 mW/cm^2 quartz-halogen illumination. Its potential versus platinum in $0.5\text{M H}_2\text{SO}_4 + 0.5\text{M Na}_2\text{SO}_4 + 1.0\text{M NaI} + 0.025\text{M I}_2$ was stable during the 1-week test.

Single-crystal n-GaAs was evaluated in several redox electrolytes. Large photopotentials and photocurrents were obtained; however, most of these were associated with photoanodic corrosion. Relatively good stability was found in the electrolyte $1\text{M Na}_2\text{Se} + 0.1\text{M Se} + 1.0\text{M NaOH}$. The open-circuit potential under illumination was -500 mV versus platinum. A short-circuit current of 16 mA/cm^2 , power conversion efficiency of about 4%, and a fill factor of 0.53 were measured. The doping and quality of the GaAs crystal was not optimum, however. A storage system of configuration n-GaAs/ $1\text{M Na}_2\text{Se} + 0.1\text{M Se} + 1\text{M NaOH}$ /Nafion/ $2\text{M NaOH}/\text{Cd}$ was assembled. The photocharge and discharge of this system were demonstrated.

Polycrystalline n-CdSe made by thermal vacuum evaporation has been evaluated. The performance and the stability of this material were strongly influenced by the nature and morphology of the substrate used. Best results were obtained by using porous titanium as a substrate. Photopotentials of -400 mV were achieved under 100 mW/cm^2 xenon light illumination. A short-circuit current density of about 20 mA/cm^2 and a power conversion efficiency of 4% were calculated. The fill factor was 0.45. The use of porous substrates had the advantage of greater CdSe adhesion and a more effective photoanode area available for illumination. The photoelectrochemical storage system n-CdSe/ $1\text{M Na}_2\text{S} + 1\text{M S} + 1\text{M NaOH}$ /Nafion/ $1\text{M Na}_2\text{Se} + 0.1\text{M Se} + 1\text{M NaOH}$ /platinized Pt and n-CdSe/ $1\text{M NaOH} + 1\text{M Na}_2\text{S} + 1\text{M S} + 0.1\text{M Na}_2\text{Se} + 0.01\text{M Se}$ /Nafion/ $2\text{M NaOH}/\text{Cd}$ were evaluated. Photocharge and electrochemical discharge have been demonstrated with both systems.

As part of the overall strategy of this program to identify efficient electrochemical photovoltaic systems for the conversion of solar energy where storage is feasible, work was also performed on an all-solid-state electrochemical photovoltaic cell containing in-situ energy storage. Here the solid-state system consisted of a homogeneous matrix cell, in which the crystal lattice structure of the reductant, oxidant, and solid electrolyte are similar. The reductant and oxidant electrodes should ideally exhibit both ionic and electronic conductivity, whereas the solid electrolyte will possess only ionic conductivity. The reductant and oxidant electrodes should contain selected redox species introduced into fixed lattice positions, where they will be expected to be immobile. The ability of this type of solid-state device to accommodate a reasonable charge capacity depends upon the solid electrolyte's possession of a larger concentration of mobile cations than is required for ionic conductivity. The solid electrolytes investigated for this solid-state device have included sodium beta alumina, rubidium silver iodide, and lithium iodide.

We have demonstrated photoactivity at the RbAg_4I_5 /cond. glass interface. Its potential can increase by several hundred millivolts upon illumination of some darkened spots at the interface. This positive photopotential could be a Dember-type photovoltage. The photoresponse was detected at wavelengths between 300 and 700 nm, with a peak at about 425 nm. Photocurrents in the cathodic as well as in the anodic direction were recorded from this interface. This process may be associated with redox reactions involving iodine at the surface of the solid electrolyte.

When CdSe was in contact with RbAg_4I_5 solid electrolyte containing iodine redox species, negative photopotentials and anodic photocurrents were detected. This is analogous to the behavior of n-type semiconductor liquid-junction solar cells. The photoresponse of the CdSe/solid electrolyte interface was seen at wavelengths up to about 800 nm, which corresponds closely to the 1.7 eV band-gap of CdSe. A small positive photopotential near 300 nm was seen in this system. This was attributed to the photoactivity of the RbAg_4I_5 solid electrolyte.

TASK OBJECTIVES AND ACHIEVEMENTS

Task 1. Identification of High-Efficiency Electrochemical Photovoltaic CellsTask 1.1. Selection of Candidate Semiconductor/Redox Couples

In alkaline electrolytes the semiconductor/redox couples selected for evaluation have included —

- a. CdSe with S^{2-}/S_n^{2-} or Se^{2-}/Se_2^{2-} as donors and Te^{2-}/Te_2^{2-} or $Cd/Cd(OH)_2$ as the acceptor
- b. GaAs with Se^{2-}/Se_2^{2-} as the donor and Te^{2-}/Te_2^{2-} or $Cd/Cd(OH)_2$ as the acceptor
- c. $MoSe_2$ with Br^-/Br_2 or Cl^-/Cl_2 as the electron donor and I^-/I_2 as the candidate electron acceptor
- d. MoS_2 with Br^-/Br_2 or Cl^-/Cl_2 as the electron donor and I^-/I_2 as the candidate electron acceptor
- e. WSe_2 with Br^-/Br_2 or I^-/I_2 as the donor and I^-/I_2 as the acceptor

In acid electrolytes, semiconductor/redox couples selected for evaluation have included —

- a. GaAs with Cu^+/Cu^{+2} , Sn^{+2}/Sn^{+4} , and Ti^{+3}/Ti^{+4} as candidate donor couples to be used in conjunction with Cr^{+2}/Cr^{+3} and Ti^{+2}/Ti^{+3} as acceptors at the cathode
- b. MoS_2 with Fe^{+2}/Fe^{+3} , Sb^{+3}/Sb^{+5} , and Br^-/Br_2 as candidate donors at the photoanode together with Cu^+/Cu^{+2} , Sn^{+2}/Sn^{+4} , and Ti^{+3}/Ti^{+4} as acceptors at the cathode
- c. $MoSe_2$ with Fe^{+2}/Fe^{+3} , Sb^{+3}/Sb^{+5} , Br^-/Br_2 , and I^-/I_2 as donors at the photoanode and Cu^+/Cu^{+2} , Sn^{+2}/Sn^{+4} , and Ti^{+3}/Ti^{+4} as acceptors at the cathode
- d. MoS_2 with Br^-/Br_2 or Cl^-/Cl_2 as donors and I^-/I_2 as the acceptor
- e. $MoSe_2$ with Br^-/Br_2 or Cl^-/Cl_2 as donors and I^-/I_2 as the acceptor
- f. WSe_2 with Br^-/Br_2 or I^-/I_2 as donors and I^-/I_2 as the acceptor.

Task 1.2. Electrochemical Measurements on Selected Single-Crystal Semiconductor/Redox Couples

The objective of this task was to evaluate the photoelectrochemical performance of single-crystal materials. Data obtained in this task were used as a guideline for analyzing the performance of the polycrystalline materials evaluated later in Task 1.3.

Single-crystal materials were ordered from the following sources:

- a. CdS, CdSe, and CdTe from Cleveland Crystals, Inc. The n-type semiconductors had the dimensions $1 \times 10 \times 10$ mm, where the 10×10 mm surface was oriented perpendicular to the c axis and the resistivity was about 1 ohm-cm.
- b. n-type GaAs from Crystal Specialties, Inc. The crystal size was $1 \times 10 \times 10$ mm, with the 10×10 mm surface in the 111 direction. The resistivity was 0.003 ohm-cm, carrier concentration was $10^{17}/\text{cm}^3$.
- c. MoSe₂ and MoS₂ single crystals from Prof. Dr. Rudolf Nitsche, University of Freiburg, Federal Republic of Germany.

The photoelectrochemical properties of the semiconductors were investigated by using a Wenking ST72 potentiostat and an Oriel 150-watt xenon light source. A schematic of the experimental setup is shown in Figure 2. The electrode potential was measured using a Wenking PPT-70 electrometer. A Tacussel-type GSTP2B pulse-sweep generator was used to control the potentiostat. The forward (anodic) and backward sweep was usually completed within 20 seconds. The current-voltage relationships of the electrodes were recorded on a Hewlett-Packard 7046 X-Y recorder.

n-MoSe₂ Single-Crystal Data

Molybdenum diselenide has already been reported to be an interesting photoelectrode with demonstrated corrosion resistance.²⁶ The single-crystal surface used in this work was the 001 plane formed by the hexagonal a_1 and a_2 axes.

Upon immersion of the MoSe₂ single crystal in the electrolyte 6M KOH + 1M NaI, photopotentials on the order of -10 mV were observed. Addition of iodine crystals to the solution increased the photopotential to about -250 mV, and a large photocurrent could be detected. The current-potential characteristics of the MoSe₂ crystal under 200 mW/cm² xenon light illumination are shown in Figure 3. The electrode potential was measured against a platinum foil counter

1. LIGHT SOURCE (150-W Xenon)
2. FILTER/MONOCROMATOR
3. QUARTZ CELL
4. WORKING ELECTRODE (Photoanode)
5. Hg/HgO REFERENCE-ELECTRODE
6. COUNTERELECTRODE
7. WENKING ST72 POTENTIOSTAT
8. TACUSSEL GSTP2B PROGRAMMER
9. WENKING PPT70 ELECTROMETER
10. HEWLETT-PACKARD X-Y-RECORDER

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Figure 2. SCHEMATIC DIAGRAM OF THE
PHOTOELECTROCHEMICAL MEASUREMENT SYSTEM

Figure 3. ANODIC PHOTOCURRENT OF MoSe_2 SINGLE CRYSTAL
IN A CELL MADE OF $\text{MoSe}_2/6\text{M KOH} + 1\text{M I}^-/\text{I}_2/\text{Pt}$

electrode. No correction was made for the light absorption in the electrolyte (1-cm path length) or for losses due to the reflection of light at the electrode surface. Under these experimental conditions, the photoanode appeared relatively stable against photoanodic dissolution. A slight granulation of the surface became apparent, however, after a few hours of operation at 30 mA/cm².

The photoelectrochemical performance of MoSe₂ in 6M HBr + 1M Br₂ is shown in Figure 4. Large photopotentials of about -470 mV and short-circuit currents of about 53 mA/cm² were detected. A power conversion efficiency of about 5% could be obtained with this photoanode — that is, a cell voltage of 0.3 volt at 33 mA/cm². The same electrode was also evaluated in the alkaline electrolyte 6M KOH + 1M KBr + 1M Br₂. Here the photopotential was only -185 mV, although the current-potential curve (Figure 5) still appeared to be good. The short-circuit current was about 28 mA/cm², that is, approximately 50% of the value in acid electrolyte. Near the resting potential, the photocurrent in the alkaline electrolyte did not rise as fast as in the acid electrolyte. The data indicate that the rate of Br⁻ photooxidation on MoSe₂ may be faster in acid than in an alkaline medium. In conjunction with this, the redox reaction of Br⁻/Br₂ on a platinized platinum electrode was studied at three different electrolyte pH ranges (Figure 6). The current densities obtained in the acid electrolyte 1M HBr + 1M Br₂ (Curve 1) were larger than the current densities in alkaline electrolyte 1M KBr + 1M Br₂ + KOH (Curve 2) or in neutral electrolyte 1M KBr + 1M Br₂ + 0.1M KOH (Curve 3). In the alkaline region the salt was not completely soluble. These results create an incentive to operate the MoSe₂ photoanode system in an acid electrolyte rather than in alkaline or neutral mediums.

MoSe₂ single crystals were also evaluated with selected redox couples in 6M HCl. The preliminary photoelectrochemical characteristics with the couples Fe⁺²/Fe⁺³, Cu⁺¹/Cu⁺², Sb⁺³/Sb⁺⁵, and Sn⁺²/Sn⁺⁴ are shown in Figures 7, 8, 9, and 10, respectively. As can be seen, photopotentials on the order of -100 to -200 mV were observed. In particular, large anodic photocurrents were observed in the presence of Cu⁺¹/Cu⁺² and Sn⁺²/Sn⁺⁴, but only small photocurrents were seen with Fe⁺²/Fe⁺³ and Sb⁺³/Sb⁺⁵. This is rather surprising, because the kinetics of Fe⁺²/Fe⁺³ are usually very fast.³⁶ In the presence of Fe⁺²/Fe⁺³ and Sb⁺³/Sb⁺⁵, the open-circuit potential of the MoSe₂ electrode in the dark was

Figure 4. CURRENT-POTENTIAL CHARACTERISTICS OF MoSe₂ SINGLE CRYSTAL
IN 6M HBr + 1M Br₂

Figure 5. CURRENT-POTENTIAL CHARACTERISTICS OF MoSe₂ SINGLE CRYSTAL
IN 6M KOH + 1M KBr + 1M Br₂

Figure 6. POTENTIAL-SWEEP (40 mV/s) POLARIZATION CURVES OF
PLATINIZED PLATINUM AT 25°C IN —
1) 1M HBr + 1M Br₂, pH 0.1; 2) 1M KBr + 1M Br₂ + KOH, pH 13.2;
3) 1M KBr + 1M Br₂ + 0.1M KOH, pH 6.9

Figure 7. CURRENT-POTENTIAL CHARACTERISTICS OF MoSe₂ SINGLE CRYSTAL IN 6M HCl + 1M Fe⁺²/Fe⁺³

Figure 8. CURRENT-POTENTIAL CHARACTERISTICS OF MoSe₂ SINGLE CRYSTAL IN 6M HCl + 1M Cu⁺¹/Cu⁺²

Figure 9. CURRENT-POTENTIAL CHARACTERISTICS OF MoSe₂ SINGLE CRYSTAL IN 6M HCl + 1M Sb⁺³/Sb⁺⁵ (The Light Was Chopped at a Frequency of 1.3/s.)

Figure 10. CURRENT-POTENTIAL CHARACTERISTICS OF MoSe₂ SINGLE CRYSTAL IN 6M HCl + 1M Sn⁺²/Sn⁺⁴.

found to be within ± 150 mV from the platinum electrode in the same solution, indicating irreversibility of the photoanode. Under similar experimental conditions, the redox couples $\text{Cr}^{+2}/\text{Cr}^{+3}$ and $\text{Ti}^{+3}/\text{Ti}^{+4}$ were evaluated. In both cases the photopotentials were only -2 and -5 mV, respectively, and photocurrents of only a few microamperes were seen.

To achieve a more effective contact to the MoSe_2 single crystal, silver was electrodeposited to its rear surface from a silver nitrate solution. A platinum-wire current collector could then be contacted effectively to the silver layer of the crystal with a conducting silver epoxy. This better contact was found to greatly improve the performance of the photoelectrode. The photoelectrochemical performance in the electrolyte $1\text{M HBr} + 1\text{M Br}_2$ is shown in Figure 11. In the dark, its equilibrium potential versus a platinum electrode was -5 mV; upon illumination the potential shifted to -490 mV. A short-circuit current of about 63 mA/cm^2 was measured. Without corrections for electrolyte absorption losses, the photoanode could be operated with a power conversion efficiency of 6.7% and a fill factor of 0.44 under approximately 200 mW/cm^2 xenon light illumination.

Transient potentiostatic techniques were performed on single-crystal MoSe_2 in $1\text{M HBr} + 1\text{M Br}_2$ as shown in Figure 12. There, a 100-mV anodic potential pulse of 10-ms duration was applied to the electrode, starting from the resting potential under xenon light illumination of approximately 200 mW/cm^2 . The resulting transient current was recorded on the scope of a Model 4202 PAR signal averager. The steady-state level was reached within 2 ms after the initiation of the pulse, and its value was only slightly lower than the peak initial value. This behavior indicates that mass transfer loss in this electrolyte is minimal. The electrolyte was not stirred during the experiment. The activation current can be obtained from the pulse experiment by extrapolating the current to time zero. These values obtained at different voltage pulses are plotted in Figure 13. The data in the low-overpotential region indicate an apparent exchange-current density of about 4.5 mA/cm^2 . This value will still depend on light intensity, concentration of the redox couple, and the electrolyte temperature.

Figure 11. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL MoSe_2 IN 1M HBr + 1M Br_2 (200 mW/cm^2 Xenon Light Illumination, E_{Pt} vs. SCE = 790 mV, Efficiency = 6.7%, Fill Factor = 0.44)

Figure 12. PHOTOCURRENT OF MoSe_2 SINGLE CRYSTAL DURING A TRANSIENT-PULSE EXPERIMENT IN 1M HBr + 1M Br_2 (A 100-mV Voltage Pulse Was Applied at Time Zero, Starting From the Open-Circuit Photopotential Under 200 mW/cm^2 Xenon Light Illumination.)

Figure 13. PLOT OF INITIAL PHOTOCURRENT OF MoSe_2 SINGLE CRYSTAL AS A FUNCTION OF THE AMPLITUDE OF THE TRANSIENT PULSE (Electrolyte: 1M HBr + 1M Br_2 , 27°C)

In 6M HCl saturated with chlorine, the potential of the MoSe₂ in the dark was 90 mV, whereas under illumination it was -650 mV versus Pt. The photoelectrochemical current-voltage characteristics are shown in Figure 14. The short-circuit current density was 110 mA/cm². From this a power conversion efficiency of about 9.9% was calculated, together with a fill factor of 0.32. This relatively low fill factor was due to the slow rise of the photocurrent near the resting potential. Later examination of the single crystal showed evidence of corrosion, which probably contributed in part to the observed high short-circuit current.

With this type of semiconductor it is well known that conduction parallel to the surface of the Van der Waals ^{9,37} plane is higher than conduction from layer to layer in the crystal. It was anticipated that partial front-surface contact would reduce the series resistance of the electrode assembly. Therefore, the silver epoxy was also allowed to contact the edges of the front surface with appropriate insulation. This photoanode was then evaluated in the redox electrolyte 1M HBr + 1M Br₂ inside a small glass cuvette. The initial open-circuit potential versus a platinum reference electrode in the same electrolyte was -130 mV in the dark and -480 mV under 200 mW/cm² illumination. The crystal was then subjected to an anodic polarization treatment at about 1 volt, whereby a current of about 5 mA/cm² flowed in the dark. After anodizing for about 1 hour, the open-circuit potential in the dark became -30 mV versus platinum, i.e., approaching more ideal behavior. This anodization technique may have passivated the steps and other imperfections of the crystal surface, perhaps by the formation of a passivating oxide layer. The current-potential characteristics of this crystal are shown in Figure 15. Here the open-circuit potential under 200 mW/cm² illumination was -490 mV versus the platinum electrode. Short-circuit current densities of about 50 mA/cm² were achieved. The power conversion efficiency was 6.2%, and the fill factor 0.55.

To identify a photoelectrochemical cell capable of being charged, using n-MoSe₂ in Br⁻/Br₂ redox electrolyte, for example, it is necessary to identify acceptor redox couples having standard potentials within 500 mV negative of Br⁻/Br₂ that also possess fast kinetics for electron exchange. It would also be desirable that the acceptor have similar charge polarity to that of the donor so that effective separation of the two redox species might be achieved using, for example, a cation exchanger membrane. As a consequence, the

Figure 14. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL MoSe_2 IN $1\text{M HCl} + 1\text{M Cl}_2$ (200 mW/cm^2 Xenon Light Illumination, E_{Pt} vs. SCE = 1140 mV , Efficiency = 9.9% ; Fill Factor = 0.32)

Figure 15. CURRENT-POTENTIAL AND POWER-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL MoSe_2 IN 1M HBr + 1M Br_2 (200 mW/cm^2 Xenon Light Illumination, $E_{\text{dark}} = -30 \text{ mV}$, $E_{\text{light}} = -490 \text{ mV}$ vs. Pt, $E_{\text{Pt}} = 810 \text{ mV}$ vs. SCE, $\eta = 6.2\%$, $\text{FF} = 0.55$, $i_{\text{sc}} = 49 \text{ mA/cm}^2$)

$\text{Br}^-/\text{Br}_2\text{-I}^-/\text{I}_2$ redox storage system was considered in a cell. Here, the photoanode was in contact with the bromine redox electrolyte while the iodine redox electrolyte at the counterelectrode was at about 500 mV negative of the bromine potential. The actual cell voltage will, of course, be dictated by the relative activities of the redox species present.

A cell of configuration $\text{MoSe}_2/1\text{M HBr} + 0.01\text{M Br}_2/\text{Nafion 315}/1\text{M HI} + 0.18\text{M I}_2/\text{Pt}$ was assembled in a two-cuvette cell as shown schematically in Figure 16. The volume of the redox electrolyte in each cuvette was 2 ml. The illuminated photoanode surface area was 0.2 cm^2 , and that of the platinum foil electrode in the iodine compartment was 2 cm^2 . Another set of 2 cm^2 platinum electrodes in each compartment was used for monitoring the cell voltage and for cell discharge. Upon shorting the MoSe_2 photoanode to its counterelectrode in the other compartment, a cell discharge current of about 0.2 mA passed. Upon illumination with approximately 200 mW/cm^2 xenon light, however, the current direction reversed and a photocurrent of about 0.8 mA flowed, charging the bromine-iodine cell. Thus, the system could be charged photoelectrochemically and discharged electrochemically upon demand.

A sequence of charge-discharge cycles is shown in Figure 17. Here, the redox cell was initially charged photoelectrochemically for about 6 hours. During this period the charging photocurrent dropped from 0.8 to 0.5 mA while the cell voltage, as measured by the auxiliary platinum electrodes, rose from 0.45 to about 0.49 V. Discharge of the cell using a 10Ω load across the auxiliary platinum electrodes resulted in an initial current of 15 mA. After approximately 1 hour this current dropped to 1 mA. The cell voltage between the auxiliary platinum electrodes also decreased from 0.49 to about 0.03 V. Upon returning to open-circuit the cell voltage was recorded as 0.45 V. The system was charged again by illuminating the photoanode for about 16 hours. Subsequent to this extended photocharge, the initial cell current and voltage during electrochemical discharge were improved, as illustrated on the right-hand side of Figure 17. This was a consequence of the higher bromine and iodide activities present after photoelectrochemical charge. The state of charge of the Br^-/Br_2 electrolyte could also be seen visually. During charge the initially yellow redox electrolyte became darker in appearance. By using a smaller load for discharge, for example, 200Ω cell currents of about 1 mA at 0.3 V could be drawn from the system for many hours.

1. Two cuvettes clamped together
2. Separator
3. n-type photoanode
4. Counterelectrode
5. Discharge electrodes
6. Sealed caps

Figure 16. SCHEMATIC DIAGRAM OF THE PHOTOELECTROCHEMICAL STORAGE CELL SYSTEM

Figure 17. CURRENT AND VOLTAGE OF THE REDOX STORAGE SYSTEM
 $\text{MoSe}_2/1\text{M HBr} + .01\text{M Br}_2/\text{Nafion 315}/1\text{M HI} + 0.18\text{M I}_2/\text{Pt}$ DURING
 PHOTOELECTROCHEMICAL CHARGE UPON ILLUMINATION (200 mW/cm^2 Xenon Light) OF THE
 MoSe_2 (0.2 cm^2) AND DURING DISCHARGE THROUGH A PAIR OF PLATINUM (2 cm^2 Each)
 ELECTRODES WITH 10Ω LOAD (Cell Voltage Was Measured Between the Platinum
 Electrodes. Electrolyte -2 ml in Each Compartment— Was Unstirred, and
 Temperature $27^\circ\text{C}.$)

The current-voltage characteristics of a $\text{Br}^-/\text{Br}_2\text{-I}^-/\text{I}_2$ redox storage cell upon electrochemical charge and discharge using a smooth platinum electrode is shown in Figure 18. Nafion 315 was found quite effective as a cell separator for preventing direct chemical reaction between the redox species. The polarization resistance calculated from the slope was $20 \Omega\text{-cm}^2$. For over 90 continuous charge-discharge cycles (of 48 minutes duration per half cycle) at 5 mA/cm^2 , electrochemical energy efficiencies of 75% were achieved.

n-MoS₂ Single-Crystal Data

The photoelectrochemical properties of single-crystal MoS₂ (0.5 mm thickness and 0.1 cm^2 effective area) in the redox electrolytes 1M HBr + 1M Br₂ and 0.02M HI + 0.02M I₂ are shown in Figures 19 and 20, respectively. Transient photocurrents were observed in the electrolyte with the I^-/I_2 couple. Here the steady-state photocurrents were much smaller than the results obtained with the Br^-/Br_2 redox electrolyte. The concentration of I^-/I_2 redox couple was kept low (0.02M), as the solution became darker at higher concentrations. Photopotentials of about -375 mV and a steady-state short-circuit current of about 0.6 mA/cm^2 were recorded in electrolyte containing the I^-/I_2 redox couple. In the Br^-/Br_2 redox electrolyte, photopotentials up to -555 mV and a short-circuit current of about 42 mA/cm^2 were achieved. The MoS₂ crystal was also tested in the electrolyte 6M HCl + 1M $\text{Fe}^{+2}/\text{Fe}^{+3}$. Photopotentials of about -140 mV and a short-circuit current of about 0.8 mA/cm^2 were obtained; the current-potential characteristics are shown in Figure 21. A similar photo-response was exhibited by MoSe₂ in $\text{Fe}^{+2}/\text{Fe}^{+3}$ redox electrolyte, as discussed earlier.

Naturally occurring MoS₂ crystals, obtained from Climax Molybdenum Company, were also investigated as photoanodes. The specimen exhibited a very good photoresponse in acid electrolyte containing Br^-/Br_2 redox couple. Photopotentials up to -425 mV and short-circuit currents around 17 mA/cm^2 were observed, as shown in Figure 22.

Some of the photoelectrochemical properties of MoSe₂ and MoS₂ photoanodes evaluated in this work are compared in Table 1.

Figure 19. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL MoS_2 IN $1\text{M HBr} + 1\text{M Br}_2$

Figure 20. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL MoS_2 IN $0.02\text{M HI} + 0.02\text{M I}_2$

Figure 21. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL MoS_2 IN $6\text{M HCl} + 1\text{M Fe}^{2+}/\text{Fe}^{3+}$

Figure 22. CURRENT-POTENTIAL CHARACTERISTICS OF NATURAL MoS_2 IN $1\text{M HBr} + 1\text{M Br}_2$

Table 1. COMPARISON OF THE PHOTOELECTROCHEMICAL PROPERTIES OF MoSe_2 AND MoS_2 SEMICONDUCTORS IN VARIOUS REDOX ELECTROLYTES

Electrode	Electrolyte	E_l^a	E_d^b	E_{Pt}^c	E_{ph}^d	I_{sc}^e
		mV				mA/cm^2
MoSe_2	6M HBr + 1M Br_2	-550	-80	785	-470	53
MoSe_2	6M KOH + 1M KBr + 1M Br_2	-550	-365	415	-185	28
MoSe_2	1M HBr + 1M Br_2	-490	-5	790	-485	63
MoSe_2	6M HCl + Cl_2	-650	-90	1140	-560	110
MoSe_2	1M KCl + Cl_2	-610	-135	1130	-475	62
MoSe_2	6M KOH + 1M KCl + Cl_2	-450	-60	410	-390	74
MoSe_2	6M KOH + 1M NaI + I_2	-300	-50	-80	-250	20
MoSe_2	6M HCl + 1M $\text{Cu}^{+1}/\text{Cu}^{+2}$	-250	0	--	-250	0
MoSe_2	6M HCl + 1M $\text{Sb}^{+3}/\text{Sb}^{+5}$	-250	-150	525	-100	0.07
MoSe_2	6M HCl + 1M $\text{Sn}^{+2}/\text{Sn}^{+4}$	-200	-80	--	-120	1.35
MoSe_2	6M HCl + 1M $\text{Fe}^{+2}/\text{Fe}^{+3}$	-200	-50	680	-150	0.4
MoSe_2	6M HCl + 1M $\text{Cr}^{+2}/\text{Cr}^{+3}$	-150	-148	400	-2	0.002
MoSe_2	6M HCl + 1M $\text{Ti}^{+3}/\text{Ti}^{+4}$	-125	-120	120	-5	0.002
MoSe_2	6M KOH + 1M SeO_2 + 1M Na_2Se	-10	150	-475	-160	0.24
MoSe_2	1M KI + 0.1M I_2	-536	-5	275	-531	32
MoSe_2	CH_3CN + 0.25M $(\text{C}_2\text{H}_5)_4\text{NCl}$ + Cl_2	-440	-25	--	-425	21
MoS_2	1M HBr + 1M Br_2	-575	-20	795	-555	42
MoS_2	.02M HI + .02M I_2	-375	+10	230	-385	0.6
MoS_2	6M HCl + 1M $\text{Fe}^{+2}/\text{Fe}^{+3}$	-210	-70	680	-140	0.8
MoS_2 (nat)	6M HCl + Cl_2	-625	-405	1140	-220	14
MoS_2 (nat)	1M KCl + Cl_2	-595	-240	1125	-300	18

^a E_l = electrode potential with light vs. platinum in the same solution.

^b E_d = electrode potential in the dark vs. platinum in the same solution.

^c E_{Pt} = the potential of the platinum vs. saturated calomel electrode.

^d E_{ph} = photopotential = $E_l - E_d$

^e I_{sc} = current density of the working electrode at E_d .

n-GaAs Single-Crystal Data

GaAs single crystals (111 orientation) were evaluated in alkaline and acid electrolytes. The current-potential characteristics of the GaAs single crystal in alkaline redox electrolytes 6M KOH + 0.25M SeO_2 + 0.25M Na_2Se , 6M KOH + 1M I^-/I_2 , and 6M KOH + 1M Br^-/Br_2 are shown in Figures 23, 24, and 25, respectively. Large photocurrents were recorded. However, with Br^-/Br_2 the electrode surface became dark, indicating rapid photoanodic decomposition of the crystal. The photopotentials were in the range of about 500 mV. The dark open-circuit potential in I^-/I_2 was -680 mV versus a platinum reference electrode present in the same electrolyte. For electrolytes containing Br^-/Br_2 , this value was -1400 mV. These large values may indicate an irreversible electrode behavior associated with corrosion potential.

The GaAs crystal was also evaluated in acid electrolytes. Figures 26 through 29 show its performance in 6M HCl + 1M $\text{Fe}^{+2}/\text{Fe}^{+3}$, 6M HCl + 1M $\text{Cr}^{+2}/\text{Cr}^{+3}$, 6M HCl + 1M $\text{Sn}^{+2}/\text{Sn}^{+4}$, and 6M HCl + 1M $\text{Cu}^{+1}/\text{Cu}^{+2}$. The photopotentials are -400, -370, -15, and -140 mV in $\text{Fe}^{+2}/\text{Fe}^{+3}$, $\text{Cr}^{+2}/\text{Cr}^{+3}$, $\text{Sn}^{+2}/\text{Sn}^{+4}$, and $\text{Cu}^{+1}/\text{Cu}^{+2}$ redox couples, respectively. In electrolytes containing $\text{Sn}^{+2}/\text{Sn}^{+4}$, the electrode became dark after the potential sweep experiment. Some red deposits (Cu) were seen after testing in electrolytes containing $\text{Cu}^{+1}/\text{Cu}^{+2}$. The deposition may have occurred when cathodic currents flowed during the potential scan in the dark. As seen in Figures 28 and 29, the dark current in $\text{Sn}^{+2}/\text{Sn}^{+4}$ and in $\text{Cu}^{+1}/\text{Cu}^{+2}$ redox electrolytes is quite significant.

Photopotentials of -245, -510, and -420 mV were observed in 6M HCl + 1M $\text{Ti}^{+3}/\text{Ti}^{+4}$, 6M HCl + 0.1M KI + 0.1M I_2 , and 6M HBr + 1M Br_2 , respectively. The current-potential curves are shown in Figures 30, 31, and 32, respectively. Quite large photocurrents were seen, but usually the electrode darkened after the test, indicating photoanodic decomposition. The crystal was also evaluated in 6M HCl + 1M SbCl_3 + 1M SbCl_5 . At ambient temperature the salts did not appear to be completely soluble. The crystal had a dark potential of -555 mV versus the platinum electrode, with the potential becoming -875 mV under illumination. The current-potential characteristics are shown in Figure 33. Although large photocurrents were obtained, the large dark potential suggested irreversible electrode behavior as a probable consequence of photoanode corrosion. Most of the data described above were obtained in the

Figure 23. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M KOH + 0.25M SeO₂ + 0.25M Na₂Se

Figure 24. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M KOH + 1M I^-/I_2

Figure 25. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M KOH + 1M Br^-/Br_2

Figure 26. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M HCl + 1M Fe²⁺/Fe³⁺

Figure 27. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M HCl + 1M Cr²⁺/Cr³⁺

Figure 28. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M HCl + 1M $\text{Sn}^{+2}/\text{Sn}^{+4}$

Figure 29. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs In 6M HCl + 1M $\text{Cu}^{+1}/\text{Cu}^{+2}$

Figure 30. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN
6M HCl + 1M $\text{Ti}^{+3}/\text{Ti}^{+4}$

Figure 31. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M HCl + 0.1M KI + 0.1M I₂

Figure 32. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M HBr + 1M Br₂

Figure 33. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M HCl + 1M SbCl₃ + 1M SbCl₅

early stages of the program, where contact to the GaAs crystal was not optimized. This might cause the slow onset of the photocurrent (low fill factor), which was often observed. The experiments were performed under high light intensity (200 mW/cm^2) so that detection of photoanodic corrosion could be accelerated.

Further work was performed using single-crystal n-type GaAs (Si-doped) obtained from Crystal Specialties Inc. The surface was oriented in the 111 direction and had an unoptimized dopant concentration of $1.3 \times 10^{18} \text{ cm}^{-3}$. Ohmic contact was made by electroplating indium and gold and annealing it at 400°C under hydrogen for two hours. The crystal was attached to a platinum wire using a silver epoxy and the whole assembly was coated with epoxy. The photoanode was etched for 10 to 15 seconds with a 1:1 mixture of 30% $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$ to matte black and dipped in 0.01M $\text{RuCl}_3 + 0.1\text{M HNO}_3$ solution for 10 seconds to improve its performance.³⁸ The photoelectrochemical performance of this photoanode was evaluated in the redox electrolyte 1M $\text{Na}_2\text{Se} + 0.1\text{M Se} + 1.0\text{M NaOH}$. The current-voltage characteristics are shown in Figure 34. The open-circuit potentials in the dark and under 100 mW/cm^2 xenon illumination were respectively -190 and -500 mV . A short-circuit current of 16 mA/cm^2 , power conversion efficiency (uncorrected for redox electrolyte absorption) of about 4%, and a fill factor of 0.53 were measured. The doping and quality of this photoanode was not optimum. Large efficiencies have been previously reported with single-crystal GaAs treated with ruthenium ion chemisorption, where solar conversion efficiencies of 12% have been observed.³⁸ It appears, however, that the greatest enhancements in efficiencies after ruthenium treatment have been observed with polycrystalline materials. Introduction of ruthenium ions onto the surface of a chemically vapor-deposited polycrystalline GaAs has resulted in solar energy conversion efficiencies up to 7.8%.⁹ Increased fill factors after such treatment³⁹ have been shown to result from reduction of the number of carrier trap sites, by the use of charge-collection scanning electron microscopy techniques.⁴⁰

Data obtained from the experiments in various redox electrolytes are compared in Table 2; large dark potentials (E_d) indicate irreversible electrode behavior. The large photocurrents obtained with GaAs in many cases were associated with electrode decomposition.

Figure 34. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL n-GaAS IN
 1M Na₂Se + 0.1M Se + 1M NaOH UNDER 100 mW/cm² XENON ILLUMINATION
 ($E_{\text{dark}} = -190$ mV, $E_{\text{light}} = -500$ mV vs. Pt, $E_{\text{Pt}} = -690$ mV vs. SCE,
 $\eta = 4\%$, $FF = 0.53$, $i_{\text{sc}} = 16$ mA/cm² Uncorrected for Light Absorption Loss in
 the Electrolyte)

Table 2. COMPARISON OF THE PHOTOELECTROCHEMICAL PROPERTIES OF GaAs SEMICONDUCTOR IN VARIOUS REDOX ELECTROLYTES

Electrolyte	E_{ℓ}^a	E_d^b	E_{Pt}^c	E_{ph}^d	I_{sc}^e -mA/cm ²
	mV				
6M KOH + 0.25M SeO ₂ + 0.25M Na ₂ Se	-1100	-490	--	-610	97
6M KOH + 1M I ⁻ /I ₂	-1240	-680	-80	-560	106
6M KOH + 1M Br ⁻ /Br ₂	-1910	-1400	415	-510	65
6M HCl + 1M Fe ⁺² /Fe ⁺³	-1090	-690	680	-400	103
6M HCl + Cr ⁺² /Cr ⁺³	-1030	-660	400	370	87
6M HCl + 1M Sn ⁺² /Sn ⁺⁴	-470	-455	-35	-15	4
6M HCl + 1M Cu ⁺¹ /Cu ⁺²	-470	-330	270	-140	44
6M HCl + 1M Ti ⁺³ /Ti ⁺⁴	-590	-345	120	-245	15
6M HCl + .1M KI + 1M I ₂	-750	-240	340	-510	54
6M HBr + 1M Br ₂	-1460	-1040	740	-420	30
6M HCl + 1M SbCl ₃ + 1M SbCl ₅	-875	-555	525	-320	7
1M Na ₂ Se + 0.1M Se + 1M NaOH	-500	-190	-690	-310	16

^a E_{ℓ} = electrode potential with light vs. platinum in the same solution

^b E_d = electrode potential in the dark vs. platinum in the same solution.

^c E_{Pt} = the potential of the platinum vs. saturated calomel electrode.

^d E_{ph} = photopotential = $E_{\ell} - E_d$.

^e I_{sc} = current density of the working electrode at E_d .

With photopotentials around -500 mV observed at the GaAs photoanode, redox couples within -500 mV of the selenide/polyselenide equilibrium redox potential could be used in the counterelectrode compartment. This restricts the number of feasible counterelectrode species available for charge by this photoanode. The redox potential of cadmium in 2M NaOH is approximately -1050 mV versus SCE, or about 300 mV negative of the selenide/polyselenide couple in alkaline solution. Cadmium electrodes in alkaline electrolytes have demonstrated excellent cycling and lifetime characteristics in nickel-cadmium batteries. The cadmium electrode used in these studies was selected from this type of battery. A storage cell of configuration GaAs/1M Na₂Se + 0.1M Se + 1M NaOH/Nafion/2M NaOH/Cd was assembled in a two-cuvette cell. Initial open-circuit potential of the n-GaAs electrode versus Cd was 350 mV in the dark and upon illumination became -100 mV. The initial cell voltage is, of course, dependent upon the charge state of the electroactive materials. At 0 mV versus cadmium counterelectrode (i.e., short circuit) a cathodic current density of 0.3 mA/cm² passed in the dark, as shown in Figure 35. Upon illumination of the photoanode (0.1 cm²) an anodic charging current of about 8 mA/cm² passed initially. This demonstrates the feasibility of illuminated n-GaAs for charging the Se²⁻/Se₂²⁻-Cd system. After approximately 1 minute, the current density dropped to half this value because of mass-transfer limitation in the unstirred system.

The current-voltage characteristics of the redox cell platinized Pt/1M Na₂Se + 0.1M Se + 1M NaOH/Nafion/2M NaOH/Cd are shown in Figure 36. As can be seen from the polarization curve, this redox couple shows good electrochemical reversibility, although, with the unstirred electrolyte used, significant polarization losses were observed.

Task 1.3. Electrochemical Measurements on Selected Polycrystalline Semiconductor/Redox Couples

Polycrystalline semiconductor electrodes were produced by utilization of the following techniques: a) pressing powders, b) vacuum evaporation, c) sputtering, and d) electrodeposition. Powders of selected materials were mixed with a binder material and pressed in a die to the shape of a tablet. An Edwards E306 thin-film evaporator was used for thermal vacuum evaporation and sputtering of selected semiconductor materials. Sputtering sources were

Figure 35. CURRENT OF n-GaAs IN THE SYSTEM 1M Na₂Se + 0.1M Se + 1M NaOH/Nafion/2M NaOH/Cd AT 0 mV BETWEEN GaAs AND Cd (The Current Reversed Its Sign Upon Illumination, Charging the System.)

Figure 36. POTENTIODYNAMIC (40 mV/s) CURRENT-VOLTAGE CHARACTERISTICS OF THE SYSTEM Pt/1M Na₂Se + 0.1M Se + 1M NaOH/Nafion 315/2M NaOH/Cd AT 27°C [Unstirred Electrolyte, Electrodes Were Platinized Platinum (1 cm²) and Porous Cadmium (1 cm²).]

obtained from Cerac, Inc. The electrodeposition of S or Se on Cd or Mo substrates was done by passing currents between the substrate and a platinum counterelectrode in appropriate electrolyte solutions. Various materials were tested for their photoresponse in both alkaline and acid solutions. Preliminary current-potential characteristics of vacuum-evaporated CdSe on iron foil, electrodeposited CdSe, electrodeposited CdS, sputtered MoSe₂, and GaAs pellets are shown in Figures 37 through 41, respectively. The properties of these photoelectrodes are summarized in Table 3.

Attempts to produce polycrystalline MoSe₂ by aqueous electrodeposition techniques followed by heating has not as yet resulted in photoactive material. MoSe₂ electrodes that are not of single-crystal quality exhibited large dark currents.

Polycrystalline n-CdSe Photoanode

We have concentrated our work with polycrystalline material on CdSe semiconductor electrodes. Thin-film CdSe electrodes were prepared by thermal vacuum evaporation of CdSe powder on a titanium foil or on SnO₂-coated glass (Corning 7059 conducting glass). The polycrystalline material on the titanium substrate was heat-treated in air at 350°C for 30 minutes and then etched in 0.1M HNO₃ for 30 seconds. In 6M KOH + 1M K₂S + 1M S, photopotentials of about -280 mV were observed. Current-potential characteristics are shown in Figure 42. The electrodes suffered from poor film adherence to the substrate, especially on conducting glass. This may have caused the photoanode to be shorted in the electrolyte, thus reducing the observed photocurrents.

Polycrystalline CdSe obtained by thermal vacuum evaporation onto a nickel foil substrate did not demonstrate superior photoelectrochemical performance over previously discussed substrates. The current-voltage properties in 6M KOH + 2.5M K₂S + 2.5M S + 0.025M K₂Se + 0.025M SeO₂ are shown in Figure 43. Photopotentials of -265 mV and short-circuit current densities of 1.8 mA/cm² were observed. A sharp increase in the anodic current was seen at higher positive potentials, possibly because of sulfidation of the nickel substrate. With such a smooth substrate, the evaporated CdSe was found to have a tendency to flake off from the nickel foil, thus leaving the nickel surface exposed to the electrolyte. Better adhesion of this polycrystalline material can be

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Figure 37. CURRENT-VOLTAGE CHARACTERISTICS OF THERMAL VACUUM EVAPORATED CdSe IN 6M KOH + 1M Na₂S

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Figure 38. CURRENT-VOLTAGE CHARACTERISTICS OF ELECTRODEPOSITED CdSe IN 6M KOH + 1M Na₂S

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Figure 39. CURRENT-VOLTAGE CHARACTERISTICS OF ELECTRODEPOSITED CdS IN 6M KOH + 1M Na₂S

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Figure 40. CURRENT-VOLTAGE CHARACTERISTICS OF SPUTTERED MoSe_2 IN 6M KOH + 1M NaI

Figure 41. CURRENT-VOLTAGE CHARACTERISTICS OF GaAs PELLET IN 6M KOH + 1M $\text{Se}^{2-}/\text{Se}_2^{2-}$

Table 3. PROPERTIES OF SOME POLYCRYSTALLINE SEMICONDUCTORS

<u>Material</u>	<u>Preparation Method</u>	<u>Comments</u>
CdSe	Thermal vacuum evaporation of CdSe powder followed by annealing in air at 425°C for 16 hr	Very good photoresponse, but adherence to Fe substrate is poor. (See Figure 37.)
CdSe	Cathodic deposition of Se ($\text{SeO}_2 + \text{H}_2\text{SO}_4$) on Cd followed by heating at 150°C for 1 hr	Good film surface, good photoresponse in 6M KOH + 1M Na_2S . (See Figure 38.)
CdS	Electrodeposition of S (from Na_2S) on Cd followed by heating at 150°C in air for 1 hr	Good film surface, good photoresponse in 6M KOH + 1M Na_2S . (See Figure 39.)
MoSe_2	Electroplating Se (from Na_2Se) on Mo followed by annealing	Poor photoresponse in 6M KOH + 1M NaI; poor film adherence; oxidation of Mo substrate.
MoSe_2	Sputtered on Mo	Poor photoresponse in 6M KOH + 1M NaI; large dark current. (See Figure 40.)
MoSe_2	Pressed powder mixture of MoSe_2 + active carbon + Teflon with Mo wire	Large dark current; very small photocurrent.
GaAs	Pellets (CERAC, Inc.) treated with SiCl_4 , heated at 400°C under H_2 for 2 hr	Photopotential (400 mV) seen in alkaline and in acid solutions; small photocurrent. (See Figure 41.)

Figure 42. CURRENT-POTENTIAL CHARACTERISTICS OF VACUUM-EVAPORATED CdSe ON Ti FOIL IN 6M KOH + 1M K₂S + 1M S

Figure 43. CURRENT-POTENTIAL CHARACTERISTICS OF VACUUM-EVAPORATED CdSe ON NICKEL FOIL IN 6M KOH + 2.5M K₂S + 2.5M S + 0.025M K₂Se + 0.025M SeO₂ ELECTROLYTE (Annealed in Air at 350°C for 30 Minutes and Etched in HCl for 30 Seconds)

achieved if porous nickel is used as a substrate. Upon evaporation of CdSe onto such a substrate, followed by heat-treatment at 350°C in air for 30 minutes, and etching in 6M HCl for 30 seconds, the photoelectrochemical performance shown in Figure 44 was obtained. Here photopotentials around -250 mV and apparent short-circuit current densities of 7.8 mA/cm² were obtained. As with the foil substrate, at high positive potentials a sharp increase was again observed in both the dark-current and the photocurrent.

Power conversion efficiencies for polycrystalline CdSe in the presence of chalcogenide/polychalcogenide redox have been reported by others as 5%⁴¹ and 6%.⁴² Although encouraging lifetimes have been demonstrated, some deterioration in photoanode performance has been attributed to chalcogenide exchange⁴³ reactions between the photoanode and the electrolyte. Such exchange reactions have been reduced by the introduction of selenium to the sulfide/polysulfide solution, which can precipitate any photoproduct cadmium ions back to lattice sites in the cadmium selenide.¹⁸ For single-crystal CdSe, efficiencies of 8% have been reported.⁴⁴

In the work reported here, performance and stability of thermally evaporated n-CdSe was found dependent on the nature and morphology of the substrate used. Best results were obtained using porous titanium as a substrate, as shown in Figure 45, where photopotentials of -400 mV were achieved under 100 mW/cm² xenon light illumination. A short-circuit current density of about 20 mA/cm² and power conversion efficiency of 4% were calculated. The fill factor, however, was around 0.45. The advantages of using porous substrates were greater CdSe adhesion and a more effective photoanode area available for illumination.

The redox potential of the alkaline sulfide/polysulfide electrolyte was about -700 mV versus SCE. Thus, with a photopotential of -400 mV, electroactive species with redox potentials between -700 and -1100 mV versus SCE might be suitable in the counterelectrode compartment of a storage cell. The two electroactive materials for the counterelectrode evaluated in this work have been Se²⁻/Se₂²⁻ (-800 mV versus SCE) and Cd (-1050 mV versus SCE). The two-compartment storage cell n-CdSe/1M Na₂S + 1M S + 1M NaOH/Nafion/1M Na₂Se + 0.1M Se + 1M NaOH/platinized Pt was assembled. Surface areas of the photoanode and platinum electrodes were 0.25 and 1 cm², respectively. The initial open-

Figure 44. CURRENT-POTENTIAL CHARACTERISTICS OF VACUUM-EVAPORATED CdSe ON POROUS NICKEL IN
 6M KOH + 2.5M K₂S + 2.5M S + 0.025M K₂Se + 0.025M SeO₂
 ELECTROLYTE (Annealed in Air at 350°C for 30 Minutes and Etched in HCl for 30 Seconds)

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Figure 45. CURRENT-POTENTIAL CHARACTERISTICS OF CdSe, THERMAL VACUUM-EVAPORATED ON POROUS Ti ELECTRODE (Electrolyte 1M Na₂S + 1M S + 1M NaOH + 0.1M Na₂Se + 0.01M Se, Unstirred, 100 mW/cm² Xenon Illumination, Efficiency = 4%, Fill Factor = 0.45, Annealed in Air at 400°C for 30 Minutes, Slow Cooling, Etched in 6M HCl for 15 Seconds)

circuit voltage of this cell in the dark was about 100 mV. Upon illumination (100 mW/cm² xenon) of the n-CdSe, a current of 2.7 mA passed initially between the photoanode and the platinum counterelectrode in the second compartment. Concurrently, the cell voltage measured via the two auxiliary platinum electrodes rose as shown in Figure 46. Here the cell was charged photoelectrochemically for about 3 hours. Upon discharge with a 100Ω load between the two auxiliary platinum electrodes, a current of about 0.5 mA at 60 mV was obtained for about 5 hours.

The current-voltage characteristics of a sulfur/selenium redox cell are illustrated in Figure 47. Although good reversibility is manifest, this system possesses an inherently low voltage, which would be of little interest for practical devices. To increase the cell voltage of n-CdSe sulfide/polysulfide-based storage cells, cadmium was evaluated as the electroactive species at the counterelectrode. The cell n-CdSe/1M NaOH + 1M Na₂S + 1M S + 0.1M Na₂Se + 0.01M Se/Nafion/2M NaOH/Cd has an initial open-circuit potential of +150 mV (CdSe electrode versus Cd) in the dark. Upon illumination (100 mW/cm² xenon light) the voltage between CdSe and Cd became -200 mV. By shorting the illuminated cell a charging photocurrent of 2.1 mA was recorded as shown in Figure 48. The cell was photocharged for 5 hours and then left at open circuit for 20 minutes. Afterwards the cell was discharged, using a 100Ω load between the platinum and cadmium electrodes. A current of about 2 mA at a cell voltage close to 175 mV flowed for 5.5 hours until the capacity of the sulfide/polysulfide system was exhausted. In the dark a short-circuit discharge current of 0.15 mA was recorded between the CdSe and Cd. A polarization curve for a S²⁻/S_n²⁻ Cd cell is shown in Figure 49. Here an open-circuit voltage of 310 mV was observed. Increasing the activity of the polysulfide species can be expected to result in larger cell voltages.

Storage Systems

Photoelectrochemical storage cells discussed in this section and under Task 1.2 are summarized in Table 4. The photopotential observed with n-MoSe₂ was found just sufficient to effect charging of the bromine-iodine redox cell, where the equilibrium cell voltage was between 0.4 and 0.5 V. From a kinetic standpoint, however, this redox system is attractive, as large short-circuit discharge current densities were obtained. The other storage systems have, in

Figure 46. CURRENT AND VOLTAGE OF THE SYSTEM 1M Na₂S + 1M S + 1M NaOH/ Nafion 315/1M Na₂Se + 0.1M Se + 1M NaOH DURING PHOTOCHARGE THROUGH 0.25-cm² CdSe/1-cm² Pt ELECTRODES AND DISCHARGE THROUGH 1-cm² PLATINIZED PLATINUM ELECTRODES WITH A 100Ω LOAD

Figure 47. POTENTIODYNAMIC (40 mV/s) CURRENT-VOLTAGE CHARACTERISTICS OF THE SYSTEM Pt/1M Na₂S + 1M S + 1M NaOH/Nafion 315/1M Na₂Se + 0.1M Se + 1M NaOH/Pt AT 27°C (Unstirred Electrolyte, Platinized Platinum Electrodes, Area of Separator = 0.5 cm²)

Figure 48. CURRENT AND VOLTAGE OF THE SYSTEM CdSe/1M NaOH + 1M Na₂S + 1M S + 0.1M Na₂Se + 0.01M Se/Nafion 315/2M NaOH/Cd DURING PHOTOCHARGE THROUGH 0.25-cm² CdSe/1-cm² Cd ELECTRODES AND DISCHARGE THROUGH 1-cm² PLATINIZED PLATINUM ELECTRODES/1-cm² Cd WITH A 100Ω LOAD

Figure 49. POTENTIODYNAMIC (30 mV/s) CURRENT-VOLTAGE CHARACTERISTICS OF THE SYSTEM Pt/1M Na₂S + 0.1M S + 1M NaOH + 0.1M Na₂Se + 0.01M Se/Nafion 315/2M NaOH/Cd AT 27°C [Unstirred Electrolyte, Electrodes Were Platinized Platinum (1 cm²) and Porous Cadmium (1 cm²).]

Table 4. PHOTOELECTROCHEMICAL CELLS WITH STORAGE

Cell System	E, mV	E _{ph} , mV	i _{photocharge} , mA/cm ²	i _{discharge} , mA/cm ²
MoSe ₂ /Br ⁻ /Br ₂ /I ⁻ /I ₂ /Pt	400 to 500	490	4 at 200 mW/cm ²	20.6
GaAs/Se ²⁻ /Se ₂ ²⁻ /Cd	250 to 350	500	8 at 100 mW/cm ²	14.6
CdSe/S ²⁻ /S _n ²⁻ /Se ²⁻ /Se ₂ ²⁻ /Pt	50 to 200	400	8 at 100 mW/cm ²	0.75
CdSe/S ²⁻ /S _n ²⁻ /Cd	300 to 400	400	10 at 100 mW/cm ²	8.25

- E = Voltage range of storage cell.
- E_{ph} = Typical photopotential of the photoanode.
- i_{photocharge} = Typical charge short-circuit photocurrent when the photoanode was illuminated at the listed light intensity.
- i_{discharge} = Short-circuit discharge current of the storage cell in the dark using platinized platinum electrodes (1 cm²) in unstirred electrolytes at 27°C.

general, lower cell voltages; however, polycrystalline GaAs and CdSe photoanodes can be readily fabricated. For n-GaAs the selenium-cadmium storage system produced only cell voltages between 250 and 350 mV, which is below the charging capacity achievable from the present state-of-the-art photoanodes.^{10,38} If one uses zinc instead of cadmium (zinc redox potential at -1500 mV versus SCE) a higher cell voltage could be realized. Photocharge of such a cell, however, would not be feasible by using n-GaAs as the photoanode in a single cell. Cells using polycrystalline CdSe do reasonably well for charging the sulfur-cadmium system where charging currents of 10 mA/cm² could be achieved. The charge-discharge characteristics of the photoelectrochemical storage cells were obtained under an unstirred electrolyte condition. The current densities that can be achieved in a stirred or flowing electrolyte system should be higher. In addition, higher voltage photoelectrochemical storage cells will require the introduction of suitable photocathode materials into the counter-electrode. This will increase the range of potential electroactive species that might be conceived for such devices.

Task 2. Development of Long-Life Electrochemical Photovoltaic Cells

Task 2.1. Identification of Photoanode Corrosion

A preliminary chemical corrosion test of GaAs, GaP, CdSe, CdTe, MoSe₂, and MoS₂ was performed in alkaline (6M KOH) and in acid (6M H₂SO₄) electrolytes. The results are summarized in Table 5. Candidates for the alkaline medium were identified as GaAs, CdSe, MoSe₂, and MoS₂; candidates for acid solution were identified as GaAs, CdTe, MoSe₂, and MoS₂.

The electrochemical stability of the selected semiconductor materials was evaluated by a) potentiodynamic cycling of the material up to 600 mV positive of the initial rest potential, and b) monitoring the decay of the anodic currents at a preset electrode potential. Some of the early results are summarized below:

In Alkaline Electrolyte (6M KOH + 1M Na₂S)

CdSe: Change in color occurred on illuminated areaa.
Anodic current decayed with time.

CdS: Anodic current changed slightly with time.

Table 5. CHEMICAL CORROSION TEST AT ROOM TEMPERATURE

Material	Description	Immersion Time in 6M KOH Electrolyte, days			Immersion Time in 6M H ₂ SO ₄ Electrolyte, days		
		0	11	23	0	11	23
		Response					
Gallium Arsenide	GaAs (gray metallic)	No change	No change	No change	No change	No change	No change
Gallium Phosphide	GaP (brownish gray metallic)	No change	Color change to light brown	No change	No change	Color change to light brown	No change
Cadmium Selenide	CdSe (gray metal)	No change	No change	No change	No change	Color change to brick red	No change
Cadmium Telluride	CdTe (gray powder)	Dissolved	No change	No change	No change	No change	No change
Molybdenum Selenide	MoSe ₂ (gray powder)	Cloudy powder	No change	No change	Cloudy powder	No change	No change
Molybdenum Sulfide	MoS ₂ (gray rod)	No change	No change	No change	No change	No change	No change

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MoSe₂ Corrosion of the molybdenum substrate or the molybdenum
and wire was observed.
MoS₂:

In Acid Electrolyte (HCl + FeCl₂)

CdSe: Dissolved.

CdS: Dissolved.

GaAs: Stable.

In Task 1 we have identified some promising semiconductor/redox electrolyte systems that have the potential to achieve high power conversion efficiencies. In many cases, however, we suspect that the large photocurrents observed may be associated with electrode corrosion. We will describe in this section the results obtained from the long-term tests using n-GaAs, n-MoSe₂, n-MoS₂, and n-WSe₂ photoanodes.

The long-term performance of single-crystal GaAs was analyzed under potentiostatic conditions in 6M HCl + 1M Cr⁺²/Cr⁺³. The open-circuit potential was -260 mV in the dark and -630 mV (versus SCE) under 200 mW/cm² xenon light illumination. When the potential was set at -400 mV versus SCE, a photocurrent of about 30 mA/cm² initially flowed. Figure 50 shows that the current decayed slowly with time. The electrode turned black, indicating electrode instability.

The long-term performance of single-crystal GaAs was also analyzed in 6M HCl + 1M Fe⁺²/Fe⁺³ solution. The open-circuit potential was 0 mV in the dark and -410 mV versus SCE under illumination. Anodizing at -200 mV versus SCE resulted in an initial photocurrent of 46 mA/cm², which slowly decayed with time as shown in Figure 51.

The long-term stability of single-crystal MoSe₂ in the acid redox electrolyte 6M HCl + Cl₂ was determined by monitoring the photocurrent with time at an applied potential 350 mV anodic of the rest potential as shown in Figure 52. After 1.5 hours the photoanode showed strong evidence of corrosion. Thus MoSe₂ under presently used experimental conditions does not appear to be stable with the Cl⁻/Cl₂ couple in acid electrolyte.

A sample of naturally occurring MoS₂ crystal was also evaluated for its long-term stability in 6M HCl + Cl₂. At 125 mV anodic from the rest potential, an initial photocurrent of about 10 mA/cm² was found. The photocurrent

Figure 50. PHOTOCURRENT OF SINGLE-CRYSTAL GaAs at -400 mV VS. SCE IN 6M HCL + $\text{Cr}^{+2}/\text{Cr}^{+3}$ AS A FUNCTION OF TIME

Figure 51. PHOTOCURRENT OF SINGLE-CRYSTAL GaAs at -200 mV VS. SCE IN 6M HCL + $\text{Fe}^{+2}/\text{Fe}^{+3}$ AS A FUNCTION OF TIME

Figure 52. DECAY OF THE PHOTOCURRENT OF SINGLE-CRYSTAL MoSe_2 IN $6\text{M HCl} + \text{Cl}_2$ AT 350 mV ANODIC FROM THE RESTING POTENTIAL (200 mW/cm^2 Xenon Light Illumination)

decreased by about 50% of its original value after 2 hours, as shown in Figure 53. Both MoSe_2 and MoS_2 as photoanodes in the redox electrolyte 1M HBr + 1M Br_2 have demonstrated excellent stability, with no apparent change in their photoelectrochemical properties. No visual change occurred in the surface after many days of operation.

The major life-limiting problem has been in identifying suitable insulating coatings for the electrode assembly. Coatings evaluated to date have included regular epoxies, silicone rubber RTV, Plexiglas, polypropylene, and paraffin wax. The greatest success has been found by using paraffin wax. Long-term testing of MoSe_2 crystal in 1M HBr + 1M Br_2 at a constant current density of 5 mA/cm^2 was performed under an approximately 100 mW/cm^2 quartz-halogen illumination with a KG-2 filter. The potential of the photoanode versus a platinum electrode stayed close to -450 mV , as shown in Figure 54. The cell was checked every day for the photopotential (-530 mV) and the short-circuit current (20 mA/cm^2). No change in current-voltage characteristics attributable to the semiconductor was observed.

A similar lifetime test for MoS_2 natural crystal is shown in Figure 55. The photopotential (-480 mV) short-circuit current (9 mA/cm^2) and operating potential (-240 mV) at 5 mA/cm^2 did not change significantly for the first 10 days. Afterwards the performance slowly became worse with time. The cell was terminated after 40 days because of deterioration and swelling of the insulating wax. The swollen wax significantly reduced incident light flux to the semiconductor. Attempts to repair the electrode assembly resulted in damage to the surface of the crystal.

The electrolyte mediums of the MoSe_2 and the MoS_2 cells were analyzed after 73 days and 40 days of operation, respectively. The analysis was done using a Perkin Elmer 603 Atomic Absorption Spectrophotometer with a Perkin Elmer HGA 2200 graphite furnace. The sensitivity limit of the unit for analysis was 5 ppb for Mo and 20 ppb for Se. In the MoSe_2 cell the molybdenum concentration was found to be $8.1 \text{ } \mu\text{g/ml}$, or about $84 \text{ } \mu\text{M}$. The selenium concentration was $13 \text{ } \mu\text{g/ml}$, or about $164 \text{ } \mu\text{M}$. The molybdenum concentration in the electrolyte of the MoS_2 cell was $7.6 \text{ } \mu\text{g/ml}$, or about $79.04 \text{ } \mu\text{M}$. We believe that these corrosion products might have been produced at the early part of the test when the electrodes were preanodized in the dark at 1 V versus platinum to improve the photoelectrochemical performance.

Figure 53. DECAY OF THE PHOTOCURRENT OF NATURAL-CRYSTAL MoS_2 IN
6M $\text{HCl} + \text{Cl}_2$ AT 125 mV ANODIC FROM THE RESTING POTENTIAL
(200 mW/cm^2 Xenon Light Illumination)

Figure 54. VOLTAGE OF SINGLE-CRYSTAL MoSe₂ VS. Pt IN 1M HBr + 1M Br₂ DURING A LONG-TERM EXPERIMENT UNDER CONSTANT-CURRENT LOAD OF 5 mA/cm² [Quartz-Halogen Illumination, Heat-Filtered (100 mW/cm²). Electrolyte Was Not Stirred. Temperature 28°C.]

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Figure 55. VOLTAGE OF NATURAL MoS₂ CRYSTAL VS. Pt IN 1M HBr + 1M Br₂ DURING A LONG-TERM EXPERIMENT UNDER CONSTANT-CURRENT LOAD OF 5 mA/cm² [Quartz-Halogen Illumination, Heat-Filtered (60 mW/cm²). Electrolyte Was Not Stirred. Temperature 27°C.]

After the long-term test in 1M HBr + 1M Br₂ we noticed a slight roughening of the Pt counterelectrode. The black platinum coating of the electrode seemed to be unstable in the electrolyte. Further work will be necessary to develop more stable catalysts.

An n-type WSe₂ semiconductor was also tested. This electrode developed a photopotential of -590 mV and generated a short-circuit current up to 32 mA/cm² under 200 mW/cm² xenon light. A power conversion efficiency of about 4.1% and a fill factor of 0.43 was calculated. The long-term performance of this single crystal was studied at a constant-current load of 5 mA/cm² under 100 mW/cm² quartz-halogen illumination. Its potential versus platinum in 0.5M H₂SO₄ + 0.5M Na₂SO₄ + 1.0M NaI + 0.025M I₂ during the long-term test is shown in Figure 56. The electrode was stable during the 1-week test.

During the course of this program, stabilization of a GaAs electrode against photoanodic corrosion has been attempted by a new technique that works like the process of cathodic protection. The protection is provided by imposing a small cathodic current on the anodic photocurrent through a separate current-regulated circuit. Preliminary results were quite encouraging for single-crystal n-GaAs in 6M KOH + 0.25M Na₂Se + 0.25M Na₂SeO₂. When an anodic photocurrent of 15 mA/cm² was passed, the electrode potential dropped slowly with time, indicating electrode corrosion. With cathodic currents (6 mA/cm²) imposed on the 15 mA/cm² anodic current, the electrode potential remained almost constant for a long period. Further work will be required to study the optimum cathodic current density needed for adequate protection at a given light intensity, anodic current load, and redox electrolyte composition.

Task 2.2. Stabilization of Semiconductor Electrodes by the Use of Nonaqueous Electrolytes

Thermally evaporated CdSe photoanode was evaluated in a variety of non-aqueous solvents containing selected redox couples in an attempt to determine nonaqueous solvent/redox couple systems compatible with CdSe.

Figure 56. THE LONG-TERM POTENTIAL OF SINGLE-CRYSTAL WSe₂ VS. PLATINUM IN 0.5M H₂SO₄ + 0.5M Na₂SO₄ + 1.0M NaI + 0.025M I₂ AT 5 mA/cm² ANODIC CURRENT LOAD DURING 100 mW/cm² QUARTZ-HALOGEN ILLUMINATION

Preliminary screening of the redox/nonaqueous electrolytes was accomplished by measuring the open-circuit photopotential versus a platinum electrode in the same solution. For those solvents showing a rapid photopotential in excess of 50 mV, the short-circuit photocurrent was also determined. For those solvents showing less than 50 mV photopotential, the main limitation appears to be either the lack of solubility of the redox couple and/or the supporting electrolyte, or slow kinetics.

Six solvents have been experimentally investigated: acetone, acetonitrile, dimethyl sulfoxide, ethanol, propylene carbonate, and 1-butanol. One-tenth gram each of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ and 0.2 gram of $KClO_4$ were placed in 20 ml of each of the six solvents. The solvents were then shaken vigorously for 20 minutes and tested for photopotential effects. The results are shown in Table 6.

Table 6. PHOTORESPONSE OF CdSe IN VARIOUS NONAQUEOUS SOLVENTS WITH $K_3Fe(CN)_6/K_4Fe(CN)_6$ AND $KClO_4$ UNDER APPROXIMATELY 20 mW/cm² ILLUMINATION

Solvent	Photopotential, mV	Comments
Acetone	--	Insoluble.
Acetonitrile	--	Only $KClO_4$ soluble.
1-Butanol	--	Insoluble.
Dimethyl Sulfoxide	98	--
Ethanol	15	--
Propylene Carbonate	160	--

In a similar manner, the six solvents were tested by using potassium sulfide and sulfur as a redox couple with potassium hydroxide as the supporting electrolyte. Once again solubility proved to be a problem. Potassium sulfide and sulfur were observed to be only very slightly soluble in acetonitrile and acetone; however, K_2S and sulfur showed moderate solubility in ethanol, 1-butanol, and propylene carbonate; and all three solids (K_2S , S, and KOH) were completely dissolved in dimethyl sulfoxide to yield a blood-red solution. The results are summarized in Table 7.

Table 7. PHOTORESPONSE OF CdSe IN VARIOUS SOLVENTS
WITH K₂S, S, AND KOH UNDER 20 mW/cm² ILLUMINATION

Solvent	Photo- potential, mV	Shorted Photo- current, μ A/cm ²	Comments
Acetone	--	--	Low solubility, green color
Acetonitrile	--	--	Low solubility, green color
1-Butanol	65	22	Yellow-brown
Dimethyl Sulfoxide	70	1.65	Blood-red
Ethanol	120	11	Amber
Propylene Carbonate	180	0.25	Yellow
H ₂ O, 1M K ₂ S/1M S, 5M KOH	160	19	Aqueous for com- parison

It was shown earlier that n-MoSe₂ gave a high apparent efficiency for solar energy conversion in chlorine-saturated HCl solution, but there was strong evidence for semiconductor corrosion. The well-known fast kinetics of the Cl⁻/Cl₂ redox couple encouraged us to evaluate this couple again in nonaqueous solvents, where the semiconductor might have greater stability. The electrolyte selected was acetonitrile containing 0.25M tetraethylammonium chloride. After bubbling with chlorine for 30 seconds, the solution became light yellow. When higher concentrations of tetraethylammonium chloride were introduced into the acetonitrile, crystallites appeared in the electrolyte solution with time after bubbling with chlorine. The photoelectrochemical performance of single-crystal MoSe₂ is shown in Figure 57. Its potential versus the platinum electrode was -25 mV in the dark and -440 mV under 200 mW/cm² xenon illumination. Short-circuit current was 21 mA/cm². The linear current-potential curve indicated a large ohmic polarization loss because of the relatively low conductivity of the nonaqueous electrolyte. The photoanode was operated at 2.0 mA/cm² continuously for over 20 hours with no apparent deterioration in performance. After this the test was discontinued because of crystallite formation in the electrolyte that blocked the incident light. Future emphasis will be on modification of the electrolyte composition to eliminate this precipitation problem.

Figure 57. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL n-MoSe₂ IN ACETONITRILE + 0.25M TETRAETHYLAMMONIUM CHLORIDE + CHLORINE (200 mW/cm² Xenon Light Illumination, Efficiency = 1%, Fill Factor = 0.23)

Task 2.3. All-Solid-State Electrochemical Photovoltaic
Cell With In-Situ Storage

The promise of high power-conversion efficiency from liquid-junction photoelectrochemical devices has dictated that narrow-band-gap materials responsive to a significant fraction of the incident solar spectrum be used, e.g., Si, GaAs, CdSe, CdS, MoSe₂, MoS₂, or WSe₂. As is well-known, however, such materials can be susceptible to photoanodic corrosion effects, particularly if the redox equilibrium potential is close to the semiconductor decomposition potential. Approaches to stabilize those semiconductors have included the evaluation of both organic and inorganic nonaqueous electrolytes containing selected redox species where the solvent species have a lower nucleophilicity than the OH⁻/H₂O couple. Although progress is being made with such nonaqueous electrolytes to address the lifetime problems, most work is at an early stage. No work has been reported to this time on photoelectrochemical devices with solid electrolytes. In fact the nature of the interface between a semiconductor and solid electrolyte is not clear. In order for a solid electrolyte to function in a photoelectrochemical device, one portion of the solid-electrolyte cell must have solid-state redox species available for reversible electrochemical reactions. This task describes a new approach for photoelectrochemical devices based upon solid electrolytes, where some enhanced stability to photoanodic (or photocathodic) corrosion effects might be realized. To some extent the viability of the overall concept would be dependent upon the accommodation of a concentration of mobile cations somewhat greater than that necessary to maintain an acceptable ionic conductivity within the solid electrolyte. Although the ionic conductivity of β -Al₂O₃ at room temperature is too low, its crystallographic structure would probably be suitable for this application, in which the a and b axes are periodically separated by Al-O-Al bonds, where the mobile cations reside. Typically sintered β -Al₂O₃ at room temperature has a conductivity of $10^{-2} \Omega^{-1} \text{cm}^{-1}$ and possesses some degree of moisture sensitivity. Hence, any photopotential generated by a semiconductor would probably be insufficient to overcome resistance losses within this solid electrolyte. Many of the highly conducting solid electrolytes investigated over the past decade have been silver-ion conductors. The most conductive of these, RbAg₄I₅, has a conductivity of $0.27 \Omega^{-1} \text{cm}^{-1}$ at ambient temperatures⁴⁵ and has found application in galvanic cells.⁴⁶ Solid electrolytes have also

been synthesized through compound formation between AgI and various substituted ammonium halides^{47,48} as well as between AgI and sulfonium iodides.⁴⁹ The single-crystal structures of certain of these unique phases have been investigated⁵⁰⁻⁵⁵ to determine the structural features that permit fast ion diffusion in solids. It was observed that the iodide ions form face-sharing polyhedra (generally tetrahedra) with the silver ions situated within these polyhedra. On the average there are two or three vacant sites per silver ion, thus permitting ready diffusion through the faces of the polyhedra.

The solid-electrolyte photoelectrochemical cell was fabricated by mixing RbAg_4I_5 powder (Research Organic Inorganic, Sun Valley, Calif.) with silver powder (Cerac, Inc.), PbI_2 , and/or iodine powder. Layers of appropriate mixtures thereof were poured inside a commercial KBr die, and the powder layers were pressed at 2000 kg/cm^2 by using a Carver laboratory press. The resulting tablet was sandwiched between a counterelectrode and a transparent semiconductor working electrode. These electrodes were mostly based upon transparent SnO_2 -coated conducting glass (Corning 7059) with a thickness of 0.032 inch and a standard resistivity of 100 ± 30 ohms per square. A small silver-wire reference electrode was inserted inside a small hole in the RbAg_4I_5 tablet.

The photoelectrochemical properties of the solid-electrolyte cell were investigated, using a Wenking ST-72 potentiostat and an Oriel 150-watt xenon light source.

Photoactivity of RbAg_4I_5

Before describing photoeffects on a semiconductor-solid electrolyte interface, a first look at the photoactivity of the solid electrolyte itself is in order. The rubidium silver iodide can be expected to be photosensitive, because binary silver halides have demonstrated photovoltaic effects.^{56,57} A cell was fabricated having the configuration: cond. glass/ $\text{PbI}_2 + \text{RbAg}_4\text{I}_5$ / $\text{RbAg}_4\text{I}_5/\text{Ag} + \text{RbAg}_4\text{I}_5$ /cond. glass. The solid-electrolyte tablet was mounted between two layers of transparent conducting glass. The tablet is made of three layers with the compositions $\text{PbI}_2 + \text{RbAg}_4\text{I}_5$, RbAg_4I_5 , and $\text{Ag} + \text{RbAg}_4\text{I}_5$, respectively. A rubidium silver iodide solid-electrolyte battery usually has a silver anode and an iodine cathode.⁵⁸ The iodine is usually complexed as, for example, in PbI_2 .

When the cond. glass/ $\text{PbI}_2 + \text{RbAg}_4\text{I}_5$ was illuminated, photopotentials in the range of 3 to 50 mV were measured. After passing anodic as well as cathodic current through this interface, however, larger photopotentials were obtained. On certain darkened spots on the electrolyte surface it was possible to measure a large potential versus the silver reference electrode; this was 450 mV in the dark and 850 mV under illumination, as is shown in Figure 58. When the light beam was not focused on the darkened spot, the photopotential was only about 5 mV. The large photopotential was still detected at wavelengths longer than $4750\text{\AA}$ when a sharp-cut filter that passes light with wavelengths longer than $4750\text{\AA}$ was inserted in the light path. The response of the cell under this condition is shown as a second deflection in Figure 58. The action spectra of the cell will be described later in more detail.

Photoexcitation of the RbAg_4I_5 will result in the formation of electron-hole pairs. The photoelectrons will diffuse from the surface into the bulk because of their much greater drift mobility than the photoholes. A net positive space charge is formed near the illuminated electrode because of the photoholes and interstitial Ag^+ ions that may be formed as a result of neutralization of trapped photoholes. These processes can lead to a positive photovoltage at the illuminated electrode, which can be described as a Dember-type photovoltage.^{57,59}

The current-voltage characteristics of the cell were analyzed by sweeping the cell voltage with a potentiostat. The cell voltage was measured as the voltage between the illuminated side versus the nonilluminated silver side. Under chopped xenon light illumination, cathodic as well as anodic photocurrents were recorded as shown in Figure 59. The photopotential and photocurrent in the solid electrolyte indicate that photoexcited carriers are produced in addition to the silver ions that existed when it was in the dark. This correlates well with the Hall effect of RbAg_4I_5 in the dark and under illumination.⁶⁰ The Hall signals in the dark are caused by the Ag^+ ion carriers; under illumination the sign of the Hall voltage is reversed. From this, and by virtue of the magnitude and temperature dependence of Hall mobility, it was concluded that photoelectrons primarily contribute to Hall signals under illumination.

At the illuminated side, photolytic iodine may also be found. The positive photopotential will lead to a larger cathodic current upon illumination. In this mode the iodine is reduced to iodide, or in other words, the cell is

Figure 58. PHOTOPOTENTIAL IN THE CELL COND.
 GLASS/PbI₂ + RbAg₄I₅/RbAg₄I₅/Ag + RbAg₄I₅/COND. GLASS
 (The Cond. Glass/PbI₂ + RbAg₄I₅ Interface Was Illuminated With 200 mW/cm² Light.)

Figure 59. CURRENT-VOLTAGE CHARACTERISTICS OF THE CELL COND. GLASS/
 $\text{PbI}_2 + \text{RbAg}_4\text{I}_5/\text{RbAg}_4\text{I}_5/\text{Ag} + \text{RbAg}_4\text{I}_5/\text{COND. GLASS}$ UNDER CHOPPED ILLUMINATION
 (200 mW/cm^2) at 25°C (The Voltage Scan Rate Was 25 mV/s.)

discharged. Under continuous illumination, the cathodic photocurrent can be drawn for many hours.

When the potential of the illuminated interface is brought to the anodic direction, iodide will be oxidized to iodine on the surface. Light may also reduce the internal resistance of the cell, thereby increasing the currents upon illumination, as shown in Figure 59. At large voltages, however, the electrolyte will decompose⁵⁸ according to $2 \text{RbAg}_4\text{I}_5 \rightarrow 4 \text{Ag} + 2 \text{RbI}_3 + 4 \text{AgI}$ with the concurrent equilibration $\text{RbI}_3 \rightleftharpoons \text{RbI} + \text{I}_2$.

Apparently the iodine that was generated might have darkened the surface. As mentioned before, the darkened spots are in the area where large photopotentials have been observed. Therefore, the photosensitivity of RbAg_4I_5 solid electrolyte that was doped with iodine was also investigated. Here the surface of the pellet was rubbed with solid iodine for a few seconds until it became light brown. This pellet was assembled between two layers of transparent conducting glass. The potential of the iodine-treated surface was measured against a silver reference electrode implanted inside the pellet. Owing to the high activity of the iodine, the potential was 661 mV in the dark. This surface immediately developed a large positive photopotential of about 100 mV upon illumination with the xenon light. The current-potential characteristics of this surface were essentially the same as shown in Figure 59, although an increase in the dark current in the anodic direction was noticed.

The dependency of the photopotential upon the wavelength of the illuminating light is shown in Figure 60. Below 300 nm essentially no photopotential was detected. This is not surprising, because the glass and the tin oxide layer on the conducting glass electrode would absorb light with wavelengths below this value. The band gap of SnO_2 is within this range, i.e., 3.8 eV, which would correspond to a wavelength of about 326 nm. The conducting glass had no photoactivity when it was tested in a liquid electrolyte. Figure 60 shows that the peak of the photoresponse of the solid electrolyte system was at a wavelength of about 425 nm and the photopotential decreased at longer wavelengths. The peak at 425 nm can be correlated to the 425-nm band in the optical absorption spectrum of RbAg_4I_5 . The spectrum actually showed four bands at 485, 425, 375, and 335 nm.⁶¹ The 425-nm band was attributed to a "forbidden" internal transition in the Ag^+ , which is actually permitted because

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Figure 60. POTENTIAL OF COND. GLASS/RbAg₄I₃ INTERFACE VS. SILVER AS A FUNCTION OF WAVELENGTH

of the tetrahedral coordination of the Ag^+ ion in RbAg_4I_5 . Anodic and cathodic photocurrents were seen up to a wavelength approaching 695 nm.

The photopotential was also measured as a function of light intensity. At 200 mW/cm^2 xenon light illumination a photopotential of about 100 mV was measured. The photopotential decreased upon attenuation of the light intensity with neutral-density filters. A plot of the photopotential versus the relative light intensity is shown in Figure 61; the photopotential is proportional to the logarithm of the light intensity.

CdSe/Solid-Electrolyte Junction

Data in the previous section showed that the RbAg_4I_5 solid electrolyte is photosensitive. The primary goal in this study was actually to see photoactivity of a semiconductor in contact with a solid electrolyte. For this study n-type CdSe was chosen, as a thin-film partially transparent electrode can be fabricated by thermal vacuum evaporation of this material on a transparent conducting glass. A cell was fabricated having the configuration CdSe on cond. glass/ $\text{I}_2 + \text{RbAg}_4\text{I}_5/\text{RbAg}_4\text{I}_5/\text{cond. glass}$. A small amount of iodine on the surface of the solid-electrolyte tablet was introduced as a redox species. The CdSe electrode was made to contact the solid electrolyte on the iodine side. In the dark the potential was 650 mV versus a silver reference electrode and it went to about 300 mV under 200 mW/cm^2 xenon light illumination. The actual light intensity reaching the CdSe/solid-electrolyte interface will be much less. Thus in this system a rapid negative photopotential was observed, as shown in Figure 62. This phenomenon is similar to the behavior of n-CdSe in liquid-junction photoelectrochemical cells.

The dependency of the CdSe electrode potential upon the wavelength of the light is shown in Figure 63. This spectrum was not corrected for the variation in the light intensity of the monochromator. The mean intensity at 625 nm was $70 \text{ } \mu\text{W/cm}^2$, and the variation at other wavelengths was $\pm 25 \text{ } \mu\text{W/cm}^2$. No photopotential was seen below 300 nm. Between 300 and 375 nm, a positive photopotential was detected. This could have the same origin as the photopotential of cond. glass/ RbAg_4I_5 seen in Figure 60. A large negative photopotential is seen in Figure 63 at wavelengths longer than 375 nm, up to about 800 nm, which corresponds closely to the 1.7-eV band gap of CdSe. Thus the

Figure 61. PHOTORESPONSE OF COND. GLASS/RbAg₄I₅/COND. GLASS
VS. INTENSITY

Figure 62. PHOTOPOTENTIAL OF $\text{CdSe/I}_2 + \text{RbAg}_4\text{I}_5/\text{RbAg}_4\text{I}_5/\text{COND.GLASS}$
(Back Illumination With 200 mW/cm^2 Xenon Light)

Figure 63. THE POTENTIAL OF CdSe IN CONTACT WITH $\text{I}_2 + \text{RbAg}_4\text{I}_5$ VS.
SILVER AS A FUNCTION OF THE WAVELENGTH OF THE LIGHT

negative photopotential can be assigned to the CdSe/solid-electrolyte interface. The photoresponse between 300 and 500 nm in Figure 63 might very well be a superposition of the positive photopotential of cond. glass/RbAg₄I₅ and of the negative photopotential of CdSe/RbAg₄I₅. The magnitude of the negative photopotential was largest at 625 nm. The dependency of this photopotential upon the intensity of the incident light was also analyzed.

Figure 64 shows the negative photopotential as a function of incident optical power. The relative scale at 10^0 corresponds to $70 \mu\text{W}/\text{cm}^2$, where the photopotential was -85 mV . With approximately $100 \text{ mW}/\text{cm}^2$ white xenon light, photopotentials up to -300 mV have been detected. At the very low light intensity of $0.7 \mu\text{W}/\text{cm}^2$ at 625 nm, a photopotential of -2 mV was still observed. This point is off from the straight line comprising the right side of the figure.

The current-potential characteristics of the CdSe electrode were studied under chopped illumination, and the result is shown in Figure 65. The open-circuit potential versus silver was 350 mV under xenon light. When the potential of the CdSe electrode was scanned in the positive direction, anodic photocurrents flowed. At higher potentials the photocurrent increased, but the dark current increased as well. When scanned in the negative direction, a small cathodic current flowed because of reduction of iodine. Initially, small anodic photocurrent deflections were seen under chopped illumination near the resting potential. At higher cathodic polarization, however, the photocurrent became cathodic. A cathodic photocurrent has been demonstrated by RbAg₄I₅ in Figure 59. Bringing the potential more cathodic than the equilibrium potential of silver resulted in a large cathodic current corresponding to reduction of silver ions to silver. When the potential was brought back to the anodic direction, an anodic current flowed from reoxidation of the silver. Usually the photopotential decreased when the electrode was brought near zero mV versus silver; this could be due to plating of silver on the electrode surface. Upon reoxidation of the silver, however, the photopotential was restored.

In summary, photoactivity in the RbAg₄I₅ solid electrolyte has been demonstrated. The positive photopotential could be a Demmer-type photovoltage. A cathodic photocurrent flowed when the cell was discharged. Illumination may yield iodine on the illuminated side and a reduced species in the bulk of the electrolyte.

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Figure 64. DEPENDENCE OF THE PHOTOPOTENTIAL OF CdSe/RbAg₄I₅ AT 625 nm ON LIGHT INTENSITY (10^0 Corresponds to $70 \mu\text{W}/\text{cm}^2$.)

Figure 65. CURRENT-POTENTIAL CHARACTERISTICS OF CdSe/I₂ + RbAg₄I₅ INTERFACE UNDER CHOPPED ILLUMINATION (Voltage Scan Rate Was 40 mV/s.)

When CdSe was in contact with the solid electrolyte containing iodine redox species, negative photopotentials and anodic photocurrents were detected. This is in analogy to the behavior of n-type semiconductor liquid-junction solar cells. For solid electrolytes the redox species are immobile, which opens up the possibility of constructing a solid-electrolyte photoelectrochemical cell with a storage capability, as shown in Figure 66.

The solid-state electrolyte device would consist of three phases in intimate contact, where in the ideal case the crystal lattice structure of the reductant, oxidant, and solid-electrolyte phases would be similar to facilitate rapid ion movement among them. The reductant and oxidant portions of the device would contain selected redox species, either introduced into fixed immobile lattice sites in the solid electrolyte (in the ideal case) or dispersed and in intimate contact with the solid electrolyte in each of the respective compartments.

The reductant and oxidant electrodes would possess both ionic and electronic conductivity, whereas the separating solid electrolyte would possess only ionic conductivity.

The following general reactions may explain the electrode reactions during charge after separation of electrons and holes in the n-type semiconductor.

At the oxidant electrode -

and at the reductant electrode -

where M_1 represents redox species, which is oxidized by an electron hole h^+ ; C^+ represents a mobile ion conductor; and M_2 represents a redox species, which is reduced by an electron e^- .

During discharge the following reaction may occur:

Figure 66. PHOTOELECTROCHEMICAL CELL WITH A SOLID ELECTROLYTE CONTAINING REDUCTANT AND OXIDANT ON EACH SIDE (The Charging Circuit Contains Rectifiers to Prevent Self-Discharge in the dark.)

The basic requirement of the redox oxidant in contact with n-type semiconductors is that it have an equilibrium potential more negative than the decomposition potential of the semiconductor and more positive than the lower edge of the semiconductor conduction band. The basic requirement of the reductant electrolyte is that its redox equilibrium potential be negative of the oxidant electrolyte and more positive than the lower edge of the semiconductor conduction band. Further work is necessary to demonstrate the practicality of this type of storage device.

We have also fabricated solid-electrolyte cells, based upon LiI, having the configuration —

Cond. Glass/CdSe/LiI + PbI₂/LiI/LiI + C + PbI₂/Cond. Glass

Without CdSe, little photopotential was observed when just the conducting glass was used as an electrode. With the CdSe thermally evaporated on the conducting glass, large photoresponses were seen as shown in Figure 67. Upon illumination with white xenon light, a positive voltage spike developed, followed by a slow positive photopotential. When the light was turned off, a negative voltage spike appeared. When the cell was illuminated with filtered xenon light so that light with wavelengths lower than 4750 Å were not transmitted, a positive spike was generated at first, followed by a negative photopotential. When the light was turned off, a negative spike developed, followed by a decay of the photopotential. In another system the CdSe was evaporated directly onto the LiI/PbI₂ phase and the cell was clamped between two conducting glasses. This cell exhibited negative photopotentials regardless of whether the xenon light was filtered (4750 Å) or not, as shown in Figure 68. Photocurrents were not observed, perhaps because of the high ionic resistivity of this solid electrolyte.

In our work with sodium beta alumina solid electrolyte, we have observed small photopotentials when using either iron oxide or CdSe as photoelectrodes, and only small photocurrents of about 1 $\mu\text{A}/\text{cm}^2$ could be obtained at room temperature. The solid-electrolyte pellet obtained from Ceramtec, Inc. (Salt Lake City), had a thickness of 0.3 cm. The ionic resistivity of this pellet at room temperature is probably too high to permit a reasonable current flow. If thin films of this material could be fabricated, one might be able to make this solid electrolyte practical.

Figure 67. PHOTORESPONSE OF COND. GLASS/CdSe/
LiI + PbI₂/LiI/LiI + C + PbI₂/COND. GLASS
(The CdSe Was Evaporated on the Conducting Glass.)

Figure 68. PHOTORESPONSE OF COND. GLASS/CdSe/
LiI + PbI₂/LiI/LiI + C + PbI₂/COND. GLASS
(The CdSe Was Evaporated on the Solid Electrolyte.)

REFERENCES CITED

1. Prince, M.B., J. Appl. Phys. 26, 534 (1955).
2. Loferski, J.J., J. Appl. Phys. 27, 777 (1956).
3. Wolf, M., Energy Convers. 14, 49 (1975).
4. Landgrebe, A.R., "DOE Division of Energy Storage Systems." Paper presented at the Second Annual Battery and Electrochemical Technology Conference, Arlington, Va., June 5-7, 1978.
5. Nelson, P.A., et al., "High Performance Batteries for Off-Peak Energy Storage and Electric Vehicle Propulsion." Progress Reports ANL-77-17, ANL-76-98, and ANL-76-33 for Contract W-31-109-eng-38. Springfield, Va.: National Technical Information Service, 1976, 1977.
6. Weber, M. and Kummer, J.T., Proc.— Power Sources Symp. 21, 37 (1967).
7. Sammells, A.F., Abstract No. 236 in Extended Abstracts, Vol. 75-2, p. 600. Princeton, N.J.: Electrochemical Society, Inc., (1975).
8. O'Donnell, P., Gahn, R.F. and Pfeiffer, W., "Redox Flow System for Solar Photovoltaic Energy Storage," Conf. Rec. IEEE Photovoltaic Spec. Conf. 12 (1976).
9. Heller, A. and Miller, B., Abstract No. 81 presented at the Division of Colloid and Surface Chemistry, 179th ACS National Meeting, Houston, March 1980.
10. Noufi, R. and Tench, D., J. Electrochem. Soc. 127, 188 (1980).
11. Gerischer, H., J. Electroanal. Chem. 82, 133 (1977).
12. Bard, A.J., J. Photochem. 10, 59 (1979).
13. Schottky, W., Z. Phys. 18, 539 (1942).
14. Spence, E., Elektronische Halbleiter, 2nd Ed., 115. Berlin: Springer 1965.
15. Dewald, J.F., Bell Syst. Tech. J. 39, 615 (1960).
16. Butler, M.A. and Ginley, D.S., J. Electrochem. Soc. 125, 228 (1978).
17. Gerischer, H., in Heller, A., Ed., Proceedings of a Conference on Electrochemistry and Physics of Semiconductor Liquid Interfaces Under Illumination, p. 1. Princeton, N.J.: The Electrochemical Society, 1977.
18. Heller, A. and Miller, B., Electrochim. Acta 25, 29 (1980).

19. Memming, R., Electrochim. Acta 25, 77 (1980).
20. Nozik, A.J., Ann. Rev. Phys. Chem. 29, 189-222 (1978).
21. Bard, A.J. and Wrighton, M.S., J. Electrochem. Soc. 124, 1706 (1977).
22. Laser, D. and Bard, A.J., J. Electrochem. Soc. 123, 1828 (1976).
23. Frank, S.M. and Bard, A.J., J. Am. Chem. Soc. 97, 7427 (1975).
24. Bolts, J.M., et al., J. Am. Chem. Soc. 101, 1378 (1979).
25. Tributsch, H., Z. Naturforsch. 32a, 972 (1977).
26. Tributsch, H., Sol. Energy Mater. 1, 257 (1979).
27. Tributsch, H. and Bennet, J.C., J. Electroanal. Chem. 81, 97 (1977).
28. Tributsch, H., Ber. Bunsenges. Phys. Chem. 81, 361 (1977).
29. Gobrecht, J., Tributsch, H. and Gerischer, H., J. Electrochem. Soc. 125, 2085 (1978).
30. Tributsch, H., J. Electrochem. Soc. 125, 1086 (1978).
31. Kautek, W., Gerischer, H. and Tributsch, H., Ber. Bunsenges. Phys. Chem. 83, 1000 (1979).
32. Tributsch, H., et al., Ber. Bunsenges Phys. Chem. 83, 655 (1979).
33. Manassen, J., Hodes, G. and Cahen, D., Proc. — Electrochem. Soc. 77-3, 34-37 (1977).
34. Manassen, J., Hodes, G. and Cahen, D., J. Electrochem Soc. 124, 532 (1977).
35. Hodes, G., Manassen, J. and Cahen, D., Nature (London) 261, 403 (1976).
36. Giner, J., Swette, L. and Cahill, K., "Screening of Redox Couples and Electrode Materials," NASA-CR-134705. Final report to NASA-Lewis on Contract NAS3-19760. Springfield, Va.: National Technical Information Service, September 1976.
37. Lewerenz, H.J., Heller, A. and DiSalvo, F.J., Abstract 103 presented at the Division of Colloid and Surface Chemistry, 179th ACS National Meeting, Houston, March 1980.
38. Parkinson, B.A., Heller, A. and Miller, B., J. Electrochem. Soc. 126, 954 (1979).
39. Johnston, W.D., et al., J. Electrochem. Soc. 127, 90 (1980).
40. Leamy, H.J., Kimerling, L.C. and Ferris, S.D., in Johari, O., Ed., Scanning Electron Microscopy, Part IV, 1, 529-38. Chicago: IIT Research Institute, 1976.

41. Russak, M.A., et al., J. Electrochem. Soc. 127, 725 (1980).
42. Noufi, R., Kohl, P. and Bard, A.J., J. Electrochem. Soc. 125, 375 (1978).
43. Heller, A., et al., J. Electrochem. Soc. 125, 1156 (1978).
44. Heller, A., Chang, K.C. and Miller, B., J. Electrochem. Soc. 124, 697 (1977).
45. Raleigh, D.O., J. Appl. Phys. 41, 1536 (1970).
46. Owens, B.B., Sprouse, J.S. and Warburton, D.L., Proc.— Power Sources Symp. 25, 8 (1972).
47. Owens, B.B., J. Electrochem. Soc. 117, 1536 (1970).
48. Owens, B.B., Christie, J.H. and Tiedemann, G.T., J. Electrochem. Soc. 118, 1144 (1971).
49. Owens, B.B., in Delahay, P. and Tobias, C.W., Eds., Advances in Electrochemistry and Electrochemical Engineering, Vol. 8, 1-61. New York: Wiley-Interscience, 1971.
50. Christie, J.H., Owens, B.B. and Tiedemann, G.T., Abstract No. 20 in Extended Abstracts, Vol. 74-2, p. 53. Princeton, N.J.: The Electrochemical Society, Inc. (1974).
51. Geller, S., Science 157, 310 (1967).
52. Geller, S. and Lind, M.D., J. Chem. Phys. 52, 5854 (1970).
53. Geller, S., Science 176, 1016 (1972).
54. Geller, S. and Owens, B.B., J. Phys. Chem. Solids 33, 1241 (1972).
55. Geller, S., Skarstad, P.M. and Wilber, S.A., J. Electrochem. Soc. 122, 332 (1975).
56. Masters, J., J. Electrochem. Soc. 117, 1378 (1970).
57. Tan, Y.T. and Trautweiler, F., J. Appl. Phys. 40, 66 (1969).
58. Owens, B.B., Oxley, J.E. and Sammells, A.F., "Applications of Halogenide Solid Electrolytes," in Geller, S., Ed., Topics in Applied Physics, Solid Electrolytes, Vol. 21. Berlin: Springer, 1977.
59. Dember, H., Physik. Z. 33, 207 (1932).
60. Kaneda, T. and Mizuki, E., Phys. Rev. Letters 29, 937 (1972).
61. Radhakrishna, S., Hariharan, K. and Jagadeesh, M.S., J. Appl. Phys. 50, 4883 (1979).

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