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ELECTROCHEMICAL PHOTOVOLTAIC CELLS

Project 65021 Quarterly Technical Progress Report
for October 15, 1979—January 15, 1980

By
Peter G. P. Ang
Robert J. Remick
Anthony F. Sammells

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SUMMARY

During the third quarter of this program, liquid junction devices based upon the semiconductors MoSe_2 , MoS_2 , GaAs, and CdSe have been evaluated. Lifetime testing of MoSe_2 and MoS_2 materials in acidic halogen electrolytes at constant current densities of 5 mA/cm^2 have shown excellent stability to date. For MoSe_2 single crystals in the electrolyte $1\text{M HBr} + 1\text{M Br}_2$, short-circuit currents of 63 mA/cm^2 were achieved with a power conversion efficiency of 6.7% for 200 mW/cm^2 xenon light illumination. Transient potentiostatic measurements made on MoSe_2 in this electrolyte indicated little diffusion control, with exchange currents being of the order of 1 to 10 mA/cm^2 . Good photoresponse of MoS_2 has been observed in $1\text{M HBr} + 1\text{M Br}_2$. The performance of the natural crystal is comparable to the performance of a single-crystal MoS_2 in this electrolyte.

CdSe thermally evaporated onto porous titanium gave efficiencies of about 4% with 100 mW/cm^2 xenon illumination.

Experimental work was initiated on the dye sensitization of Fe_2O_3 and TiO_2 materials. Of the twelve dyes evaluated, little enhancement of the photoresponse of these materials was noted.

Solid-state photoelectrochemical cells have been fabricated, based upon LiI. Cells of the configuration — cond. glass $\text{CdSe/LiI} + \text{PbI}_2/\text{LiI/LiI} + \text{C} + \text{PbI}_2/\text{cond. glass}$ — were fabricated. Photoresponses up to 150 mV were observed.

INTRODUCTION

The proposed program is directed toward evaluation of semiconductor/redox couples systems that show acceptable solar energy conversion efficiency and have the potential for energy storage in a redox cell. The work is organized as follows:

1. Select suitable semiconductor/redox couples based on their relative positions in the energy diagram.
2. Test the photoelectrochemical properties of single-crystal semiconductor materials in the redox electrolytes.
3. Test the photoelectrochemical properties of polycrystalline semiconductor materials in the redox electrolyte.
4. Determine the chemical stability of the single-crystal and polycrystalline materials in the redox electrolytes.
5. Evaluate all solid-state photoelectrochemical devices based upon solid electrolytes.

Emphasis during this reporting period has been placed upon the transition metal dichalcogenides MoSe_2 and MoS_2 , where with the former material power conversion efficiencies of 6.7% have been achieved with 200 mW/cm^2 xenon light illumination.

TASK OBJECTIVES AND ACHIEVEMENTS

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

During this reporting period photoelectrochemical measurements were performed using the photoanodes MoSe_2 , MoS_2 , GaAs, and CdSe. Performance characteristics of these photoanodes were evaluated in electrolytes containing the following redox couples: Cl^-/Cl_2 , Br^-/Br_2 , I^-/I_2 , $\text{Se}^{2-}/\text{Se}_2^{2-}$, and $\text{S}^{2-}/\text{S}_n^{2-}$. Experimental results obtained from these semiconductor/redox interfaces will be discussed in Task 1.2.

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

A single-crystal photoanode of MoS_2 was plated with silver on its back side and contacted to a platinum wire current collector, using a conducting silver epoxy. A second coating of either epoxy or wax was then applied to electrically insulate this current collector from the redox electrolyte.

The photoanode surface area visible for illumination was 0.1 cm^2 . In general, the chemical stability of the insulating coating has been found to be the major life-limiting component of the semiconductor electrode assembly. The photoelectrochemical properties of MoS_2 in $1\text{M HBr} + 1\text{M Br}_2$ and in $0.02\text{M HI} + 0.02\text{M I}_2$ are shown in Figure 1 and Figure 2, respectively. Transient photocurrents were observed in the I^-/I_2 containing electrolyte, whereas with Br^-/Br_2 the photocurrents reached the steady-state value almost immediately. Of these two redox couples, the largest steady-state currents were found with the Br^-/Br_2 redox electrolyte. However, this can, in part, be explained by the lower concentration of I^-/I_2 (0.02M) used in these experiments, chosen because of the high light absorbance of this electrolyte. A photopotential of about -375 mV and steady-state short-circuit currents of about 0.6 mA/cm^2 were recorded in this I^-/I_2 containing electrolyte. The cell was illuminated with 200 mW/cm^2 xenon light. For the Br^-/Br_2 redox electrolyte, photopotentials up to -555 mV and a short-circuit current of about 42 mA/cm^2 were observed. The MoS_2 crystal was also tested in the electrolyte $6\text{M HCl} + 1\text{M Fe}^{+2}/\text{Fe}^{+3}$. Here 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 3. A similar photo-response was exhibited by MoSe_2 in $\text{Fe}^{+2}/\text{Fe}^{+3}$ redox electrolyte as reported earlier.¹

The photoelectrochemical performance of single-crystal MoSe_2 in alkaline electrolytes containing $\text{Se}^{2-}/\text{Se}_2^{2-}$ as the redox couple was evaluated. For the electrolyte composition $6\text{M KOH} + 1\text{M SeO}_2 + 1\text{M Na}_2\text{Se}$, photopotentials of -160 mV and short-circuit currents of 0.24 mA/cm^2 were achieved. The current-potential characteristics are shown in Figure 4. Improved current collection has been achieved with MoSe_2 single crystals by first electrodepositing silver from a silver nitrate solution onto the back side of the crystal. The platinum wire current collector was then contacted to this silver layer by use of a conducting silver epoxy. This procedure was found to greatly improve electrode performance. The photoelectrochemical performance of such a MoSe_2 electrode in the electrolyte $1\text{M HBr} + 1\text{M Br}_2$ is shown in Figure 5. Its potential versus a platinum electrode in the same solution was -5 mV in the dark and -490 mV under xenon light illumination. Short-circuit current of about 63 mA/cm^2 was measured. The photoanode could be operated with a power conversion efficiency of about 6.7% and a fill factor of 0.44 under the approximately 200 mW/cm^2 xenon light illumination used. A heat-absorbing filter was inserted in the light path.

Figure 1. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL MoS_2 IN 1M HBr + 1M Br_2

Figure 2. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL MoS_2 IN 0.02M HI + 0.02M I_2

Figure 3. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL MoS₂ IN 6M HCl + 1M Fe²⁺/Fe³⁺

Figure 4. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL MoSe_2 IN 6M KOH + 1M SeO_2 + 1M Na_2Se

Figure 5. CURRENT-POTENTIAL CHARACTERISTICS OF
 SINGLE-CRYSTAL MoSe₂ IN 1M HBr + 1M Br₂
 (200 mW/cm² Xenon Light Illumination, E_{Pt} Vs. SCE = 790 mV,
 Efficiency = 6.7%, Fill Factor = 0.44)

These preliminary performance characteristics can still be improved with better selection of crystal surface and contacts. Our data showed that the MoSe_2 photoanode performed significantly better in acidic electrolyte with Br^-/Br_2 redox couple than in any other redox electrolyte evaluated to date.

The MoSe_2 electrode was also tested in 6M HCl bubbled with chlorine gas. The electrode potential versus platinum in the same solution was -90 mV in the dark and -650 mV under illumination. The current-voltage characteristics are shown in Figure 6. At -90 mV the short-circuit current density was 110 mA/cm^2 . A power conversion efficiency of about 9.9% was calculated, and the fill factor was 0.32. The relatively low fill factor was due to the slow rise of the photocurrent near the resting potential. The stability of this electrode was also studied and will be discussed later in Task 2.1.

Transient potentiostatic techniques were performed on single-crystal MoSe_2 in 1M HBr + 1M Br_2 as shown in Figure 7. There, a 100-mV anodic potential pulse of 10-ms duration was applied to the electrode, starting from the resting potential under approximately 200 mW/cm^2 xenon light illumination. 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 8. From the data in the low-overpotential region we obtain 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. Further work in this direction will be performed in the future.

In the October 1979 quarterly report we have shown that very good polarization characteristics for MoSe_2 as well as for platinized platinum electrodes were found with Br^-/Br_2 in acidic solution. Since we have proposed to study a photoelectrochemical storage system based on $\text{n-MoSe}_2/\text{Br}^-/\text{Br}_2/\text{I}^-/\text{I}_2/\text{Pt}$, it would be of interest also to study the polarization characteristics of platinum in electrolytes with I^-/I_2 redox couple. The results of a potential sweep experiment on platinized platinum at different pH ranges are shown in Figure 9. Curve 1 was obtained in 1M HI + 1M I_2 , pH 0.1; curve 2 in 1M KI + 1M I_2 + 0.1M KOH,

Figure 6. CURRENT-POTENTIAL CHARACTERISTICS OF
SINGLE-CRYSTAL MoSe_2 IN 6M HCl + BUBBLED Cl_2
(200 mW/cm^2 Xenon Light Illumination, E_{Pt} Vs. SCE = 1140 mV,
Efficiency = 9.9%, Fill Factor = 0.32)

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Figure 7. 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 8. PLOT OF INITIAL PHOTOCURRENT OF MoSe₂ SINGLE-CRYSTAL AS A FUNCTION OF THE AMPLITUDE OF THE TRANSIENT PULSE (Electrolyte: 1M HBr + 1M Br₂, 27°C)

Figure 9. POTENTIAL-SWEEP (40 mV/s) POLARIZATION CURVES OF PLATINIZED PLATINUM AT 25°C IN —

1. 1M HI + 1M I₂, pH 0.1
2. 1M KI + 1M I₂ + 0.1M KOH, pH 9.0
3. 1M KI + 1M I₂ + KOH, pH 13.1.

pH 9.0; and curve 3 in 1M KI + 1M I₂ + KOH at pH 13.1. We can see that a reduction process is favored at low pH (curve 1), while the anodic oxidation is better at high pH (curve 3). The good reduction process of I₂ on Pt at low pH range is compatible with the great performance of MoSe₂ for the photo-oxidation of Br⁻ at low pH range. A storage system with Br⁻/Br₂ and I⁻/I₂ redox couples is being constructed in the laboratory. Separator materials that will be tested include Daramic, Nafion and thirsty glass.

Single-crystal GaAs has been investigated in the electrolyte 6M HCl + 1M SbCl₃ + 1M SbCl₅, although at ambient temperatures the salts were not completely soluble in the acid solution. This single-crystal material was found to have 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 10. Although large photocurrents were obtained, the large dark potential is not encouraging.

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

Using naturally-occurring MoS₂, the preliminary photoelectrochemical properties were evaluated. As shown in Figure 11, this material demonstrated a very good photoresponse in acid electrolyte with Br⁻/Br₂ redox couple. Photopotentials up to -425 mV and short-circuit currents of about 17 mA/cm² were observed. With acid electrolyte containing Cl⁻/Cl₂ as a redox couple, photopotentials up to -200 mV and short-circuit currents of about 14 mA/cm² were observed. The current-voltage characteristic of the MoS₂ photoanode is shown in Figure 12. The electrode potential in the dark was -405 mV, and under illumination it was -625 mV versus a platinum electrode in the same solution. The large dark potential suggested an irreversible electrode behavior.

New attempts to produce polycrystalline MoSe₂ by electrodeposition and heating technique have not yet produced photoactive material. Preparation is underway to electrolytically produce samples via high-temperature molten salt techniques.²

Attempts to make polycrystalline CdSe by thermal vacuum evaporation on nickel foil did not produce significant improvement over the film evaporated previously on iron foil. The current-voltage properties in 6M KOH + 2.5M K₂S + 2.5M S + 0.025M K₂Se + 0.025M SeO₂ are displayed in Figure 13. Photopotentials of -265 mV and short-circuit currents of about 1.8 mA/cm² were

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Figure 10. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M HCl + 1M SbCl₃ + 1M SbCl₅

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Figure 11. CURRENT-POTENTIAL CHARACTERISTICS OF NATURAL MoS₂ IN 1M HBr + 1M Br₂

Figure 12. CURRENT-POTENTIAL CHARACTERISTICS OF NATURAL-CRYSTAL MoS_2 IN 6M HCl + BUBBLED Cl_2 (200 mW/cm^2 Xenon Light Illumination, E_{Pt} Vs. SCE = 1140 mV)

Figure 13. CURRENT-POTENTIAL CHARACTERISTICS OF VACUUM-EVAPORATED CdSe ON NICKEL FOIL IN 6M KOH + 2.5M K_2S + 2.5M S + 0.025M K_2Se + 0.025M SeO_2 ELECTROLYTE (Annealed in Air at 350°C for 30 Minutes and Etched in HCl for 30 Seconds)

observed. A sharp increase in the anodic current was seen at higher potential, perhaps due to sulfidation of the nickel substrate. The CdSe film has a tendency to flake off from the nickel foil, thus leaving the nickel surface exposed to the electrolyte. Better results were obtained when a porous nickel electrode (Gould, Inc.) was used as a substrate for the CdSe film. After heating at 350°C in air for 30 minutes and etching in 6M HCl for 30 seconds, the results shown in Figure 14 were obtained. Photopotentials of about -250 mV and short-circuit current densities of approximately 7.8 mA/cm² were obtained. At the high anodic potential region, a sharp increase in the dark- and photo-current was observed again.

Using porous titanium as a substrate, the CdSe gave 20 mA/cm² short-circuit current in 6M KOH + 2.5M K₂S + 2.5M S as the electrolyte, as shown in Figure 15, where efficiencies of 4% were achieved with 100 mW/cm² xenon illumination. The fill factor was 0.45.

The enhanced sensitization of wider band-gap semiconductor materials with selected dyes has been evaluated, using Fe₂O₃ and TiO₂ with dyes listed in Table 1. Photoanodes comprised of polycrystalline Fe₂O₃ and TiO₂ were supported, respectively, on iron and titanium wires. Initial experiments were directed toward determining if these stable semiconductors could, in fact, be sensitized to respond to a wider fraction of the solar spectrum. Later experiments were then directed towards evaluating whether such dyes affected the reaction kinetics of the photoanodic reaction.

For enhanced sensitization of a photoanode to an increased fraction of the solar spectrum three criteria must be met: 1) electrons lying in partially-filled molecular orbitals must be available for photoexcitation to either a higher unoccupied orbital or into the continuum (photoionized), 2) the dye excited-state energy level must lie above the conduction band of the photoanode, and 3) the energy difference between the ground state and the excited state of the dye molecule must be less than the semiconductor band-gap. To determine the compatibility of the selected dyes with the electrolytes in which they were to be evaluated, their solubility in ethanol and in 6M KOH and their respective color change in the electrolyte were identified. Only phthalocyanine was found to be insoluble in ethanol. As a result, a suspension of phthalocyanine was prepared by mixing the dye with ethanol in an ultrasonic vibration apparatus. Of the dyes tested, only Eosin-Y was found to be soluble in 6M KOH. Ethanolic

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Figure 14. CURRENT-POTENTIAL CHARACTERISTICS OF VACUUM-EVAPORATED CdSe ON POROUS NICKEL IN 6M KOH + 2.5M K_2S + 2.5M S + 0.025M K_2Se + 0.025M SeO_2 (Electrode Annealed in Air at 350°C for 30 Minutes and Etched in HCl for 30 Seconds)

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Figure 15. CURRENT-POTENTIAL CHARACTERISTICS OF CdSe, THERMAL VACUUM-EVAPORATED ON POROUS Ti ELECTRODE (Electrolyte 6M KOH + 2.5M K₂S + 2.5M S, 100 mW/cm² Xenon Illumination, Efficiency = 4%, Fill Factor = 0.45, Annealed in Air at 350°C for 30 Minutes, Slow Cooling, Etched in 6M HCl for 15 Seconds)

Table 1. SENSITIZATION DYES FOR Fe_2O_3 AND TiO_2 ELECTRODES

Acridine Orange

8-Anilino-1-naphthalene sulfonic acid ammonium salt (8-ANS)

Eosin-Y

Merocyanine 540

Methylene Blue

Neutral Red

Phthalocyanine

Rhodamine B

Rose Bengal

8-p-toluidino-1-naphthalene sulfonic acid (8-TNSA)

6-p-toluidino-2-naphthalene sulfonic acid (6-TNSA)

2-p-toluidinylnaphthylene-6-sulfonate (2-TN6S)

solutions of the dyes were placed dropwise into an excess of 6M KOH, and color changes were noted. Acridine orange, Eosin-Y, merocyanine, methylene blue, and neutral red were all observed to change color in base, as shown in Table 2.

Photoanodes made of Fe_2O_3 or TiO_2 were prepared by heating $1/2\text{-cm}^2$ metal foils to redness in air. The photoanodes were placed in a quartz vessel containing 6-molar potassium hydroxide, a platinum counterelectrode, and a mercury/mercuric oxide reference electrode.

In the first experimental series, light from a xenon lamp, filtered to eliminate all wavelengths shorter than $4750\text{\AA}$ and having an intensity after the filter of $45\text{ milliwatts/cm}^2$, was used to illuminate the photoanode under test. In this manner light with a spectral energy just below that required to activate the photoanode was available. Electrodes were prepared by coating the exposed semiconductor surface with an alcohol solution of dye and drying in air.

A cyclic voltammogram, made by scanning to 700 mV positive of the rest potential, was used to compare the photocurrent under filtered illumination with the dark current for anodes both with and without dye coatings.

In this filtered illumination the photocurrent for an unsensitized photoanode was only about 1% to 5% higher than the dark current.

If a dye is capable of sensitizing the photoanode to wavelengths of light extending beyond the threshold of the filter, a significant increase in photocurrent should be noted. However, none of the 12 dyes tested were observed to give significant enhanced photocurrents on either iron oxide or titanium dioxide photoanodes under these experimental conditions.

The second experimental series was conducted using a xenon lamp filtered to provide a spectrum equivalent to AM-1 solar radiation. Under these conditions, the photocurrent associated with the oxidation of OH^- on unsensitized photoanodes was several orders of magnitude higher than the dark current. In these tests a photoanode was placed in a quartz vessel containing 6M KOH subjected to a homogeneous beam of nearly parallel light. Cyclic voltammograms for the photoanodes were then compared with and without dye added to the electrolyte.

Table 2. PHYSICO-CHEMICAL PROPERTIES OF SOME DYES

<u>Dye</u>	<u>6M KOH + (C₂H₅OH + dye)</u>	<u>6M KOH + dye</u>	<u>Ethanol</u>
Acridine orange	orange to red	no cc, i	s
8-ANS	no cc	no cc, i	s
Eosin yellow	yellow to brown	no cc, s	s
Merocyanine 540	purple to yellow	no cc, i	s
Methylene blue	blue to violet	green to blue, i	s
Neutral red	red to yel-orange.	no cc, i	s
Rose bengal	no cc	no cc, i	s
8-TNSA	green to brown	no cc, i	δc
6-TNSA	no cc	no cc, i	δs
2-TN6S	pink to clear	no cc, i	δs
Rhodamine B	no cc	no cc, i	s
Phthalocyanine	no cc	no cc, i	i

cc = color change

i = insoluble

s = soluble

δ = partially

Of the 12 dyes tested, none were found to enhance the photocurrent of either the iron oxide or titanium dioxide semiconductor electrodes. However, acridine orange, 8-TNSA, 6-TNSA, and 2-TNGS were observed to reduce the anodic currents. This phenomenon could be the result of the attenuation of the light by the dye layer, or by the electrochemical insulation of the electrode surface by the dye layer.

In conclusion, none of the 12 dyes listed in Table 1 have proved to enhance the photooxidation of OH^- species on polycrystalline iron oxide or titanium dioxide electrodes. Further work on photosensitization will be done in the future with dissolved redox species, e.g., H_2O_2 . We have demonstrated that H_2O_2 drastically increased the photocurrents of iron oxide photoanodes.³

Task 2. Development of Long-Life Electrochemical Photovoltaic Cells

Task 2.1. Identification of Photoanode Corrosion

To date, both MoSe_2 and MoS_2 photoanodes appear to be very stable in electrolytes containing 1M HBr /1M Br_2 redox couples, with no change being apparent on the semiconductor surface visually after many days of operation. The major life-limiting problem of the electrode assembly has been in identifying suitable insulating coatings between the electrolyte and the silver epoxy used in making electronic contact to the semiconductor. Coatings evaluated to date have included regular epoxies, silicone rubber RTV, Plexiglas, polypropylene and paraffin wax. 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 lamp with a KG-2 filter. The potential of the photoanode versus a platinum electrode stayed close to -450 mV since the beginning of the test on January 21, 1980, as shown in Figure 16. The cell was checked every day for the photopotential (-530 mV) and the short-circuit current (20 mA/cm^2), and no change has been observed until today.

A similar lifetime test for MoS_2 natural crystal, starting from February 3, 1980, is shown in Figure 17. 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. Both of these electrodes are operative as of the writing of this report.

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Figure 16. VOLTAGE OF SINGLE-CRYSTAL MoSe_2 VERSUS Pt IN 1M HBr + 1M Br_2
DURING A LONG-TERM EXPERIMENT UNDER CONSTANT-CURRENT LOAD OF 5 mA/cm^2
[Quartz-Halogen Illumination, Heat-Filtered (100 mW/cm^2).
Electrolyte Was Not Stirred. Temperature 28°C , Started on January 21, 1980]

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Figure 17. VOLTAGE OF NATURAL MoS_2 CRYSTAL VERSUS Pt IN 1M HBr + 1M Br_2
DURING A LONG-TERM EXPERIMENT UNDER CONSTANT-CURRENT LOAD OF 5 mA/cm^2
[Quartz-Halogen Illumination, Heat-Filtered (60 mW/cm^2)).
Electrolyte Was Not Stirred. Temperature 27°C , Started on February 4, 1980]

MoSe₂ showed very good photoresponse in 6M HCl + Cl₂, as described in Task 1.2. The long-term stability of this photoanode was studied by monitoring the photocurrent at a potential of 350 mV anodic from the resting potential. During the experiment, chlorine was constantly bubbled in the electrolyte. A rapid decrease in the photocurrent was noticed, as shown in Figure 18. After running the test for 1.5 hours, the electrode was examined, and it showed strong evidence of corrosion. Thus, MoSe₂ did not appear to be stable in acid electrolyte with Cl⁻/Cl₂ redox couple. The long-term stability of natural MoS₂ in 6M HCl + Cl₂ was evaluated. At 125 mV anodic from the rest potential, an initial photocurrent of about 10 mA/cm² was measured. The photocurrent decreased by about 50% within a two-hour period, as shown in Figure 19. The long-term stability of MoS₂ and MoSe₂ in neutral and alkaline solutions of Cl⁻/Cl₂ couple seems to be better than in the acid solution. This finding will be investigated further and will be reported next month.

During this reporting period we have attempted to stabilize an electrode against photoanodic corrosion 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 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 conducted to study the optimum amount of cathodic current needed for complete protection at various light intensities, anodic current load, and redox couple concentration.

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

Cadmium selenide was thermal-vacuum evaporated on a nickel foil and annealed at 350°C for 1/2 hour in air. The foil was then sealed to the end of a glass tube in such a manner that only the CdSe was exposed to the electrolyte. This CdSe photoanode was then immersed in a variety of solvents containing various redox couples in an attempt to find a nonaqueous solvent/redox couple compatible with CdSe. Preliminary screening of the solvents and redox couples was accomplished by measuring the open-circuit photopotential versus a platinum

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Figure 18. DECAY OF THE PHOTOCURRENT OF SINGLE-CRYSTAL MoSe_2
IN 6M $\text{HCl} + \text{Cl}_2$ AT 350 mV ANODIC FROM THE RESTING
POTENTIAL (200 mW/cm^2 Xenon Light Illumination)

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Figure 19. 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)

electrode in the same solution. For those solvents showing a rapid photo-response 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 the lack of solubility of the redox couple and/or the supporting electrolyte.

Six solvents were 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 2/10 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 3.

In a similar manner the six solvents were tested, using potassium sulfide and sulfur as a redox couple with potassium hydroxide as the supporting electrolyte. Once again, solubility proved to be a problem. K_2S 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. All three solids (K_2S , S, and KOH) were completely dissolved in DMSO to yield a blood-red solution. The results are shown in Table 4.

Further work will be conducted to optimize the solubility and the absorption characteristics of the nonaqueous redox systems. The halogen redox couples will also be studied, since their well-known fast kinetic properties may be beneficial for nonaqueous systems.

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

Although photocurrents and photovoltages have been previously reported on cells based upon the solid electrolyte $RbAg_4I_5$, some question remains as to the relative photoactivity of the semiconductor materials present at the oxidant electrode and of that of the solid electrolyte. To gain some insight into this question, solid-state cells based upon LiI of configuration -

cond. glass CdSe/LiI + PbI_2 /LiI/LiI + C + PbI_2 /cond. glass

were fabricated. Without CdSe, little photopotential was observed when using just the conducting glass as an electrode. With the CdSe thermally evaporated on the conducting glass, large photoresponses were seen as shown in Figure 20. Upon illumination with white xenon light, a positive voltage spike followed

Table 3. 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	--

Table 4. PHOTORESPONSE OF CdSe IN VARIOUS NONAQUEOUS SOLVENTS
WITH K_2S , S, AND KOH UNDER 20 mW/cm² ILLUMINATION

Solvent	Photo- potential, mV	Shorted Photo- current, $\mu A/cm^2$	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_2S /1M S, 5M KOH	160	19	Aqueous for com- parison

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Figure 20. PHOTORESPONSE OF CONDUCTING-GLASS
 $\text{CdSe/LiI} + \text{PbI}_2/\text{LiI/LiI} + \text{C} + \text{PbI}_2/\text{CONDUCTING GLASS}$
 (The CdSe Was Evaporated on the Conducting Glass.)

by a slow positive photopotential developed. When the light was turned off, a negative voltage spike appeared. When the cell was illuminated with filtered xenon light such that light with wavelengths lower than $4750\text{\AA}$ are not transmitted, we got at first a positive spike 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/PbI_2 phase, and the cell was clamped between two conducting glass. This cell exhibited negative photopotentials regardless of whether the xenon light was filtered ($4750\text{\AA}$) or not, as shown in Figure 21. Photocurrents were not observed, perhaps because of the high ionic resistivity of this solid electrolyte at room temperature. Attempts will be made in the future to make thin-film cells so that the cell resistance can be reduced. Also, the origin of the photoresponse will be further analyzed.

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Figure 21. PHOTORESPONSE OF CONDUCTING-GLASS
 $\text{CdSe/LiI} + \text{PbI}_2/\text{LiI/LiI} + \text{C} + \text{PbI}_2/\text{CONDUCTING GLASS}$
 (The CdSe Was Evaporated on the Solid Electrolyte.)

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