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MASTER

ELECTROCHEMICAL PHOTOVOLTAIC CELLS

Project 65039 Quarterly Technical Progress Report

For the Period August 1 Through October 31, 1980

**Peter G. P. Ang
Anthony F. Sammells**

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**Prepared by
Institute of Gas Technology
IIT Center, 3424 S. State Street
Chicago, Illinois 60616**

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INTRODUCTION

Liquid-junction photoelectrochemical cells can be used either for the direct conversion of solar energy to electricity or to generate stored chemical species available for later electrochemical discharge. The objective of this program is to identify experimental approaches for electrochemical photovoltaic cells that not only show promise of high power-conversion efficiencies but also have the potential to achieve long life and the capacity for energy storage.

The work is organized as follows:

1. Selection of High-Efficiency Semiconductor Photoelectrode/Electrolyte Systems
2. Development of Long-Life Electrochemical Photovoltaic Cells
3. Development of an All Solid-State Electrochemical Photovoltaic Cell With In-Situ Storage
4. Demonstration of Laboratory-Size Photoelectrochemical Cell With Redox Storage.

This program is directed toward identifying a suitable match between the proposed semiconductor and the redox species present in aqueous, nonaqueous, and solid electrolytes for achieving the necessary performance and semiconductor stability requirements. Emphasis is on aqueous electrolyte-based systems where fast kinetics are favored. The proposed systems will be compatible with convenient storage of the electroactive species generated and their later electrochemical discharge in a redox cell.

TASK OBJECTIVES AND ACHIEVEMENTS

Task 1. Selection of High-Efficiency Semiconductor Photoelectrode/Electrolyte SystemsTask 1.1. Evaluation of Single-Crystal Systems

During this reporting period we evaluated the following semiconductor electrode/redox couple systems:

- p-GaP/1M Na₂S + 0.1M S
- p-GaP/1M Na₂S + 1M S + 1M NaOH
- p-Si/1M Na₂S + 1M S + 1M NaOH
- p-ZnTe/1M Na₂S + 0.1M S.

Task 1.2. Characterization of Single-Crystal Systems

P-type GaP (Zn doped, $1.2 \times 10^{18}/\text{cm}^3$) single crystal, obtained from Atom-ergic Chemetals Corp., was studied during this period. Contact to the crystal was made by electrodepositing indium and zinc and then annealing the crystal at 400°C under hydrogen for 2 hours. A nickel wire was attached to the contact area using a conducting silver epoxy; the electrode assembly was then insulated with epoxy and wax. The crystal was tested as a photocathode in a solution of 1M Na₂S + 0.1M S (redox potential of -690 mV versus SCE). The potential of the GaP electrode versus a platinum reference electrode in the same solution was -150 mV in the dark and 80 mV under 200 mW/cm² xenon illumination. At the dark potential, the short circuit photocurrent was -0.5 mA/cm². The current-potential characteristics of this electrode under chopped illumination are shown in Figure 1. The electrode potential was scanned from its open-circuit potential under illumination to the cathodic direction. The photocurrent was small, and the electrode exhibited poor fill factor. Larger photocurrents were obtained in an alkaline solution of 1M Na₂S + 1M S + 1M NaOH, as shown in Figure 2. The potential of the p-GaP electrode versus a platinum reference electrode in the solution was -60 mV in the dark and 75 mV under illumination. Photocurrent at the position of the dark potential was -0.6 mA/cm².

Our data indicate that p-GaP generates photopotential only up to 200 mV in magnitude. Very large photocurrents can be obtained in 1M HI + 0.18M I₂ solution, but only small photocurrents can be obtained in the sulfide/polysulfide system.

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Figure 1. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL p-GaP IN 1M Na₂S + 0.1M S ($E_{\text{dark}} = -150$ mV; $E_{\text{light}} = 80$ mV versus Pt)

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Figure 2. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL p-GaP IN 1M S + 1M Na₂S + 1M NaOH ($E_{\text{dark}} = -60$ mV; $E_{\text{light}} = 75$ mV versus Pt)

P-type ZnTe single crystal (Cleveland Crystals Inc., 111 orientation, resistivity 6 ohm-cm) was studied during this period. Contact to the crystal was made by depositing indium on its back side. A nickel wire was attached to the contact area using a conducting silver epoxy, and the electrode assembly was properly insulated with epoxy. The crystal (0.2 cm^2 surface area) was tested as a photocathode in a solution of $1\text{M Na}_2\text{S} + 0.1\text{M S}$ (redox potential of -690 mV versus SCE). The surface of the crystal was etched for 10 seconds in HF/HNO_3 solution before the experiment. The potential of the ZnTe electrode versus a platinum reference electrode in the same solution was -50 mV in the dark and $+5 \text{ mV}$ under $200 \text{ mW}/\text{cm}^2$ xenon illumination. At the dark potential, the short-circuit photocurrent was $-0.5 \text{ mA}/\text{cm}^2$. The current-potential characteristics of this electrode under chopped illumination are shown in Figure 3. The electrode potential was scanned from its open-circuit potential under illumination to the cathodic direction. The photocurrent was small, and the electrode exhibited poor fill factor. Larger photocurrents were obtained after cathodization at -2 V , as shown in Figure 4. However, the fill factor is still poor. Upon repeated etching, an increasingly n-type character appeared as the electrode developed negative photopotentials.

Task 1.3. Surface Treatment Characterization

Further work has been done to improve the photoelectrochemical properties of a variety of semiconductors by introducing metals and/or catalysts on the electrode surface. A gradual increase in the photocurrent of p-Si was produced after the crystal was repeatedly electrodeposited with nickel from an aqueous NiCl_2 solution. The current-potential characteristics of this electrode in $1\text{M Na}_2\text{S} + 1\text{M S} + 1\text{M NaOH}$ solution are shown in Figure 5. The open-circuit potential versus a platinum reference electrode in the same solution was -100 mV in the dark and -40 mV under $200 \text{ mW}/\text{cm}^2$ xenon light illumination. The absolute value of the open-circuit potential varied from experiment to experiment. The photopotential, however, was always about 50 mV . This value is quite small compared with the 400 mV photopotential of an uncoated p-Si electrode. (See Project No. 65039 April-July Quarterly Report.) After nickel electrodeposition, the photocurrent of the p-Si crystal became three times as large. This phenomenon could be caused by the electrocatalytic activity of the nickel toward the sulfide/polysulfide redox couple. Note that, as reported previously in the April-July Quarterly Report, we had found no improvement in photocurrent when the

Figure 3. CURRENT-POTENTIAL CHARACTERISTICS OF p-ZnTe SINGLE CRYSTAL IN 1M Na₂S + 0.1M S

Figure 4. CURRENT-POTENTIAL CHARACTERISTICS OF p-ZnTe SINGLE CRYSTAL IN 1M Na₂S + 0.1M S AFTER ETCHING AND CATHODIZATION

crystal was just dipped in NiCl_2 solution. New ways to improve the magnitude of the photopotential are still being sought. We have also coated the p-Si electrode surface with either platinum, gold, or chromium. None give significant improvement in the photoelectrochemical performance.

Further work was done to improve the photoelectrochemical properties of p-Si by introducing metals and/or catalysts on the electrode surface. A gradual increase in the photocurrent of p-Si was produced after the crystal was repeatedly electrodeposited with nickel from an aqueous NiCl_2 solution. Further improvement was obtained by cathodizing the electrode at -2 V versus a platinum reference electrode in the solution for several minutes. The current-potential characteristics of this electrode in $1\text{M Na}_2\text{S} + 1\text{M S} + 1\text{M NaOH}$ solution are shown in Figure 6. The open-circuit potential versus a platinum reference electrode in the same solution was -150 mV in the dark and +50 mV under 200 mW/cm^2 xenon light illumination. The absolute value of the open-circuit potential, however, varied from experiment to experiment. Further work is being conducted to improve the fill factor of the electrode.

Task 1.4. Characterization of Polycrystalline System

The labeling of the figure for CdSe in the April-July Quarterly Report was incorrect. For clarification the corrected version will be described here. We fabricated CdSe photoanodes by a new, simple technique. CdSe powder (Apache Chemical, Inc., 99.99%) was mixed with water, and the slurry was brushed onto a porous titanium substrate. After air drying, the electrode was heat treated at 400°C in air for 1 hour. It was then etched with 6M HCl for 10 seconds. The photoelectrochemical properties of this electrode are shown in Figure 7. The open-circuit potential versus a platinum reference electrode in the solution was -70 mV in the dark and -500 mV under 200 mW/cm^2 xenon light illumination. A short-circuit current density of about 11 mA/cm^2 was achieved. The power-conversion efficiency and fill factor were 1.34% and 0.49, respectively.

During this period we also investigated another technique to make CdSe electrodes. First, cadmium was deposited onto a porous titanium electrode by rubbing cadmium pellets onto the electrode surface. Then selenium was electrodeposited by passing a cathodic current in an aqueous solution of $\text{SeO}_2 + \text{H}_2\text{SO}_4$. The electrode was then annealed at 400°C in air for 1 hour. In $1\text{M Na}_2\text{S} + 1\text{M S} + 1\text{M NaOH}$ solution, the electrode demonstrated good photoresponse. The performance

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Figure 5. CURRENT-POTENTIAL CHARACTERISTICS OF NICKEL-PLATED p-Si SINGLE CRYSTAL IN 1M Na_2S + 1M S + 1M NaOH ($E_{\text{dark}} = -100$ mV; $E_{\text{light}} = -40$ mV versus Pt)

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Figure 6. CURRENT-POTENTIAL CHARACTERISTICS OF NICKEL-PLATED p-Si IN 1M Na_2S + 1M S + 1M NaOH AFTER CATHODIZATION ($E_{\text{dark}} = -150$ mV; $E_{\text{light}} = 50$ mV versus Pt)

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Figure 7. CURRENT-POTENTIAL CHARACTERISTICS OF CdSe SLURRY ON POROUS TITANIUM SUBSTRATE IN 1M Na₂S + 1M S + 1M NaOH ($E_{\text{dark}} = -70$ mV; $E_{\text{light}} = -500$ mV versus Pt; $i_{\text{SC}} = 11$ mA/cm²; $\eta = 1.3\%$; FF = 0.49)

improved further after etching for a total of 20 seconds in 6M HCl. The results are shown in Figure 8. The open-circuit potential versus a platinum reference electrode in the solution was -150 mV in the dark and -500 mV under 200 mW/cm² xenon light illumination. A short-circuit current density of 21 mA/cm² was achieved. The power-conversion efficiency and fill factor were 2.8% and 0.51, respectively.

During this quarter we made attempts to produce other polycrystalline materials, for example, indium selenide. This was made by first rubbing indium onto a porous titanium electrode and then electrodepositing selenium from a solution of SeO₂ in H₂SO₄. The electrode was then annealed at 400°C in a hydrogen atmosphere for 1 hour. It was tested in a solution of 1M Na₂S + 1M S + 1M NaOH. The open-circuit potential versus a platinum reference electrode in the solution was -160 mV in the dark and -170 mV under illumination. Upon

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Figure 8. CURRENT-POTENTIAL CHARACTERISTICS OF CdSe ELECTRODE MADE BY ELECTRODEPOSITION OF Se ON Cd/POROUS TITANIUM ELECTRODE (Electrolyte 1M Na₂S + 1M S + 1M NaOH: $E_{\text{dark}} = -130$ mV; $E_{\text{light}} = -500$ mV versus Pt; $i_{\text{SC}} = 21$ mA/cm²; $\eta = 2.8\%$; FF = 0.51)

scanning the potential in the anodic direction, some photocurrents were detected on top of a dark current (Figure 9). The dark current rose sharply at potentials above 75 mV, perhaps because of sulfidation of the electrode. Further work is being performed to improve the characteristics of this electrode.

Figure 9. CURRENT-POTENTIAL CHARACTERISTICS OF INDIUM SELENIDE ON POROUS TITANIUM ELECTRODE IN 1M Na_2S + 1M S + 1M NaOH

Attempts were made to produce polycrystalline layered compounds, e.g., MoSe_2 , MoS_2 , and WSe_2 by rubbing the material onto a porous titanium electrode. In some cases, the electrodes were annealed at 400° or 800°C under a hydrogen atmosphere for 1 hour. To date, however, no photoresponse could be obtained from these electrodes. Large anodic and cathodic dark currents were obtained from these electrodes in solutions containing halogen redox couples. These electrodes will be excellent for use in the redox cell where the stored electrochemical energy is discharged. The performance of these electrodes are described in Task 4.

Task 1.5. Characterization of Polycrystalline Surface Treatment

A CdSe electrode was made by rubbing Cd and electroplating Se onto a porous titanium electrode. This electrode was dipped in a CoCl_2 solution to incorporate cobalt onto the electrode. Cobalt and its sulfide have been reported as good electrocatalysts for the sulfide/polysulfide redox system.¹ The electrode was annealed at 400°C under nitrogen for 1 hour. After etching for 10 seconds in 6M HCl the photoelectrochemical response shown in Figure 10 was obtained. The dark potential was -130 mV, and the potential under 200 mW/cm^2 xenon light was -420 mV versus a platinum electrode in the solution. A photocurrent of 12 mA/cm^2 flowed at -130 mV versus platinum. This electrode exhibited quite a large anodic dark current, perhaps because of the presence of excess cobalt on the surface. The photocurrent is slightly larger compared with the graph shown in Figure 7.

Task 1.6. Sample Deliveries

A sample of vacuum-evaporated CdSe on a porous titanium substrate is being delivered to SERI. The electrode has been annealed in air at 350°C for 1 hour.

Task 2. Development of Long life Electrochemical Photovoltaic Cells

Task 2.1. Lifetime Testing of Aqueous Systems

Long-term testing was started on p-GaP (zinc doped, 1.2 to $1.5 \times 10^{18}/\text{cm}^3$) in $1\text{M HI} + 0.1\text{M I}_2$. The photocathode (0.1 cm^2 surface area) was illuminated with a quartz-halogen lamp (about 100 mW/cm^2) and connected to a platinum counter electrode (1 cm^2 surface area) through a 100 ohm load. The open-circuit voltage of the cell was 100 mV under illumination and 20 mV in the dark. With the load, the cell voltage dropped to about 70 mV. This voltage was recorded as a function of time as shown in Figure 11. During the first few days performance increased slightly. Apparently the surface of the crystal was etched continuously by the solution. After the 5th day the voltage started to decline, and after the 10th day it decreased rapidly. The p-GaP electrode was examined on the 14th day, and evidence of surface corrosion was seen. The silver-epoxy contact to the crystal was also loose.

Task 2.2. Lifetime Testing of Nonaqueous Systems

In the previous annual report we showed that n-MoSe₂ has a high power-conversion efficiency (about 9.9% in chlorine-saturated HCl solution. The electrode, however, showed strong evidence of corrosion. The well-known fast

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Figure 10. CURRENT-POTENTIAL CHARACTERISTICS OF CoCl_2 -TREATED CdSe ELECTRODE MADE BY ELECTRODEPOSITION OF Se ON Cd/POROUS TITANIUM ELECTRODE ($E_{\text{dark}} = -130$ mV; $E_{\text{light}} = -420$ mV versus Pt; Electrolyte 1M Na_2S + 1M S + 1M NaOH)

kinetics of the Cl^-/Cl_2 redox couple encouraged us to evaluate this couple in nonaqueous solvents, where the semiconductor might have greater stability. We are preparing to study transition metal dichalcogenides in acetonitrile. The redox couple chosen is tetrabutylammonium chloride/chlorine. Tetrabutylammonium chloride has a high solubility in acetonitrile. Previously, when tetraethylammonium chloride was used, some white precipitates gradually appeared in the solution after many hours. This phenomenon will be investigated further.

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Figure 11. VOLTAGE OF THE ILLUMINATED p-GaP/1M HI + 0.1M I₂/Pt UNDER 100 OHMS LOAD AS A FUNCTION OF TIME

Task 3. All Solid-State Electrochemical Photovoltaic Cell With In-Situ Storage

Task 3.1. Selection of System

Solid electrolyte systems selected for evaluation include RbAg₄I₅, LiI, and beta-alumina.

Task 3.2. Evaluation of Systems

The photoresponse of CdSe in contact with I₂ + RbAg₄I₅ solid electrolyte has been demonstrated and reported in the Project No. 65039 annual report for 1979. This work was continued this quarter using CdS. The material (99.99% CdS, Apache Chemicals, Inc.) was vacuum-evaporated on glass. Thus, a cell of configuration

$\text{CdS/I}_2 + \text{RbAg}_4\text{I}_5/\text{RbAg}_4\text{I}_5/\text{Cond. glass}$ was assembled. The potential of the CdS electrode versus a silver wire implanted in the RbAg_4I_5 was 650 mV in the dark. Under 200 mW/cm^2 xenon light the potential became 400 mV. Thus, a negative photopotential was obtained. No significant current could be obtained from the cell, perhaps because of the low conductivity of the CdS/solid electrolyte interface. Further work is necessary to understand the nature of the semiconductor/solid electrolyte interface.

Task 3.3. Status of Technology-Sample Delivery

Not applicable this quarter.

Task 4. Demonstration of a Laboratory-Size Photoelectrochemical Storage Cell

Task 4.1. Preliminary System Evaluation

Work was continued on the evaluation of electrocatalysts for the halogen redox couples. A porous titanium electrode was coated with WSe_2 , and the electrode was sintered at 600°C under nitrogen for 1 hour. Good polarization characteristics were obtained close to the performance of the MoSe_2 electrode described in the Project No. 65039 April-July Quarterly Report. The polarization characteristics of the WSe_2 electrode in $1\text{M HBr} + 1\text{M Br}_2$ are shown in Figure 12. The polarization resistance was $0.47\Omega\text{-cm}^2$. The performance of this electrode in $1\text{M HI} + 0.18\text{M I}_2$ is also quite good, as shown in Figure 13. There, a polarization resistance of about $0.80\Omega\text{-cm}^2$ was obtained.

In the previous quarterly report we showed that MoSe_2 is a good electrocatalyst in HBr/Br_2 electrolyte. This material was also found to be a good electrocatalyst for the HI/I_2 as well as the KI/I_2 electrolyte. The catalyst was rubbed onto a porous titanium electrode and then annealed. Polarization curves in these two electrolytes are shown in Figures 14 and 15, respectively. The performance of the electrode was strongly influenced by the amount of electrocatalyst deposited on the porous titanium electrode. Some electrocatalyst materials did not adhere well to the porous structure when the electrode was sintered at 400°C . Better adherence was obtained by sintering at 800°C under an inert gas atmosphere. The data indicate that the transition metal dichalcogenide layer compounds are good electrocatalysts for the halogen redox couples.

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Figure 12. POLARIZATION CHARACTERISTICS OF WSe_2 ON POROUS TITANIUM IN 1M HBr + 1M Br_2 (Scan Rate = 50 mV/s; Temperature = 28°C; Unstirred Electrolyte)

Task 4.2. Lifetime and Performance Testing

The MoSe_2 -coated porous titanium electrode for the redox cell was tested for its long-term stability in 1M HBr + 1M Br_2 solution. An anodic current of 125 mA/cm^2 was passed. After about 5 hours of steady operation the welded contact area between the porous electrode and the titanium wire became corroded. On the next day the porous electrode was found at the bottom of the cell. Apparently the titanium support material corroded in the solution when an anodic current was passed. A similar electrode acting as the counterelectrode passed with cathodic current was found to be stable for many days. Other support materials, for example, graphite, carbon, and reticulated vitreous carbon, will be tested in the future.

Figure 13. POLARIZATION CHARACTERISTICS OF WSe_2 ON POROUS TITANIUM IN 1M HI + 0.18M I_2 (Scan Rate = 50 mV/s; Temperature = 28°C; Unstirred Electrolyte)

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Figure 14. POLARIZATION CHARACTERISTICS OF MoSe_2 ON POROUS TITANIUM IN 1M HI + 0.18M I_2 (Scan Rate = 50 mV/s; Temperature = 28°C; Unstirred Electrolyte)

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Figure 15. POLARIZATION CHARACTERISTICS OF MoSe_2 ON POROUS TITANIUM IN 1M KI + 0.1M I_2 (Scan Rate = 50 mV/s; Temperature = 28°C; Unstirred Electrolyte)

A redox storage system Pt/1M HBr + 1M Br₂/Nafion 315/1M HI + 0.1M I₂/Pt was assembled in a two-cuvette system as described previously. Its long-term charge-discharge characteristic was monitored. When glass cuvettes were used, the cell had a tendency to crack within a period of between several hours and a few days after filling with the solutions. Apparently the Nafion separator swelled and expanded upon wetting by the solutions. Because the Nafion was epoxied to the walls of the cuvettes, the force of the expansion could have strained the glass and caused it to crack. No cell cracking was seen, however, when polystyrene cuvettes were used, perhaps because they are flexible enough to accomodate some strain. One disadvantage of the polystyrene cuvette is that the halogen redox solutions stain the walls. These cells have been electrochemically charged and discharged for more than 2 weeks with no apparent loss in capacity.

We continued our work on the sulfur-cadmium storage system for the CdSe photoanode. Although the solubility of cadmium ions in KOH solution is quite small, there is a possibility that trace amounts of cadmium ions or sulfide species migrate across the membrane separator. We conducted an accelerated study to see the effects of cadmium ions and sulfide species on the conductivity of Nafion 315 membrane. For this purpose a solution of about 1M CdSO₄ was placed on one side of the membrane, and a solution of 1M Na₂S + 1M S + 1M NaOH was placed on the other side. Voltage pulses of 20 V peak to peak, 10 ms pulse duration at a frequency of 100 hertz were applied through platinum electrodes to drive cadmium ions and sulfide species from the solution into the membrane. The ionic conductivity of the membrane, as measured from the current flowing across the membrane, declined rapidly during this process. Within minutes the current dropped from about 100 mA/cm² to a few mA/cm². There is a possibility that the cadmium ions and the sulfide species recombine and block the pores of the membrane so that they reduce its conductivity. In the future we will evaluate the lifetime of the membrane in the presence of a limited amount of cadmium ions in KOH solution.

Task 4.3. Status of Technology - Sample Delivery

Not applicable this quarter.

References

1. Hodes, G., Manassen, J. and Cahen, D., J. Electrochem. Soc., 127, 544, (1980).