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ELECTROCHEMICAL PHOTOVOLTAIC CELLS

Quarterly Technical Progress Report for April 15–July 31, 1980

By
Peter G. P. Ang
Anthony F. Sammells

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Project 65039 Quarterly Technical Progress Report
For the Period April 15 Through July 31, 1980

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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
TASK OBJECTIVES AND ACHIEVEMENTS	2
Task 1. Selection of High-Efficiency Semiconductor Photoelectrode-Electrolyte Systems	2
Task 1.1. Evaluation of Single-Crystal Systems	2
Task 1.2. Characterization of Single-Crystal Systems	2
Task 1.3. Surface Treatment Characterization	9
Task 1.4. Characterization of Polycrystalline Systems	10
Task 1.5. Characterization of Polycrystalline Surface Treatments	11
Task 1.6. Sample Deliveries	11
Task 2. Development of Long-Life Electrochemical Photovoltaic Cells	11
Task 3. All Solid-State Electrochemical Photovoltaic Cell With <u>In Situ</u> Storage	11
Task 3.1. Selection of Systems	11
Task 3.2. Evaluation of Systems	11
Task 3.3. Status of Technology-Sample Delivery	12
Task 4. Demonstration of Laboratory-Size Photoelectrochemical Storage Cell	12
Task 4.1. Preliminary System Evaluation	12
Task 4.2. Lifetime and Performance Testing	15
Task 4.3. Status of Technology-Sample Delivery	15

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
1	Current-Potential Characteristics of Single-Crystal p-GaP	3
2	Current-Potential Characteristics of Single-Crystal p-GaAs	4
3	Current-Potential Characteristics of p-Si in 1M HI + 0.18M I ₂	5
4	Current-Potential Characteristics of p-Si in 1M Na ₂ S + 0.1M S	5
5	Current-Potential Characteristics of p-Si in 1M Na ₂ S + 1M S + 1M NaOH	6
6	Current-Potential Characteristics of p-GaAs in 1M Na ₂ S + 0.1M S	7
7	Current-Potential Characteristics of p-GaAs in 1M Na ₂ S + 1M S + 1M NaOH	7
8	Current-Potential Characteristics of p-GaAs in 1M Na ₂ S + 1M S + 1M NaOH + 0.1M Na ₂ Se	8
9	Current-Potential Characteristics of p-Si in 1M Na ₂ S + 1M S + 1M NaOH After Dipping in 1M NiCl ₂ Solution	9
10	Current-Potential Characteristics of p-GaAs in 1M Na ₂ S + 1M S + 1M NaOH + 0.1M Na ₂ Se After Ruthenium Treatment	10
11	Current-Potential Characteristics of CdSe Slurry, Sintered on Porous Titanium Substrate in 1M Na ₂ S + 1M S + 1M NaOH	12
12	Polarization Characteristics of Hot-Pressed MoSe ₂ in 1M HBr + 1M Br ₂ at 27°C	14
13	Polarization Characteristics of MoSe ₂ on Porous Titanium in 1M HBr + 1M Br ₂	14

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 objectives of this program are 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. 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 its 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 have evaluated the following semiconductor electrode/redox couple systems:

The bromine/iodine redox storage system has a voltage between 0.4 and 0.5 volt depending on the state of charge of the redox couples. A good n-MoSe_2 will have sufficient photopotential to charge this cell. By using two photosystems, however, the combined photopotential will be more effective for charging the storage cell.

Task 1.2. Characterization of Single-Crystal Systems

The photoelectrochemical properties of single-crystal n-MoSe_2 photoanodes have been described in previous reports. P-type GaP (Zn doped, $1.2 \times 10^{18}/\text{cm}^3$) single-crystal, obtained from Atomergic Chemetals Corp., has been studied during this period. Contact to the crystal was made by electrodepositing indium and zinc and then annealing it at 400°C under hydrogen for 2 hours. A nickel wire was attached to the contact area using a conducting silver epoxy, and the electrode assembly was then insulated with epoxy and wax. The crystal was tested as a photocathode in an acidic solution of $1\text{M HI} + 0.18\text{M I}_2$ (redox potential of 236 mV versus SCE). The potential of the GaP electrode versus a platinum reference electrode in the same solution was -20 mV in the dark and 120 mV under $200 \text{ mW}/\text{cm}^2$ xenon light illumination. Due to the dark color of the solution, the actual intensity of the incident light at the electrode surface was expected to be about half this value. At the dark potential, the short-circuit photocurrent was $30 \text{ mA}/\text{cm}^2$. 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. Large

photocurrents were generated although the photopotential was relatively small. The power conversion efficiency of this electrode was low, about 1.7%, because of the small photopotential. The fill factor was about 0.42. This electrode can be coupled to an n-type MoSe_2 photoanode to photocharge a bromine-iodine redox storage system.

Figure 1. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL p-GaP

During this period, we have also studied the photoelectrochemical properties of p-type GaAs. The crystal was doped with zinc (acceptor concentration of $3.9 \times 10^{18} \text{ cm}^{-3}$). Contact to the crystal was made by electroplating gold and indium and then heating at 400°C under hydrogen for 2 hours. The surface (111 face) was etched in concentrated H_2SO_4 -30% H_2O_2 (1:1) solution for 10 seconds. This electrode was tested in 1M HI + 0.18M I_2 solution. The open-circuit potential versus a platinum reference electrode in the solution was -20 mV in the dark and 140 mV under 200 mW/cm^2 xenon light. We measured a photocurrent of about 17 mA/cm^2 at the dark potential (-20 mV). The current-potential characteristics of this electrode are shown in Figure 2. Because of the small photopotential, the power conversion efficiency was small, about 1.1%. The fill factor was about 0.39.

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Figure 2. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL p-GaAs

Single-crystal p-type Si was characterized in 1M HI + 0.18M I₂. The crystal, obtained from Atomergic Chemetals Corp., has a resistivity of 1.5 to 3 Ω-cm. Contact to the wafer was made by evaporating aluminum and then annealing it at 400°C under hydrogen for 2 hours. A nickel wire was attached to the contact area using a conducting silver epoxy, and the electrode assembly was insulated with epoxy and wax. The current-potential characteristics of this electrode are shown in Figure 3. The open-circuit potential versus a platinum reference electrode in the solution was -150 mV in the dark and -100 mV under 200 mW/cm² xenon illumination. Due to electrolyte absorbance, the incident light at the electrode surface was estimated at 100 mW/cm². As shown in Figure 3, the photocurrent started to flow only at relatively high cathodic overpotentials. No photocurrent could be detected near the open-circuit potential. This is in contrast to the behavior of p-GaP and p-GaAs in the same electrolyte reported in the previous paragraphs.

The p-Si electrode was further tested in 1M Na₂S + 0.1M S solution. In this case, the open-circuit potential versus platinum was -500 mV in the dark and 0 mV under 200 mW/cm² xenon illumination. The change in electrode potential with light intensity was rapid. The current-potential characteristics of this electrode are shown in Figure 4. Although large photopotentials were obtained, the photocurrents generated, especially near the open-circuit potential, were small. Apparently, the rate of electron transfer

Figure 3. CURRENT-POTENTIAL CHARACTERISTICS OF p-Si IN 1M HI + 0.18M I₂
 (E_{dark} = -340 mV; E_{light} = -190 mV vs. Pt; E_{Pt} =
 236 mV vs. SCE; 200 mW/cm² Xenon Light)

Figure 4. CURRENT-POTENTIAL CHARACTERISTICS OF p-Si IN 1M Na₂S +
 0.1M S (E_{dark} = -500 mV; E_{light} = 0 mV vs. Pt; E_{Pt} =
 -690 mV vs. SCE; 200 mW/cm² Xenon Light)

from the silicon surface to the redox species in the solution is quite slow. Pretreatment of the electrode surface by etching (HF + HNO₃ solution, 10 seconds) as well as cathodic treatment generally improved the photoelectrochemical response of the silicon electrode. The cathodic photocurrent apparently was associated with reduction of the polysulfide species as well as hydrogen evolution on the silicon surface. In an alkaline solution (1M Na₂S + 1M S + 1M NaOH) the photoresponse shifted toward more positive

potentials, as shown in Figure 5. The performance of the p-Si might be improved further by surface modification.

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Figure 5. CURRENT-POTENTIAL CHARACTERISTICS OF p-Si IN 1M Na₂S + 1M S + 1M NaOH ($E_{\text{dark}} = -400$ mV; $E_{\text{light}} = 50$ mV vs. Pt; $E_{\text{Pt}} = -710$ mV vs. SCE; 200 mW/cm² Xenon Light)

Further work with the p-GaAs electrode has been done. The crystal was tested in three solutions containing S²⁻/S_n²⁻ redox couple. The results obtained in 1M Na₂S + 0.1M S, in 1M Na₂S + 1M S + 1M NaOH, and in 1M Na₂S + 1M S + 1M NaOH + 0.1M Na₂Se are shown in Figures 6, 7, and 8, respectively. Photopotentials around 100 mV were obtained with all three solutions. The photocurrents, however, were larger when the solution was made alkaline (Figure 7), and further increased when Na₂Se was added into the solution (Figure 8). Near the open-circuit potential, however, the photocurrents were always small. The power-conversion efficiency of this electrode is still very small. An improvement might be possible, for example, by introduction of surface catalysts.

A p-type photocathode operating in S²⁻/S_n²⁻ redox electrolyte can be coupled to n-MoSe₂ in I⁻/I₂ redox electrolyte. This iodine/sulfide redox storage system has a voltage of about 1 volt. The characteristics of this system are being studied.

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Figure 6. CURRENT-POTENTIAL CHARACTERISTICS OF p-GaAs IN 1M Na₂S + 0.1M S ($E_{\text{dark}} = -75$ mV; $E_{\text{light}} = 25$ mV vs. Pt; $E_{\text{Pt}} = -690$ mV vs. SCE; 200 mW/cm² Xenon Light)

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Figure 7. CURRENT-POTENTIAL CHARACTERISTICS OF p-GaAs IN 1M Na₂S + 1M S + 1M NaOH ($E_{\text{dark}} = 0$ mV; $E_{\text{light}} = 80$ mV vs. Pt; $E_{\text{Pt}} = -710$ mV vs. SCE; 200 mW/cm² Xenon Light)

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Figure 8. CURRENT-POTENTIAL CHARACTERISTICS OF p-GaAs IN 1M Na₂S + 1M S + 1M NaOH + 0.1M Na₂Se ($E_{\text{dark}} = -40$ mV; $E_{\text{light}} = 80$ mV vs. Pt; 200 mW/cm² Xenon Light)

Task 1.3. Surface Treatment Characterization

An attempt has been made to improve the photoelectrochemical properties of p-Si and p-GaAs by introducing catalysts on the electrode surface. The large dark open-circuit potentials of Si versus Pt in solutions with S^{2-}/S_n^{2-} redox couple (Figures 4 and 5) indicate an irreversible electrode behavior. This p-type electrode is, however, quite attractive because of its large photopotential (about 500 mV). When this electrode was dipped in 1M $NiCl_2$ solution for a few seconds, rinsed in water, and then tested again in 1M Na_2S + 1M S + 1M NaOH, the dark open-circuit potential became more positive. The photopotential decreased slightly, to 390 mV. The current-potential characteristics, shown in Figure 9, however, did not change much as compared with Figure 5. A similar phenomenon was observed upon dipping the electrode in chloroplatinic acid solution. By electroplating platinum onto the electrode surface, the dark open-circuit potential can be brought to a value close to 0 mV versus platinum. In this case, the photopotential became smaller, about 100 mV. The amount and type of catalyst will be further optimized.

Figure 9. CURRENT-POTENTIAL CHARACTERISTICS OF p-Si IN 1M Na_2S + 1M S + 1M NaOH AFTER DIPPING IN 1M $NiCl_2$ SOLUTION ($E_{dark} = -300$ mV; $E_{light} = 90$ mV vs. Pt; $E_{Pt} = -710$ mV vs. SCE; 200 mW/cm² Xenon Light)

It is known in the literature that the performance of n-GaAs can be significantly improved by dipping in 0.1M HNO_3 + 0.01M RuCl_3 solution. We have tried to see if a similar treatment can improve the photoelectrochemical properties of p-type GaAs. The current-potential characteristics of this electrode in 1M Na_2S + 1M S + 1M NaOH + 0.1M Na_2Se before Ru^{+3} treatment are shown in Figure 8. After dipping in the ruthenium solution for 10 seconds, the results shown in Figure 10 were obtained. The dark open-circuit potential became 0 mV versus Pt. Larger dark current as well as photocurrent can be seen. This treatment will be further improved in the future.

Figure 10. CURRENT-POTENTIAL CHARACTERISTICS OF p-GaAs IN 1M Na_2S + 1M S + 1M NaOH + 0.1M Na_2Se AFTER RUTHENIUM TREATMENT ($E_{\text{dark}} = 0$ mV; $E_{\text{light}} = 90$ mV vs. Pt; 200 mW/cm^2 Xenon Light)

Task 1.4. Characterization of Polycrystalline Systems

Polycrystalline CdSe was studied beginning in the third month of the program. Good results were obtained in the previous year using CdSe evaporated onto porous

titanium substrate, where adherence of the film to the substrate was excellent. During this period, we have made a photoanode by a new and simpler 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 11. 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 about 21 mA/cm² was achieved. The power conversion efficiency and fill factor were 2.8% and 0.51, respectively.

Task 1.5. Characterization of Polycrystalline Surface Treatments

Work has been initiated for improving the performance of CdSe by a combination of techniques involving a variety of annealing temperatures (300°C to 700°C) and etchant and surface modifiers/catalysts. Experimental work directed toward this goal will be reported in the next quarterly report.

Task 1.6. Sample Deliveries

Not applicable this quarter.

Task 2. Development of Long-Life Electrochemical Photovoltaic Cells

Not covered in the milestone chart for this month.

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

Task 3.1. Selection of Systems

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

Task 3.2. Evaluation of Systems

One of the problems of the solid-electrolyte systems is the high internal resistance of the electrolyte. To overcome this, a very thin solid-electrolyte pellet (0.1 to 0.2 mm thick) of RbAg₄I₅ was fabricated. This pellet, however, has a problem with its mechanical rigidity: It has a tendency to crack when squeezed between two electrodes. We evaluated procedures to fabricate thin-film solid electrolytes. It is feasible to fabricate RbAg₄I₅ by thermal vacuum evaporation of RbAg₄I₅. With enough care, one may also be able to evaporate LiI. The beta-alumina, however, may be quite difficult to evaporate due to its ceramic character. Also, the sodium released upon evaporation of beta-alumina may be dangerous when it comes into contact with air.

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Figure 11. CURRENT-POTENTIAL CHARACTERISTICS OF CdSe SLURRY, SINTERED ON POROUS TITANIUM SUBSTRATE IN 1M Na₂S + 1M S + 1M NaOH. ($E_{\text{dark}} = -130$ mV; $E_{\text{light}} = -500$ mV vs. Pt; $i_{\text{SC}} = 21$ mA/cm²; $\eta = 2.8\%$; FF = 0.51)

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

Photoelectrochemical storage systems that will be evaluated are –

a. Aqueous System b. Nonaqueous System

Further work has been performed using the HBr/Br₂ electrolyte. As reported in our previous final report, we have noticed a slight roughening or etching of the platinum counterelectrode after the long-term test (about 90 days) in 1M HBr + 1M Br₂. When a platinized platinum electrode was used, the black platinum coating had a tendency to flake off from the surface of the electrode. We, therefore, searched for other catalysts that are more stable. Our experiments with n-MoSe₂ single crystal have indicated that this material is extremely stable in HBr/Br₂ electrolyte. Therefore, we studied the electrocatalytic behavior of this material. An electrode was fabricated from a hot-pressed MoSe₂ (Cerac, Inc.). The electrode was attached to a nickel wire using conducting silver epoxy, and the assembly was properly isolated from the electrolyte using epoxy and wax. The polarization characteristics of this electrode in 1M HBr + 1M Br₂ are shown in Figure 12. Very large currents were obtained. Thus, this material exhibited good catalytic activity toward the Br⁻/Br₂ redox couple. This electrode did not show photoactivity.

Further work was performed by depositing MoSe₂ onto a porous structure to increase the effective surface area of the electrode. The hot-pressed MoSe₂ was rubbed on both sides of a porous titanium electrode (Gould 6525). Contact of the electrode to a titanium wire was made by spot welding. The electrode was annealed at 400°C under nitrogen gas for 1 hour. Figure 13 shows the current-voltage characteristics of this electrode in 1M HBr + 1M Br₂. This electrode demonstrated very good reversibility toward the halogen redox couples and showed very high current densities. Polarization resistance of about 0.35 Ω-cm² was obtained from the slope near the resting potential. The electrode potential was first scanned in the cathodic direction, starting from its resting potential, and the subsequent scan was in the anodic direction. The electrolyte was not stirred. Therefore, mass-transfer effects were noticed, especially in the cathodic scan, because of rather low bromine concentration.

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Figure 12. POLARIZATION CHARACTERISTICS OF HOT-PRESSED MoSe_2 IN 1M HBr + 1M Br_2 At 27°C

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Figure 13. POLARIZATION CHARACTERISTICS OF MoSe_2 ON POROUS TITANIUM IN 1M HBr + 1M Br_2 (Scan Rate = 50 mV/sec; Temperature = 28°C ; Unstirred Electrolyte)

Task 4.2. Lifetime and Performance Testing

A photoelectrochemical redox storage system having the configuration –

is being assembled. The cell for photocharge is assembled from two cuvettes that are clamped together. A Nafion membrane is used for ionic communication between the two electrolytes. The electrolytes can be circulated to another two-cuvette system where the redox couples can be discharged.

The long-term photocharge/discharge characteristics of the system were monitored. The voltage of the redox storage cell changed between 0.4 and 0.5 volt depending on the state of the charge of the system. After being in the 1M HI + 0.18M I₂ solution for a few days, the adherence of the p-GaP electrode to the silver epoxy became poor perhaps because of electrolyte seepage to the contact area. After a few days of operation, we noticed pitting of the GaP photocathode surface. The long-term stability of the GaP will be further monitored.

Some plumbing problems were encountered in the electrolyte circulation; for example, electrolyte leakage and an air bubble trapped in the circulation system. The compatibility of a variety of tubing materials (tygon, Teflon, vinyl, etc.) with the electrolytes are being evaluated.

Task 4.3. Status of Technology-Sample Delivery

Not applicable this quarter.

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