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ELECTROCHEMICAL PHOTOVOLTAIC CELLS

Quarterly Technical Progress Report for Period July 15–October 15, 1979

By
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MASTER

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**Project 65021 Quarterly Technical Progress Report
For the Period July 15 Through October 15, 1979**

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

**Prepared by
Institute of Gas Technology
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October 1979

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SUMMARY

During the second quarter of this program we have evaluated the photoelectrochemical performance of single-crystal MoSe_2 and GaAs, polycrystalline CdSe, and cells with RbAg_4I_5 solid electrolyte. MoSe_2 electrode exhibited very good photoresponse in electrolytes containing Br^-/Br_2 redox couple. The photopotential and photocurrent were larger in acid than in alkaline electrolyte. A power conversion efficiency of about 5% was achieved under 200 mW/cm^2 Xenon light illumination in the acid medium. The catalytic activity of a platinumized platinum electrode toward Br^-/Br_2 redox couple was also better in acid electrolyte than in alkaline electrolyte. Higher current densities were obtained in the acid medium. The MoSe_2 was found to have good stability in acid and alkaline electrolytes; however, it will be necessary to protect the electrolyte against evaporation of the bromine, oxidation by air, or photo-decomposition.

GaAs was tested in alkaline electrolytes containing $\text{Se}^{2-}/\text{Se}_n^{2-}$, I^-/I_2 or Br^-/Br_2 redox couple and in acid electrolytes containing $\text{Fe}^{+2}/\text{Fe}^{+3}$, $\text{Cr}^{+2}/\text{Cr}^{+3}$, $\text{Sn}^{+2}/\text{Sn}^{+4}$, $\text{Cu}^{+1}/\text{Cu}^{+2}$, $\text{Ti}^{+3}/\text{Ti}^{+4}$, I^-/I_2 or Br^-/Br_2 . Large anodic dark currents were observed in solutions containing $\text{Sn}^{+2}/\text{Sn}^{+4}$ or $\text{Cu}^{+1}/\text{Cu}^{+2}$. The large photo-effects found with the other redox couples were usually accompanied by electrode darkening and decrease in photocurrent with time.

Polycrystalline electrodes have been made by thermal vacuum evaporation of CdSe on titanium foil or SnO_2 -coated glass. The CdSe still suffered from poor adherence to the substrates and, therefore, poor photoresponse.

A solid electrolyte photoelectrochemical cell was fabricated giving photopotentials of about 300 mV at current densities of about 0.1 mA/cm^2 under 200 mW/cm^2 Xenon light illumination. The cell has the configuration —

The photoresponses of cells made with the RbAg_4I_5 solid electrolyte were improved over that reported last quarter after using SnO_2 -coated transparent conducting glass. The origin of the positive photopotential is still obscure since it may be a mixture of Dember-type photovoltage, electrolyte photolysis and photoinduced charge transfer between the electrode and the solid electrolyte. The solid electrolyte cell has the potential of having storage capabilities.

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.

Significant results are the good photoresponse of single-crystal MoSe_2 with Br^-/Br_2 redox couple in acid electrolyte. The best data showed a current density of about 33 mA/cm^2 at 0.3 V cell voltage under 200 mW/cm^2 Xenon light illumination. The maximum power efficiency obtained was about 5%.

In addition we have tested some solid electrolyte photoelectrochemical cells which have the potential of energy conversion and storage. These cells were based on the silver ion conducting RbAg_4I_5 solid electrolyte. This quarter we have demonstrated that this system exhibited photopotentials and photocurrents.

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 during this quarter included:

- MoSe_2 with Br^-/Br_2 as the electron donor and I^-/I_2 as the candidate electron acceptor
- CdSc with $\text{S}^{2-}/\text{S}_n^{2-}$ or $\text{Sc}^{2-}/\text{Sc}_n^{2-}$ as the donor and $\text{Tc}^{2-}/\text{Te}_n^{2-}$ as the candidate acceptor
- GaAs with $\text{Se}^{2-}/\text{Se}_n^{2-}$ as the donor and $\text{Te}^{2-}/\text{Te}_n^{2-}$ as the candidate acceptor.

In acid electrolytes the semiconductor/redox couples selected during this quarter included:

- MoSe_2 with Br^-/Br_2 as the electron donor and I^-/I_2 as the candidate acceptor
- GaAs with $\text{Fe}^{+2}/\text{Fe}^{+3}$ as the electron donor and $\text{Cr}^{+2}/\text{Cr}^{+3}$ as the candidate acceptor

The photoelectrochemical properties of MoSe_2 and GaAs in a variety of redox electrolytes were evaluated this quarter and are described in Task 1.2.

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

Single-crystal materials were obtained from sources as described in the first quarterly report.¹ The semiconductor was attached to a nickel wire with a conducting silver epoxy. A second coating of regular epoxy was later applied to insulate the rest of the electrode assembly from the electrolyte so that only the semiconductor-electrolyte interface was illuminated. In most cases the cell was illuminated with approximately 200 mW/cm^2 of light from a 150 Watt Xenon lamp equipped with a heat-absorbing filter.

Photoelectrochemical measurements were performed using MoSe_2 and GaAs single-crystals. The current-potential characteristics were obtained with a potentiostat. The MoSe_2 (001 plane) was tested in aqueous acid and alkaline electrolytes containing either Br^-/Br_2 or I^-/I_2 redox couples. The photoelectrochemical performance in 6M HBr + 1M Br_2 is shown in Figure 1. Large photopotentials of about -470 mV and short-circuit current of about 53 mA/cm^2 were detected. A cell efficiency of about 5% could be obtained with this photoanode, i.e., a cell voltage of 0.3 V at 33 mA/cm^2 . The same electrode was also evaluated in the alkaline electrolyte 6M KOH + 1M KBr + 1M Br_2 . There the photopotential was only -185 mV, although the current-potential characteristic (Figure 2) still appeared to be good. The short-circuit current was about 28 mA/cm^2 , i.e., approximately 50% of the value in acid electrolyte. Near the resting potential the photocurrent in alkaline electrolyte does not rise as fast as in the acid electrolyte. The data indicates that the rate of Br^- photo-oxidation on MoSe_2 may be faster in acid than in alkaline medium. In conjunction with this the redox reaction of Br^-/Br_2 on a platinized platinum electrode was studied at three different electrolyte pH ranges (Figure 3).

Figure 1. CURRENT-POTENTIAL CHARACTERISTICS OF MoSe_2 SINGLE-CRYSTAL
IN 6M HBr + 1M Br_2

Figure 2. CURRENT-POTENTIAL CHARACTERISTICS OF MoSe₂ SINGLE-CRYSTAL
IN 6M KOH + 1M KBr + 1M Br₂

Figure 3. POTENTIAL-SWEEP (40 mV/sec) 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

Larger current-densities were obtained in acid electrolyte 1M HBr + 1M Br₂ (Curve 1) compared to the current densities in alkaline electrolyte 1M KBr + 1M Br₂ + KOH (Curve 2) and in neutral electrolyte 1M KBr + 1M Br₂ + 0.1M KOH (Curve 3). In the alkaline region the salt was not completely soluble. Based on these results there is an incentive to operate the MoSe₂ photoanode system in acid electrolyte rather than in alkaline or neutral medium. In using bromine we have experienced that the cell has to be sealed tightly to prevent bromine evaporation from the electrolyte.

The performance of the MoSe₂ single-crystal was also tested in acid electrolyte (6M HCl) using 1M Cr⁺²/Cr⁺³ and 1M Ti⁺³/Ti⁺⁴ as redox species. In both cases the photopotential was only -2 mV and -5 mV, respectively, and photocurrents of only a few microamperes were seen. From these results it would appear that the position of these two redox couples is above the lower edge of the conduction band of MoSe₂, and consequently would be of no interest with MoSe₂ as a photoanode.

GaAs single-crystal (111 orientation) was tested in alkaline and acid electrolytes. The current-potential characteristics of the GaAs single-crystal in 6M KOH + 0.25M SeO₂ + 0.25M Na₂Se, 6M KOH + 1M I⁻/I₂, and 6M KOH + 1M Br⁻/Br₂ are shown in Figures 4, 5, and 6, respectively. Large photocurrents could be recorded, however, with Br⁻/Br₂, 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⁻/I₂ was -680 mV versus a platinum reference electrode dipped in the same solution. In electrolytes containing Br⁻/Br₂, this value was -1400 mV. These large values may indicate an irreversible electrode behavior associated with corrosion potential.

The GaAs crystal was also tested in an acid electrolyte. Figures 7, 8, 9, and 10 show its performance in 6M HCl + 1M Fe⁺²/Fe⁺³, 6M HCl + 1M Cr⁺²/Cr⁺³, 6M HCl + 1M Sn⁺²/Sn⁺⁴, and 6M HCl + Cu⁺¹/Cu⁺². The photopotentials are 400 mV, 370 mV, 15 mV, and 140 mV in Fe⁺²/Fe⁺³, Cr⁺²/Cr⁺³, Sn⁺²/Sn⁺⁴, and Cu⁺¹/Cu⁺² redox couples, respectively. In electrolytes containing Sn⁺²/Sn⁺⁴, the electrode became dark after the potential sweep experiment. Some red deposits (Cu) were seen after testing in electrolytes containing Cu⁺¹/Cu⁺². The deposition may have occurred when cathodic currents flowed during the potential scan in the dark. As seen in Figures 9 and 10, the dark current in Sn⁺²/Sn⁺⁴ and in Cu⁺¹/Cu⁺² redox electrolytes is quite significant.

Figure 4. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M KOH + 0.25M SeO_2 + 0.25M Na_2Se

Figure 5. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M KOH + 1M I⁻/I₂

Figure 6. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs 1N 6M KOH + 1M Br⁻/Br₂

Figure 7. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs in 6M HCl + 1M Fe²⁺/Fe³⁺

Figure 8. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M HCl + 1M Cr⁺²/Cr⁺³

Figure 9. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL
GaAs IN 6M HCl + 1M $\text{Sn}^{+2}/\text{Sn}^{+4}$

Figure 10. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL
GaAs IN 6M HCl + 1M $\text{Cu}^{+1}/\text{Cu}^{+2}$

Photopotentials of -245 mV, -510 mV and -420 mV were observed in $6M$ $HCl + 1M$ Ti^{+3}/Ti^{+4} , $6M$ $HCl + 0.1M$ I^-/I_2 , and in $6M$ $HBr + 1M$ Br_2 , respectively. The current-potential curves are shown in Figures 11, 12, and 13, respectively. Quite large photocurrents were seen, but usually the electrode darkened after the test, indicating photoanodic decomposition. Data obtained from the experiments in various redox electrolytes are compared in Table 1; large numbers in the dark potential (E_d) indicate an irreversible electrode behavior. The large photocurrents obtained with GaAs in many cases were associated with electrode decomposition. Attempts will be made in the future to stabilize the GaAs electrode.

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

During this reporting period we prepared several CdSe photoanodes. Thin-film electrodes were prepared by thermal vacuum evaporation of CdSe powder on a titanium foil or on SnO_2 -coated glass (Corning 7059 glass). The electrode made on the titanium foil was heat-treated in air at $350^\circ C$ for 30 minutes and then etched in $0.1M$ HNO_3 for 30 seconds. In $6M$ $KOH + 1M$ $K_2S + 1M$ S , photopotentials of about -280 mV were observed. The current-potential characteristic is shown in Figure 14. The electrodes suffered from poor film adherence to the substrate, especially on the surface of the conducting glass. This may have caused the photoanode to be shorted in the electrolyte, thus reducing the observed photocurrents. The adherence of the film will be improved in the future by modifications to the substrate temperature during evaporation.

Task 2. Development of Long-Life Electrochemical Photovoltaic Cells

Task 2.1. Identification of Photoanodic Corrosion

Candidate photoanodes that showed promise in Tasks 1.2 and 1.3 were further evaluated for their long-term stability. $MoSe_2$ showed very good stability in aqueous acid electrolytes and in alkaline electrolytes, either with Br^-/Br_2 or I^-/I_2 redox couple, as shown, for example, in Figure 15. Here the $MoSe_2$ electrode was operated in $6M$ $HBr + 1M$ Br_2 at 280 mV anodic from its resting potential. A constant photocurrent of about 40 mA/cm² could be drawn for hours. In a few instances we have noticed a slight decrease of the photocurrent. However, the original photocurrent could be restored after a new solution was used. Thus, the stability of the electrolyte redox couple against evaporation, air oxidation or photodecomposition will have to be analyzed further.

Figure 11. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M HCl + 1M $\text{Ti}^{+3}/\text{Ti}^{+4}$

Figure 12. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL
GaAs IN 6M HCl +.1M KI +.1M I₂

Figure 13. CURRENT-POTENTIAL CHARACTERISTICS OF SINGLE-CRYSTAL GaAs IN 6M HBr + 1M Br₂

Table 1. COMPARISON OF THE PHOTOELECTROCHEMICAL PROPERTIES OF DIFFERENT SEMICONDUCTORS IN VARIOUS REDOX ELECTROLYTES

Electrode	Electrolyte	E_{ℓ}	E_d	E_{Pt}	E_{ph}	I_{sc}
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
GaAs	6M KOH + 0.25M SeO ₂ + 0.25M Na ₂ Se	-1100	-490	--	--	97
GaAs	6M KOH + 1M I ⁻ /I ₂	-1240	-680	--	--	106
GaAs	6M KOH + 1M Br ⁻ /Br ₂	-1910	-1400	--	--	65
GaAs	6M HCl + 1M Fe ⁺² /Fe ⁺³	-1090	-690	680	-400	103
GaAs	6M HCl + Cr ⁺² /Cr ⁺³	-1030	-660	400	-370	87
GaAs	6M HCl + 1M Sn ⁺² /Sn ⁺⁴	-470	-455	-35	-15	4
GaAs	6M HCl + 1M Cu ⁺¹ /Cu ⁺²	-470	-330	270	-140	44
GaAs	6M HCl + 1M Ti ⁺³ /Ti ⁺⁴	-590	-345	120	-245	15
GaAs	6M HCl + .1M KI + .1M I ₂	-750	-240	340	-510	54
GaAs	6M HBr + 1M Br ₂	-1460	-1040	740	-420	30
CdSe	6M KOH + 1M K ₂ S + 1M S	-380	-100	-625	--	4

E_{ℓ} = electrode potential (mV) with light vs. platinum in the same solution

E_d = electrode potential (mV) in the dark vs. platinum in the same solution

E_{Pt} = the potential (mV) of the platinum vs. saturated calomel electrode

I_{sc} = current density of the working electrode at E_d (mA/cm²)

E_{ph} = photopotential = $E_{\ell} - E_d$ (mV).

In most cases the large photocurrent of GaAs was accompanied by electrode decomposition.

Figure 14. CURRENT-POTENTIAL CHARACTERISTICS OF VACUUM-EVAPORATED CdSe
ON Ti FOIL IN 6M KOH + 1M K_2S + 1M S

Figure 15. STABILITY OF THE PHOTOCURRENT OF SINGLE-CRYSTAL MoSe_2 AT 280 mV ANODIC FROM RESTING POTENTIAL OR -200 mV FROM Pt ELECTRODE IN 6M HBr + 1M Br_2 UNDER $200 \text{ mW}/\text{cm}^2$ LIGHT ILLUMINATION

During operation of the MoSe_2 single-crystal in $6\text{M KOH} + 1\text{M KBr} + 1\text{M Br}_2$ erosion on the front surface was noted in one instance. Apparently the electrolyte managed to penetrate the layered structure of the MoSe_2 crystal and once reaching the current collector (silver epoxy contact) caused a short-circuit between the illuminated crystal and the silver epoxy. The erosion of the crystal may be due to high local current densities associated with the short-circuit. This will be further investigated in the future by appropriately scaling the semiconductor electrode to prevent electrolyte seepage.

The long-term performance of single-crystal GaAs was analyzed under potentiostatic conditions in $6\text{M HCl} + 1\text{M Cr}^{+2}/\text{Cr}^{+3}$. The open-circuit potential was -260 mV in the dark and -630 mV (vs. SCE) under illumination. When the potential was set at -400 mV vs. SCE, a photocurrent of about 30 mA/cm^2 initially flowed. Figure 16 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 a $6\text{M HCl} + 1\text{M Fe}^{+2}/\text{Fe}^{+3}$ solution. The open-circuit potential was 0 mV in the dark and -410 mV vs. SCE under illumination. Potentiostating at -200 mV vs. SCE resulted in an initial photocurrent of 46 mA/cm^2 , which slowly decayed with time as shown in Figure 17. The instability of the electrode will be further investigated.

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

This task was inactive during this quarter.

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

In this quarter we have studied photoeffects of cells having RbAg_4I_5 as the solid electrolyte. A rubidium silver iodide solid electrolyte battery usually has a silver anode and iodine cathode² with the iodine usually complexed, as in PbI_2 , for example. The cells were generally fabricated by pressing the appropriate powder mixtures at about 2000 kg/cm^2 . As current collectors we have used SnO_2 -coated transparent conducting glass (Corning 7059 glass). In previous months we have used a nickel-chrome wire mesh as the current collector. In a cell of configuration $\text{glass-SnO}_2/\text{PbI}_2 + \text{RbAg}_4\text{I}_5/\text{RbAg}_4\text{I}_5/\text{C} + \text{PbI}_2 + \text{RbAg}_4\text{I}_5/\text{SnO}_2\text{-glass}$ we have seen photopotentials of about 50 mV when the left side of

Figure 16. 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 17. PHOTOCURRENT OF SINGLE-CRYSTAL GaAs at -200 mV VS. SCE IN $6\text{M HCl} + \text{Fe}^{+2}/\text{Fe}^{+3}$ AS A FUNCTION OF TIME

the above cell (i.e., the $\text{PbI}_2 + \text{RbAg}_4\text{I}_5$ side) was illuminated. Upon illumination of the other side photopotentials of about -25 mV were observed. When CdSe powder was mixed in the electrolyte near the illuminated side, i.e., in a cell of configuration glass $\text{SnO}_2/\text{PbI}_2 + \text{CdSe} + \text{RbAg}_4\text{I}_5/\text{RbAg}_4\text{I}_5/\text{C} + \text{PbI}_2 + \text{RbAg}_4\text{I}_5/\text{SnO}_2$ glass, photopotentials of about -150 mV were observed (Figure 18). There was a rapid negative photopotential which decayed slowly in the dark.

When CdSe was evaporated in the SnO_2 -coated glass, i.e., giving the cell glass $\text{SnO}_2/\text{CdSe}/\text{PbI}_2 + \text{RbAg}_4\text{I}_5/\text{RbAg}_4\text{I}_5/\text{C} + \text{PbI}_2 + \text{RbAg}_4\text{I}_5/\text{SnO}_2$ glass photopotentials of about 350 mV were observed (Figure 19). The cell potential in the dark was about -50 mV initially (illuminated CdSe side negative). Upon illumination with about 200 mW/cm^2 Xenon light, the cell potential rose to $+280$ mV. The cell voltage seems not to be very stable initially; however, after anodic and cathodic currents were passed briefly the cell voltage stabilized itself at -400 mV in the dark and -50 mV under illumination. Apparently after current was passed through the cell, the CdSe electrode came to equilibrium with Ag^+ in the electrolyte, since it assumes a resting potential in the dark close to the potential of a silver electrode. When the potential of the CdSe electrode was scanned in the cathodic direction, photocurrents of about $85 \text{ } \mu\text{A/cm}^2$ were recorded (Figure 20). The current was small, apparently due to rather high ohmic resistance of the cell. The nature of this photoeffect may depend a lot on the interaction of CdSe with the electrolyte and with the SnO_2 . We believe that larger photopotentials and photocurrents can be obtained once the photoactive interface is optimized.

Another cell which contains silver powder in the counterelectrode was fabricated. This cell had the configuration — Cond.glass/ $\text{CdSe}/\text{PbI}_2 + \text{RbAg}_4\text{I}_5/\text{RbAg}_4\text{I}_5/\text{Ag} + \text{RbAg}_4\text{I}_5/\text{Cond.glass}$. This cell had an initial voltage of about 150 mV versus the counterelectrode which contains silver. After a cathodic current was passed briefly on the CdSe electrode, the cell voltage stabilized itself at near zero volts. This procedure apparently increased the activity of silver near the CdSe electrode. When the cell was illuminated with white Xenon light (about 200 mW/cm^2) on the CdSe side, a large photovoltage of about $+360$ mV was observed (Figure 21). The rise and decay of the photovoltage was rapid. Slight reduction in the photovoltage was noticed when the light beam was filtered so that only light with wavelengths longer than $4750 \text{ } \text{\AA}$ was passed.

Figure 18. PHOTOPOTENTIAL OF A SOLID-ELECTROLYTE CELL MADE OF:
Glass-SnO₂/PbI₂ + CdSe + RbAg₄I₅/RbAg₄I₅/C + PbI₂ + RbAg₄I₅/SnO₂-glass

Figure 19. PHOTOPOTENTIAL OF A SOLID-ELECTROLYTE CELL MADE OF:
Glass-SnO₂/CdSe/PbI₂ + RbAg₄I₅/RbAg₄I₅/C + PbI₂ + RbAg₄I₅/SnO₂-glass

Figure 20. CURRENT-VOLTAGE CHARACTERISTICS OF A SOLID-ELECTROLYTE CELL MADE OF:
 Glass-SnO₂/CdSe/PbI₂ + RbAg₄I₅/RbAg₄I₅/C + PbI₂ + RbAg₄I₅/SnO₂-glass
 (Light was Chopped)

Figure 21. PHOTOPOTENTIAL IN THE CELL
Cond. glass/CdSe/PbI₂ + RbAg₄I₅/RbAg₄I₅/Ag + RbAg₄I₅/Cond. glass

When the potential of the CdSe electrode was scanned in the cathodic direction, a significant cathodic photocurrent was detected under chopped light illumination (Figure 22). A small anodic current was seen in the dark since the resting potential in the dark was close to 0 mV. Anodic photocurrent was also observed while scanning in the anodic direction. The cathodic photocurrent could be maintained for a few hours, as shown in Figure 23. Here, a photocurrent of about 0.15 mA/cm^2 could be obtained at a cell voltage of 0.2 V. The current increased slightly initially and then declined slowly. When the photocurrent was driven in the anodic direction by setting the cell voltage at 650 mV, it decreased rapidly by 50% in about 20 minutes. The photoresponse may have originated from a number of photoelectrochemical processes in the system, for example, Dember-type^{3,4} photovoltage, photolytic processes in the electrolyte, and charge transfer between the electrode and the solid electrolyte. This will be further investigated in the future.

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Figure 22. CURRENT-VOLTAGE CHARACTERISTICS OF THE CELL
Cond. glass/CdSe/PbI₂ + RbAg₄I₅/RbAg₄I₅/Ag + RbAg₄I₅/Cond. glass
(Under Chopped Illumination at 25°C)

Figure 23. CATHODIC PHOTOCURRENT OF THE CELL WITH THE CONFIGURATION -
 Cond. glass/CdSe/PbI₂ + RbAg₄I₅/RbAg₄I₅/Ag + RbAg₄I₅/Cond. glass - AT A CELL VOLTAGE OF 0.2V.
 THE CdSe SIDE OF THE CELL WAS ILLUMINATED WITH APPROXIMATELY 200 mW/cm² XENON LIGHT