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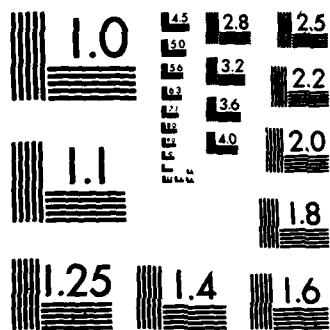
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Contract No. N00014-83-C-0108

INTERIM TECHNICAL REPORT 0001AC

AD A 128646

CHARACTERIZATION OF ILLUMINATED SEMICONDUCTOR/
SOLID-ELECTROLYTE JUNCTIONS.

PHOTOELECTROCHEMICAL INVESTIGATION OF A POLY(ETHYLENE OXIDE) CELL

by

Anthony F. Sammells and Peter G. P. Ang

Prepared for publication in
The Journal of the Electrochemical Society

May 1, 1983

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 0001AC	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Characterization of Illuminated Semiconductor/ Solid-Electrolyte Junctions. Photoelectrochemical Investigation of a Poly(ethylene Oxide) Cell	5. TYPE OF REPORT & PERIOD COVERED Technical March 1 - April 30 1983	
	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) Anthony F. Sammells and Peter G. P. Ang	8. CONTRACT OR GRANT NUMBER(s) N00014-83-C-0108	
9. PERFORMING ORGANIZATION NAME AND ADDRESS ELTRON RESEARCH INC. 710 E. Ogden Ave. Naperville, IL 60540	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR051-826	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research/Chemistry Program Arlington, Virginia 22217	12. REPORT DATE May 1, 1983	
	13. NUMBER OF PAGES	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release: Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Submitted to the Journal of the Electrochemical Society		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. <input checked="" type="checkbox"/> ABSTRACT (Continue on reverse side if necessary and identify by block number) Photoelectrochemical effects have been observed with solid-state cells using a poly(ethylene oxide).NaSCN solid polymer electrolyte containing a Na ₂ S/S redox couple. Photoeffects were observed at the interface of this electrolyte with p-InP, n-GaAs, and in a two-photoelectrode cell of configuration p-InP/PEO-NaSCN,Na ₂ S,S/n-CdS. In this latter cell, photopotentials of 540 mV were generated using 100 mW/cm ² quartz iodine illumination.		

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PHOTOELECTROCHEMICAL INVESTIGATION OF A POLY(ETHYLENE OXIDE) CELL

by

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The modification of poly(ethylene oxide) (PEO) into an alkali ion conducting polymer solid electrolyte by its formation of solid solutions with several alkali metal salts has been well documented over the last few years (1-5). Although the ionic conductivities of such materials are quite low ($\approx 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at ambient temperature), particularly in comparison to aqueous electrolytes, this in part can be compensated for by their fabrication into thin electrolyte samples. Such solid polymer electrolyte materials can conveniently be prepared by evaporation of methanol solutions containing PEO and an appropriate alkali ion salt onto a suitable substrate. Formation of a thin solid polymer electrolyte layer is then achieved typically by annealing under vacuum at temperatures below 120°C . Transference number (6) measurements for PEO/NaSCN-based solid polymer electrolytes have shown predominant alkali ion conductivity.

Recently some preliminary photocurrent/voltage data were reported on a solid-state photoelectrochemical (PEC) cell consisting of PEO/KI, I_2 as a solid polymer redox electrolyte prepared on a tin oxide conducting substrate in intimate contact to a n-Si photoanode. This photoanode was initially coated with platinum and subsequently protected from photoanodic corrosion effects by a layer of polypyrrole (7). The substitution of alternate redox electrolytes for the aqueous systems predominantly pursued in photoelectrochemical cells is one approach to address photoanodic corrosion effects at the illuminated photoelectrode/electrolyte interface. Alternative redox electrolytes have included organic nonaqueous (8) ambient-temperature molten salts (9) and inorganic solid electrolytes (10). These latter electrolytes have been previously discussed by us at the solid-state interface of n-CdSe with the silver-ion conducting solid electrolyte RbAg_4I_5 . With this solid electrolyte, however, photoactivity was detected even in the absence of a semiconductor junction, a probable consequence of the spontaneous photoreduction of Ag^+ and/or the presence of a Demer-type

photovoltage (11). Because of such interfering photoeffects with silver-ion conducting solid electrolytes, there is an obvious incentive to investigate PEC phenomena using alternative redox solid electrolytes where the opportunity for photoeffects by the solid electrolyte is less likely to occur.

In work discussed here, PEC measurements have been made on the solid polymer electrolyte PEO/NaSCN, containing $\text{Na}_2\text{S}/\text{S}$ as an introduced redox species. The fact that various redox couples can be incorporated into these alkali-ion conducting polymeric materials may give us the opportunity to use such modified materials in photoelectrochemically rechargeable cells where the stored energy via oxidized or reduced species within the electrolyte and close to the photoelectrode, could be later electrochemically discharged. This would require that the redox species incorporated within the polymer be essentially immobile. In mainly crystalline PEO electrolyte, ionic conduction is predominantly via an alkali ion transport mechanism along polymer helical chains, whereas for more amorphous PEO materials, a configurational entropy dominated transport process has been suggested (12).

Aqueous liquid-junction PEC cells with storage, having the general configuration $\text{p-InP}/\text{S}^{2-}, \text{S}_n^{2-}/\text{I}^-, \text{I}_2/\text{n-WSe}_2$ have previously been investigated by us (13). Here the relatively high ionic conductivity of the aqueous electrolytes used allowed large interelectrode distances to be tolerated. For PEO-based cells, however, small interelectrode distances are essential to minimize internal resistance losses. To identify an analogous two-photoelectrode solid-state cell based upon PEO requires that one of the photoelectrodes be transparent, to ensure illumination of both photoelectrode/redox electrolyte interfaces. The use of p-InP as a photocathode in such devices would, as a consequence, preclude the use of n-WSe₂ as the second photoelectrode.

The PEO-based redox electrolyte was prepared by introducing PEO (Aldrich Chemical Co., MW 600,000) and NaSCN into anhydrous methanol in a 4.5:1 molar

ratio of the polymer repeat unit, as discussed by others (6). With continuous stirring was slowly added an equimolar (0.1M) solution of Na_2S and S up to a sulfide concentration corresponding to 1/10 that of NaSCN. During addition of the sulfide species to the PEO/NaSCN solution, the mixture was initially yellow, but became colorless after stirring for 30 minutes. Upon standing for several weeks, some precipitation became evident from this solution. A PEC cell was prepared by initially placing a drop of freshly prepared PEO/NaSCN/ Na_2S ,S solution onto the surface of a Nesatron tin-doped indium oxide conducting glass electrode and allowed to dry in the atmosphere. This was then treated under vacuum at 75°C for one hour. The p-InP photocathode was obtained from Crysta Comm. Inc. (Zn doped $6 \times 10^{16} \text{cm}^{-3}$, <111> surface used) and had a resistivity of $0.6 \Omega\text{cm}$. Ohmic contact was made by first sputtering a thin layer of gold, followed by electrodeposited Zn and later another layer of sputtered gold. The electrode was annealed at 475°C for 1 minute. Initial attempts to make contact of this photoelectrode to the solid polymer redox electrolyte on the conducting glass met with mixed results. Reproducible contact was made by introducing a drop of the PEO containing methanol solution onto the photocathode and after drying, lightly pressing onto the already cured polymer electrolyte present on the conducting glass surface. Final curing of this cell was performed under vacuum for two hours at 75°C .

The initial photoelectrochemical performance of the cell

p-InP/PEO.NaSCN, Na_2S ,S/conducting glass
is shown in Figure 1 under 100 mW/cm^2 quartz iodine illumination. Positive photopotentials of 200mV were observed. Upon potentiostatting the p-InP at -1.2V versus its dark potential, cathodic photocurrents of $\approx 10 \mu\text{A/cm}^2$ were observed. The rather high photoelectrode bias voltage required to achieve such photocurrents and the poor fill factor are in part symptomatic of the

highly resistant polymer electrolyte used. The photoelectrochemical oxidation of the $\text{Na}_2\text{S}/\text{S}$ couple incorporated into PEO was also investigated on n-GaAs. The n-GaAs single crystal was obtained from Crystal Specialties Inc. and had a carrier density of $10^{16}/\text{cm}^3$ after silicon doping. Ohmic contact to the semiconductor was made by thin-film evaporation of a 88Au/12Ge alloy. The $\langle 111 \rangle$ face was used in these experiments after initially etching in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ before drying and coating with PEO/ $\text{NaSCN}, \text{Na}_2\text{S}, \text{S}$. This photoanode was contacted to a Nesatron conducting glass electrode and annealed in an analogous manner to that discussed previously for p-InP. A photocurrent/potential curve for this cell is shown in Figure 2. Here the initial photopotential obtained was -150 mV using $100 \text{ mW}/\text{cm}^2$ quartz iodine illumination. Anodic photocurrents of $9 \mu\text{A}/\text{cm}^2$ were obtained after subjecting the cell to a 1.5 V positive bias. Because of the opaque nature of gallium arsenide, however, this photoanode cannot be used in a two-photoelectrode cell where p-InP is used as a photocathode.

The requirements necessary for a two-photoelectrode solid-state PEC cell using a solid polymer electrolyte are not only that one of the photoelectrodes be transparent, but also that the redox species incorporated into the PEO not corrode the photoelectrodes during illumination. Although we have found the redox kinetics of halogens introduced into PEO, in general, higher than for the $\text{Na}_2\text{S}/\text{S}$ couple, we have not to this time been able to fabricate a two-photoelectrode cell which fulfills the above requirements using a halogen as one of the redox couples.

As a result, we have fabricated the solid-state two-photoelectrode cell p-InP/PEO. $\text{NaSCN}, \text{Na}_2\text{S}, \text{S}/\text{n-CdS}$, using single-crystal photoelectrodes. The n-CdS single crystal was obtained from Cleveland Crystal. Ohmic contact to the material was made by initially contacting with a gallium-indium eutectic followed by silver epoxy and curing at 150°C for 1 hour. The two-

photoelectrode cell was prepared by placing a drop of the PEO redox electrolyte onto the surface of each electrode, allowing to dry in the atmosphere and partially curing at 60°C under vacuum for 1 hour. The two electrodes were lightly pressed together to make effective contact and then finally cured at 75°C for one hour. The cell is shown schematically in Figure 3. The dark open-circuit voltage was 560mV. Upon illumination through the n-CdS photoanode to the solid-state junctions of the redox PEO with both these photoelectrodes under 100mW/cm² quartz iodine illumination, a 540 mV photopotential was generated. The photoresponse of this electrode is shown in Figure 4. The voltage between the two photoelectrodes could exceed 1000 mV. However, upon potentiostatting this cell to 0 V under illumination, currents only in the 0.3 μA range were observed as a result of the high resistivity of the electrolyte.

We conclude that although PEO-based redox electrolytes offer the opportunity to fabricate solid-state PEC cells, their eventual practicality into small devices is contingent upon increasing the PEO ionic conductivity. Compensation of this present limitation by the use of small interelectrode spacing greatly increases the susceptibility to cell shorting during fabrication.

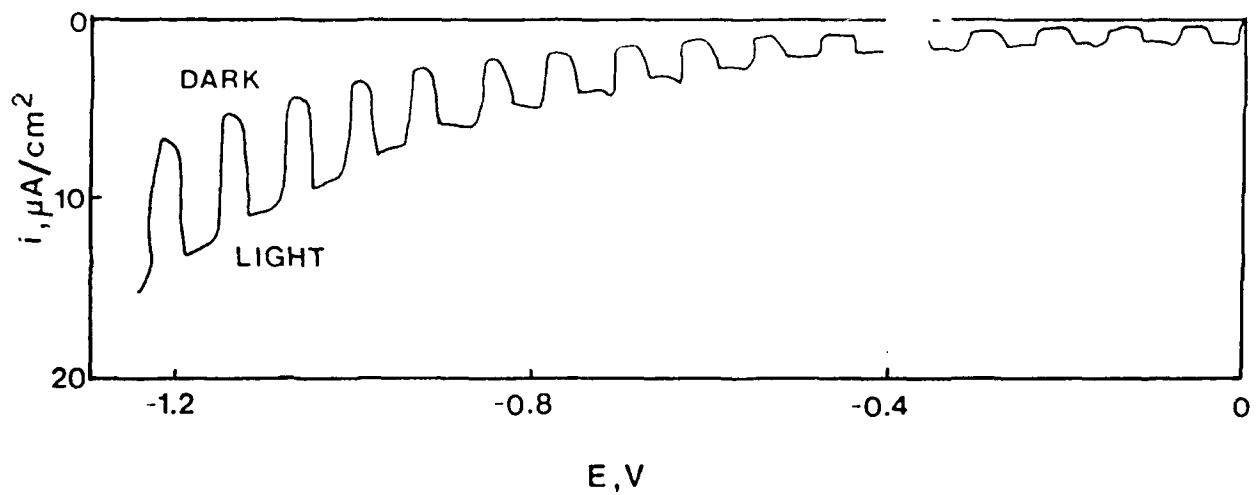


Figure 1. CURRENT-VOLTAGE CURVE FOR THE CELL $p\text{-InP}/\text{PEO.NaSCN,Na}_2\text{S,S/}$
COND. GLASS WITH AND WITHOUT $100\text{mW}/\text{cm}^2$ QUARTZ IODINE
ILLUMINATION.

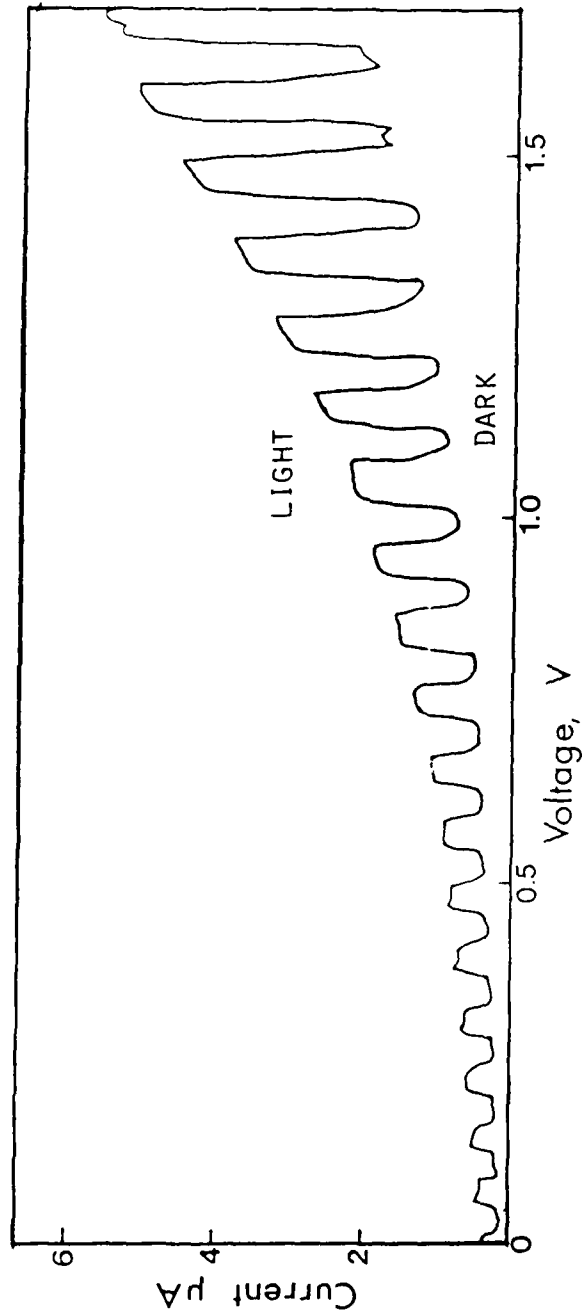


Figure 2 CURRENT-VOLTAGE CURVE FOR THE CELL
n-GaAs/PEO.NaSCN, $\text{Na}_2\text{S}_2\text{S}_8/\text{COND. GLASS WITH}$
AND WITHOUT 100 mW/cm^2 QUARTZ IODINE
ILLUMINATION.

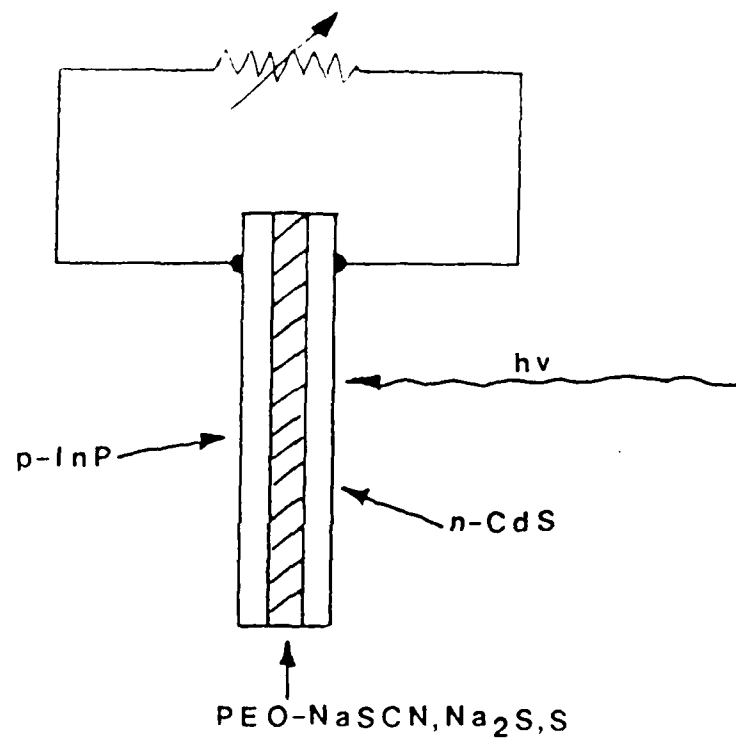


Figure 3. SCHEMATIC DIAGRAM OF CELL
 $p\text{-InP/PEO-NaSCN, Na}_2\text{S, S/n-CdS}$

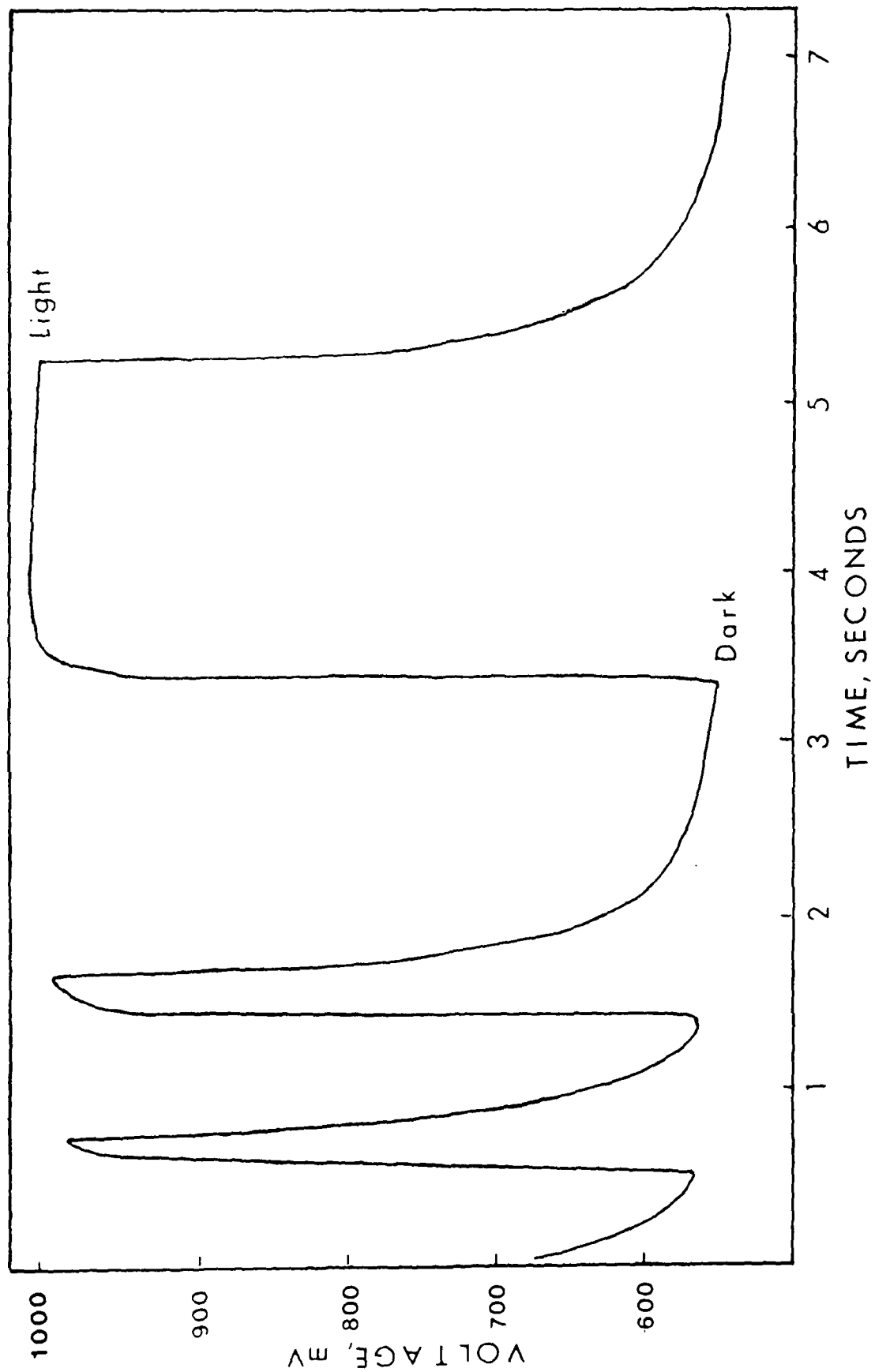


Figure 4. VARIATION OF VOLTAGE WITH TIME FOR CELL p-InP/PEO-NaSCN, Na₂S, S/n-CdS WITH AND WITHOUT ILLUMINATION (100mW/cm² QUARTZ IODINE ILLUMINATION).

ACKNOWLEDGMENT

This work was supported by the Office of Naval Research under contract # N00014-83-C-0108.

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