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ELECTROCHEMICAL PHOTOVOLTAIC CELLS/STABILIZATION AND
OPTIMIZATION OF II-VI SEMICONDUCTORS

First Technical Progress Report for Period April 15-June 30, 1980

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FIRST TECHNICAL PROGRESS REPORT

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1.0 ABSTRACT

The overall goal of this program is to provide the basis for designing a practical electrochemical solar cell based on the II-VI compound semiconductors. Emphasis is on developing new electrolyte redox systems and electrode surface modifications which will stabilize the II-VI compounds against photodissolution without seriously degrading the long-term solar response. The bulk electrode material properties are also being optimized to provide the maximum solar conversion efficiency and greatest inherent electrode stability.

Because of delays in negotiating the follow-on contract, this report covers only about 10 man-weeks of effort.

Factors limiting the short circuit current of the n-CdSe/methanol/ferro-ferricyanide system (which we have shown to be stable) to 17.5 mA/cm^2 have been identified. The principal limiting factor is apparently specific adsorption of hexacyanoferrate species on the electrode surface which occurs at higher redox couple concentrations and slows the overall charge transfer process. Ion pairing also occurs, resulting in a low mass transport rate (smaller diffusion coefficients and increased solution viscosity), and probably enhances the degree of specific adsorption. Improvements in the performance of this system will require mitigation of the interactions between the redox species and the electrode surface, e.g., via electrolytes with reduced ion-pairing tendencies or the use of electrode surface films.

Photoelectrochemically generated polypyrrole films have been shown to protect CdX photoanodes from dissolution while permitting electron exchange with the electrolyte. Current effort is directed toward improving the film adhesion and optimizing the performance characteristics.

2.0 PROJECT DESCRIPTION

To date, the best performance for electrochemical solar cells has been attained with n-type cadmium chalcogenide (CdX , where $X = \text{S}, \text{Se}$ or Te) [1-15] and n-GaAs [16] electrodes stabilized by chalcogenide/polychalcogenide redox couples (e.g., $\text{Se}^{2-}/\text{Se}_x^{2-}$) in aqueous electrolytes. Photogenerated holes, which would otherwise lead to destruction of the semiconductor lattice, are preferentially consumed in the redox reaction. Solar AM2 conversion efficiencies of 7 to 8% for CdX single crystals [10], 6% for thin CdX polycrystalline films [1], and 9% for GaAs single crystals [16] have been reported. Unfortunately, although photodissolution is almost completely suppressed in such systems, the photocurrents deteriorate with time, especially at higher light intensities. In the case of CdX , this has been shown to involve chalcogenide exchange between the electrolyte and the electrode surface, possibly via photo-oxidation followed by reprecipitation [17-20]. Recently, Noufi, *et al.* [1] have demonstrated that conversion efficiencies are higher and degradation is slower for mixed polycrystalline CdS/CdSe electrodes. Chemical modification of n-GaAs electrodes by RuCl_3 solutions has also been shown [21] to increase solar conversion efficiencies for single crystals to 12% in $\text{Se}^{2-}/\text{Se}_x^{2-}$, although long-term stability has not been established.

These results demonstrate both the promise and the problems associated with stabilization of narrow-band-gap semiconductors for use in electrochemical solar cells. Most studies to date have emphasized cell characterization rather than materials development, so that only the more common semiconductors and a few redox systems have been investigated. In spite of this, decent power conversion efficiencies (6%) for thin polycrystalline films have been demonstrated. To evolve a stable acceptably efficient cell, however, a more systematic approach involving a wider spectrum of materials and more emphasis on materials characterization is needed. The most promising possibilities include organometallic redox systems in both aqueous and nonaqueous media, chemically modified electrode surfaces, and other solid solution electrodes. Surface chemical modification is particularly attractive since the

electrolyte redox system could then be varied over a wider range to improve conversion efficiencies and perhaps obtain more desirable reaction products (e.g., fuels). Unfortunately, the synthetic chemistry knowledge required for chemically modifying II-VI electrode surfaces is not available and has to be developed.

The focus of the present program is on stabilizing II-VI semiconductors against photodissolution, with the ultimate goal of attaining a practical electrochemical solar cell. These materials have bandgap energies which are sufficiently small (1.4 to 2.4 eV) to permit capture of a reasonable fraction of the solar spectrum, and their flatband potentials are generally very negative in aqueous electrolytes so that cell voltages are large and an external voltage bias is not required for maximum efficiency. Solid solution formation also provides added flexibility for both the bandgap and flatband potential, as well as the electrode stability. In addition, thin film fabrication techniques, which will most probably be required for any economical solar cell, are reasonably advanced for this class of materials.

The program emphasis is on developing new electrolyte redox systems and electrode surface modifications which will stabilize the II-VI compounds against photodissolution without seriously degrading the long-term solar response. A cooperative effort involving electrochemistry, synthetic chemistry, and materials characterization provides the mutual feedback necessary to evolve a practical compromise between the interfacial chemistry and the device characteristics. Work is concentrated on the polycrystalline thin films needed for large area, economical solar cells, although single crystal electrodes are used to elucidate some of the surface chemistry. Obviously, much of the chemical knowledge required for redox system design and electrode surface modification is similar, so that considerable synergy exists between these two parallel approaches.

As an integral part of the program, the bulk electrode materials properties are being optimized in concert with the stabilization studies to provide the maximum solar conversion efficiency and greatest inherent elec-

trode stability. Various II-VI semiconductors and appropriate binary mixtures within this class are being evaluated for stability and solar conversion efficiency in the various redox electrolytes. The effects of the method of film preparation (e.g., vapor deposition, sputtering), annealing treatments, and the type and concentrations of dopants on the film properties are also under investigation.

A critical facet of this program involves materials characterization. Chemical changes in the electrode surface resulting from deliberate chemical modifications or photoelectrochemical evaluation are detected by x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS), energy dispersive analysis of x-rays (EDAX), and/or low energy electron diffraction (LEED). Morphological changes in grain size or porosity are followed by scanning electron microscopy (SEM). Hall, conductivity, and a.c. impedance measurements are used to determine the concentrations, mobilities, and lifetimes of charge carriers in the semiconductor materials. The presence and properties of electrode surface states and trap levels are being investigated in situ by photocapacitance spectroscopy, an extremely promising new technique.

This broad interdisciplinary approach permits full advantage to be taken of the synergy which exists between the various facets of the program and of the understanding and insight provided by thorough materials characterization. Actual electrochemical solar cells are also built to test concepts and provide additional feedback for further materials development, as well as a better basis for comparing the emerging electrochemical and solid state solar cell technologies.

3.0 TECHNICAL PROGRESS DESCRIPTION

3.1 Development of New Electrolyte Redox Couples

3.1.1 Methanol/Ferro-Ferricyanide

Under last year's program, n-CdSe photoanodes were shown to be stable in the methanol/ferro-ferricyanide system. Under tungsten-halogen illumination of about AM1 intensity (85 mW/cm^2), the current at a single crystal n-CdSe photoanode remained constant at 6 mA/cm^2 (conversion efficiency of $\sim 3.5\%$) for 29 days in a stirred methanol electrolyte containing 0.4 M each of tetraethylammonium $\text{Fe}(\text{CN})_6^{3-/4-}$ plus 0.1 M tetraethylammonium fluoroborate. It was also demonstrated that the stability of n-CdSe photoanodes in methanol/ferro-ferricyanide is not sensitive to traces of water.

Based on these very encouraging results, experiments were then performed using more efficient n-CdSe electrode materials. The best output parameters for n-CdSe ($\sim 5\%$ conversion efficiency, $\text{FF} \approx 0.5$) were obtained for electrodes with 5×10^{16} carriers/ cm^3 in methanolic solutions containing 0.25 M each of chemically prepared $\text{Fe}(\text{CN})_6^{3-/4-}$ species. The measured open circuit voltage was very close to the maximum value expected for this system (0.7 V). Photocurrent measurements as a function of light intensity indicated that the maximum stable short circuit current is 17.5 mA/cm^2 in stirred solutions and 7.5 mA/cm^2 in unstirred solutions (at 95 mW/cm^2). Transient photocurrents were larger at the higher light intensities but rapidly decayed to the steady values.

Under the current program, the factors limiting the attainable photocurrent in the n-CdSe/methanol/ferro-ferricyanide system were determined. The possibilities included inadequate mass transport of the redox species in the electrolyte and decreased redox reaction rate caused by ion pairing or specific adsorption of one or both of the electroactive species. The inherent electrode kinetics for the ferro-ferricyanide couple in methanol were studied by cyclic voltammetry at a rotating Pt disc electrode. Kinematic viscosity

measurements were also made as a function of the redox couple concentration so that the relative effects of changes in the fluid flow characteristics, reactant diffusion coefficients, and electron transfer rate could be ascertained. The dependence of the photocurrent for n-CdSe photoanodes on light intensity was determined in both the methanol/ferro-ferricyanide and aqueous polysulfide systems as a means of detecting solid state limitations. Some earlier measurements were repeated as a check.

Figure 1 shows plots of the diffusion limiting currents (i_L) for the ferro-ferricyanide reaction at a rotating Pt disc electrode as a function of the redox couple concentration. For both the anodic and cathodic branches, i_L goes through a maximum at about 0.15 M $\text{Fe}(\text{CN})_6^{3-/4-}$. Also, at concentrations above 0.05 M, specific adsorption becomes significant as indicated by higher "Tafel" slopes (180-250 mV/decade) than obtained at lower concentrations (~120 mV/decade). The decrease in i_L at higher concentrations could result from a decrease in the diffusion coefficient of the hexacyanoferrate species, stemming from increased ion pairing, and/or an increase in the electrolyte viscosity. That i_L is practically diffusion limited at all redox couple concentrations is shown by the Levich plots [22] in Fig. 2.

Figure 3 shows plots of the diffusion coefficients for the $\text{Fe}(\text{CN})_6^{3-/4-}$ species (calculated from the Levich equation) and the electrolyte kinematic viscosity (measured with a Cannon-Fenske viscometer) vs the redox couple concentration. The viscosity is practically constant at low $\text{Fe}(\text{CN})_6^{3-/4-}$ concentrations but increases sharply at about 0.2 M, which corresponds approximately to the maximum in the diffusion limiting current for the redox reaction (0.15 M). However, the diffusion coefficient decreases by almost an order of magnitude (from 28×10^{-6} to 3×10^{-6} cm^2/sec) from 0.01 to 0.1 M $\text{Fe}(\text{CN})_6^{3-/4-}$, indicating that considerable ion pairing occurs even at relatively low redox couple concentrations.

The relative effects of the electrolyte kinematic viscosity (ν) and the diffusion coefficients (D) in reducing the diffusion limiting currents can best be seen by plotting $D^{2/3}$ and $\nu^{-1/6}$, which are the terms appearing in the Levich equation [22].

Fig. 1 Diffusion limited currents vs the $\text{Fe(CN)}_6^{3-/4-}$ concentration for a rotating 0.13 cm^2 Pt disc electrode in methanol/ $0.1 \text{ M Et}_4\text{NBF}_4$ electrolyte containing equal concentrations of the oxidized and reduced species. The scan rate was 20 mV/sec and i_L was determined at an overvoltage of 1.00 V in each case.

Fig. 2 Levich plots [22] for the $\text{Fe(CN)}_6^{3-/4-}$ reaction at a rotating Pt disc electrode in methanol/0.1 M Et_4NBF_4 (conditions same as for Fig. 1).

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Fig. 3 Plots of the diffusion coefficients (D) of $\text{Fe(CN)}_6^{3-/4-}$ species and the kinematic viscosity of 0.1 M $\text{Et}_4\text{NBF}_4/\text{methanol}$ solutions as functions of the $\text{Fe(CN)}_6^{3-/4-}$ concentration.

$$i_L = 1.94 \times 10^7 C_R D_R^{2/3} \nu^{-1/6} \omega^{1/2}$$

where i_L is in mA/cm², C_R is the concentration of reactant in moles/ml, D_R is the reactant diffusion coefficient in cm²/sec, ν is the electrolyte kinematic viscosity in cm²/sec, and ω is the disc electrode rotation rate in rpm. Such plots are shown in Fig. 4. $\nu^{-1/6}$ decreases linearly and relatively slowly (note scale difference) with $\text{Fe}(\text{CN})_6^{3-/4-}$ concentration whereas $D^{2/3}$ decreases sharply to about 0.1 M and then more gradually. Thus, the decrease in i_L at concentrations above 0.15 M results from a combination of the effects of $\nu^{-1/6}$ and $D^{2/3}$.

Plots of the short circuit photocurrent at single crystal n-CdSe photoanodes in 0.25 M $\text{Fe}(\text{CN})_6^{3-/4-}$ /methanol and in aqueous polysulfide electrolytes vs light intensity are shown in Fig. 5. The linear plot (passing through the origin) for the aqueous system indicates that solid state limitations are not predominant. Therefore, the nonlinearity in the methanol/ $\text{Fe}(\text{CN})_6^{3-/4-}$ plot and the upper limit of 17.5 mA/cm² for the steady-state photocurrent are apparently associated with specific adsorption of hexacyanoferrate species on the electrode surface which slows the overall electron transfer rate. This is consistent with the transient photocurrents (at the higher light intensities) decaying to the steady state value (Fig. 5), and with the higher "Tafel" slopes (on Pt) for higher redox couple concentrations. The adsorbed species are probably ion-paired since the viscosity data indicate that ion pairing is prevalent at $\text{Fe}(\text{CN})_6^{3-/4-}$ concentrations above 0.1 M. Note that the diffusion limiting currents for the redox reaction are apparently too high (30 mA/cm² at 900 rpm) to limit the photoanode current to 17.5 mA/cm², but a direct comparison cannot be made since the n-CdSe photoanodes were not in a configuration amenable to rotation (magnetic stirring was used instead).

3.1.2 Other Redox Electrolytes

Since a key advantage of electrochemical photovoltaic cells (i.e., good efficiencies with polycrystalline materials) would be lost if backside

Fig. 4 Plots of $D^{2/3}$ and $\nu^{-1/6}$ for the data in Fig. 3

Fig. 5 Short circuit currents vs light intensity (tungsten-halogen lamp) for n-CdSe electrodes in 0.25 M tetraethylammonium $\text{Fe}(\text{CN})_6^{3-/4-}$ /0.1 M Et_4NBF_4 /methanol and in aqueous 2.2 M Na_2S /0.1 M S/0.1 M NaOH electrolytes

illumination were required, we are initially considering only relatively transparent redox couples for stabilization of CdX photoanodes. Couples to be investigated include: $\text{Co}(2,2'\text{-bipyridyl})_3^{3+/2+}$, $\text{Fe}(\text{EDTA})^{1-/2-}$, $\text{Fe}^{+3/+2}$ and $\text{Fe}(\text{CN})_4(2,2'\text{-bipyridyl})^{1-/2-}$ in various solvents. All of these couples have been synthesized or can be readily generated in situ from available materials.

3.2 Chemical Modification of the Electrode Surface

3.2.1 Electrochemically Generated Polymer Films

In principle, the problem of photoanode degradation could be overcome by the use of an electrically conducting polymer film on the electrode. By acting as a barrier to ion/solvent transport, such an insoluble film would prevent photodegradation while permitting electron exchange with the electrolyte. Good adhesion, uniformity and interfacial charge transport properties are expected for electrochemically generated films since deposition is initiated at the interface by electrochemical oxidation/reduction. Electrodeposition of polypyrrole films, having conductivities in the 10 to $100 \Omega^{-1} \text{ cm}^{-1}$ range, on Au and Pt electrodes has recently been reported [23-25]. Under this program, we have photoelectrochemically generated polypyrrole films on semiconductor electrodes and are currently evaluating the characteristics of the resulting photoanodes.

Initially, films were deposited potentiostatically on Pt and illuminated single crystal n-CdX and n-GaAs electrodes from acetonitrile solution containing 0.1 M pyrrole and 0.1 M Et_4NBF_4 . Deposition on the illuminated semiconductor electrodes begins at less anodic potentials ($0 - 0.2 \text{ V}$ vs. SCE) than on Pt (0.8 V) and was generally performed at 0.2 V on CdX and 0.45 V on GaAs (for which the current was about $100 \mu\text{A}/\text{cm}^2$). Based on the charge passed, the film thickness was usually in the 100 monolayer range (assuming $50 \mu\text{C}/\text{cm}^2$ per monolayer).

Polypyrrole films undergo a reversible electrochemical reaction evidenced by anodic/cathodic cyclic voltammetry peaks at 0.2 V on Pt and just anodic of the flatband potentials on the illuminated semiconductor elec-

trodes. This intrinsic film reaction apparently involves anion exchange with the solution. When $\text{Fe}(\text{CN})_6^{3-}$ is incorporated into the film instead of BF_4^- , the voltammetry peaks occur at the potential of the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple and exhibit the characteristics of a surface bound electroactive species. This indicates that the redox reaction is occurring within the matrix of the film, a very exciting observation.

Cyclic voltammetric studies were performed for polypyrrole-coated CdX electrodes, with and without illumination, in aqueous solutions containing redox couples covering a range of potentials (V_R), i.e., $\text{Fe}^{2+/3+}$ (0.53 V vs SCE), $\text{Fe}(\text{CN})_6^{3-/4-}$ (0.12 V), and $\text{Fe(III)EDTA/Fe(II)EDTA}$ (0.00 V). The pH was also varied widely to produce large shifts in the flatband potential (V_{fb}), which is not possible for the bare electrodes since CdX materials are chemically unstable in acidic solutions. Flatband potentials for the coated electrodes were generally comparable to those for the bare electrodes, but open circuit voltages (V_{oc}) were somewhat less than expected ($V_{oc} = V_R - V_{fb}$) because of appreciable dark currents. A summary of V_{oc} values is given in the Table I. Similar studies with polypyrrole-coated n-GaAs yielded the expected V_{oc} values and small dark currents. In all cases, polypyrrole films were found to protect the semiconductor from photodegradation while permitting charge transfer to the electrolyte.

Table I. Open Circuit Voltages for CdX Photoanodes in Various Redox Electrolytes.

Redox Couple	pH	V_{oc} (V vs SCE)	
		CdSe	CdTe
$\text{Fe}^{2+/3+}$	2	0.70	0.55
$\text{Fe}(\text{CN})_6^{3-/4-}$	1	0.30	0.20
	12	0.90	0.80
	14	1.0	0.90
Fe(II/III) EDTA	8	0.6	0.50

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The key problem at this point is peeling of the polypyrrole film which usually occurs after about 10 minutes under illumination in aqueous solutions. We are presently investigating various surface pretreatments and constant current deposition as means of improving film adhesion. Recent results are very encouraging. Films obtained on both CdX and GaAs electrodes at constant current appear to be significantly more adherent (are physically much more difficult to remove from the substrate). Also, one coated GaAs electrode for which the surface was photoelectrochemically roughened prior to deposition operated for about 7 hours as a photoanode without signs of deterioration.

3.3 Optimization of the Bulk Electrode Material

No work was performed on this task during the past quarter.

3.4 Development of Photocapacitance Spectroscopy

No work was performed on this task during the past quarter.

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