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THE DEVELOPMENT OF ELECTROCHEMICAL PHOTOVOLTAIC CELLS

Third Technical Progress Report for November 1, 1979—January 31, 1980

By
H. J. Byker
R. E. Schwerzel
V. E. Wood
A. E. Austin
E. W. Brooman

March 7, 1980

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Battelle
Columbus Laboratories
Columbus, Ohio

U.S. Department of Energy

Solar Energy

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THIRD TECHNICAL PROGRESS REPORT
FOR THE PERIOD
NOVEMBER 1, 1979 TO JANUARY 31, 1980

on

THE DEVELOPMENT OF ELECTROCHEMICAL
PHOTOVOLTAIC CELLS

to

THE SOLAR ENERGY RESEARCH INSTITUTE

March 7, 1980

by

H. J. Byker, R. E. Schwerzel and
V. E. Wood

Other Program Members
A. E. Austin and E. W. Brooman

Contract No. XP-9-8002-2

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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ABSTRACT

The development of stable, efficient, electrochemical photo-voltaic cells based on silicon and gallium arsenide in non-aqueous electrolyte systems is being investigated. The effect of surface condition of silicon electrodes on electrochemical and physical characteristics has been studied. An electrode-supporting electrolyte interaction in acetonitrile has been identified which leads to etching of the surface. Improved performance can result, which has practical significance. Gallium arsenide electrodes have been electrochemically characterized in cells containing propylene carbonate with a ferrocene/ferricenium redox additive. Degradation of the ferricenium salt under illumination has been investigated. Other redox couples studied to date have not given promising results. Long-term stability experiments have been deferred while a better understanding of electrode behavior is being obtained.

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INTRODUCTION

An electrolyte solution in contact with a semiconductor electrode is the essential feature of a photoelectrochemical solar cell, which is the analog of a metal-semiconductor junction solar cell. These photoelectrochemical cells, or electrochemical photovoltaic cells as they are sometimes called, are potentially an alternative to the expensive solid state solar cells for aerospace and terrestrial power generation. The goal of this research program is the development of practical, low cost electrochemical photovoltaic cells with long-term stability and power conversion efficiencies of greater than 10% of the incident solar radiation. Liquid junctions with thin film semiconductors of polycrystalline or amorphous materials are considered to be the candidates for electrochemical photovoltaic cells to meet these goals.

Previous studies of photoelectrochemical systems have focused mainly on aqueous electrolyte solutions with inorganic redox additives

taking part in the charge transfer reactions at the electrodes. The use of organic redox additives in organic (non-aqueous) solvents opens up many possibilities for photoelectrochemical systems which offer several advantages over those using water.

The photo-assisted dissolution of the small band gap semiconductor electrodes usually occurs in aqueous systems, where water itself can be an integral part of the decomposition reactions. The use of anhydrous, organic solvents should hinder such dissolution reactions, since the semiconductor decomposition products generally are not solvated as well by nonaqueous liquids as they are by water. Nonaqueous, aprotic solvents are also stable over a greater range of electrode potentials, and allow the use of a wide range of organic and organo-metallic redox couples which are not soluble in water.

An objective of Battelle's research program is the identification of appropriate redox couples for the stabilization of electrochemical photovoltaic cells based on silicon or gallium arsenide electrodes in nonaqueous, aprotic, organic electrolytes. The feasibility of developing a stable, efficient electrochemical photovoltaic cell utilizing an organic solvent system will be demonstrated and the physical and chemical parameters limiting the performance of such cells will be determined. Battelle believes that for electrochemical photovoltaic cells to become a viable commercial proposition, emphasis must be placed on long life (cell stability) as well as performance (cell efficiency).

The planned approach is to select possible redox couples and investigate their electrochemical and photoelectrochemical behavior in the presence of illuminated silicon and gallium arsenide electrodes. The effect of semiconductor surface preparation techniques on these reactions will also be studied. Systems demonstrating good conversion efficiency will be selected for stability tests. The most promising electrolyte systems will then be chosen for investigation with polycrystalline and amorphous thin film electrodes. If specific degradation mechanisms can be identified, approaches for controlling the degradation, hence improving the stability of these cells, will be recommended.

EXPERIMENTAL PROGRAM

The experimental program is divided into two principal tasks. The first task is concerned with the development of an efficient electrochemical photovoltaic cell, and is broken into four subtasks as follows:

- Task 1.1 Electrode Materials Selection, Acquisition and Cell Fabrication
- Task 1.2 Electrochemical Characterization of Materials and Cell Performance
- Task 1.3 Physical Characterization of Electrode Materials
- Task 1.4 Experiments with Polycrystalline Materials.

The second task is concerned with identifying and controlling degradation mechanisms, and investigating long-term cell stability. There are four subtasks also, namely:

- Task 2.1 Cell Materials Selection and Cell Fabrication
- Task 2.2 Long-Term Degradation Studies
- Task 2.3 Determination of Degradation Mechanisms
- Task 2.4 Experiments to Control Degradation.

Work performed in this third technical progress reporting period centered on activities involving Tasks 1.1, 1.2, 1.3, and 2.3. A description of the accomplishments on these tasks is given below.

Task 1.1: Electrode Materials Selection, Acquisition and Cell Fabrication

Details of this activity were given in the second technical progress report dated November 21, 1979. During the current reporting period experiments have been conducted with the acetonitrile solvent, dried by a technique involving distillation over calcium hydride under dry argon, and with propylene carbonate solvent also purchased from Burdick and Jackson Laboratories, Inc.

Some effort was expended on the identification and evaluation of additional redox couples. For example, studies have been made of I^-/I_3^- , phenazine compounds, Cu^+/Cu^{++} and Hg^+/Hg^{++} in acetonitrile containing tetrabutyl ammonium fluoborate at platinum and n-Si electrodes. None of these exhibited promising characteristics^(1,2). The search for useful redox additives is being continued.

In this report emphasis will be placed upon the use of ferrocene/ferricenium tetrachloroferrate as a redox couple. The latter salt was identified as being more soluble in the solvents of interest than those used previously, namely ferricenium fluoborate and ferricenium nitrate.

Task 1.2: Electrochemical Characterization of Materials and Cell Performance

Experiments have been conducted with cells containing n-silicon and n-gallium arsenide photo-electrodes and platinum counter-electrodes in acetonitrile or propylene carbonate solvents.

Silicon Cell Studies: Effects of Surface Treatment

The use of silicon in electrochemical photovoltaic cells has been limited primarily by the poor stability of the silicon surface exposed to the electrolyte solution. Although photoanodic dissolution of n-type silicon does not appear to be the problem it is for some other n-type semiconductor materials (particularly III-V and II-VI compounds) the silicon surface readily forms a passivating layer of oxide in the presence of water. This problem should be preventable in a deoxygenated, water-free, organic solvent, as used in our experimental program.

It was our original expectation that a commercially polished, defect-free silicon surface, which only was etched to removed oxide prior to use, would be the most desirable condition for a silicon photoelectrode. This is in fact true for a metal Schottky diode on silicon materials. Although we have observed that well behaved differential capacitance curves in acetonitrile can be obtained with such electrode surfaces, no under-potential has been observed for the photoelectrochemical oxidation of ferrocene at such an electrode.

Laser and Bard⁽³⁾ observed that polished, unetched silicon electrodes were more active electrochemically than etched electrodes, and the former behaved in a nearly metallic fashion. In such cases it may be that the electron transfer from the electrolyte to the silicon electrode is mediated by a mechanically induced surface species, which could serve to trap photogenerated holes near the surface where they can react with materials in solution.

Figure 1 shows the results of an experiment with an n-type silicon electrode which was polished with 1.5 μm diamond paste, rinsed in absolute methanol and left unetched. The silicon was obtained from Monsanto Electronic Materials Division and was phosphorus doped to a resistivity of 3 to 6 ohm-cm. The [111] face was exposed to the solution. A sputtered titanium-silver ohmic contact on the back of the electrode was determined, by mercury diode analysis⁽⁴⁾, to add a series resistance of 31 ohms to the cell. The electrolyte solution consisted of 0.001 M ferrocene and 0.1 M tetrabutylammonium fluoborate in acetonitrile. The acetonitrile had been distilled from CaH_2 under dry argon. A three electrode cell, with an Ag/Ag^+ reference half-cell and a platinum wire counter-electrode, was assembled in a dry box. The solution was purged with purified argon.

The top curve (Curve a) in Figure 1 shows an oxidation wave for ferrocene at n-silicon in the dark. The peak current density is similar to that expected for a platinum electrode. Note, however, the existence of a large anodic current which begins to flow at about +1.0 volt vs Ag/Ag^+ . We interpret this behavior as being the result of a photoelectrochemical etching process, and is not believed to be due to oxide formation on the n-silicon via reaction with residual water in the electrolyte system. The defect surface caused by polishing with a relatively large grit material allows the electrode to act in a metallic manner, but this also causes the electrode to be very reactive itself. We tentatively propose that at certain active sites the silicon reacts anodically with the tetrafluoborate ions of the supporting electrolyte, and the silicon at these sites is etched away by the following net oxidation reaction:

FIGURE 1. OXIDATION OF FERROCENE AT POLISHED
n-TYPE SILICON IN ACETONITRILE

On the second sweep in the dark (Figure 1, Curve b) the ferrocene is oxidized more easily than on the first sweep and this is not the expected observation if the large anodic current had been due to oxide formation, and passivation of the surface. The second anodic current increase also takes place at a less positive potential.

The third sweep (Curve c) also in the dark, shows a small positive shift in peak potential and a slight reduction in the peak current density. Five more sweeps (not shown) continue to show this same general trend in behavior.

The fourth voltammogram shown (Curve d) is for the oxidation of ferrocene with white light illumination (40 mW/cm^2) from an ELH lamp. This sweep was run immediately after the previously described voltammograms. For illustrative purposes, a cyclic voltammogram (dashed curve) of ferrocene at a platinum electrode is superimposed on the curve for silicon. The current density scale for the n-silicon electrode should be multiplied by a factor of 1.1 in order to correspond with the current density at platinum. The two superimposed curves show that ferrocene is oxidized more easily at the illuminated n-silicon electrode than at platinum, a phenomenon not observed with an etched, defect-free silicon surface.

These experiments illustrate a fundamental difference between the oxidation reaction at silicon and at gallium arsenide. For example, at n-type silicon the difference in the oxidation wave with and without illumination is a relatively small change in potential and current, whereas at a n-type gallium arsenide electrode it is very difficult to obtain any oxidation current in the dark.

The results of a comparable experiment, with a similarly prepared n-type silicon electrode, involving ferrocene oxidation in propylene carbonate is shown in Figure 2. This solution was 0.05 M in ferrocene and 0.1 M in tetrabutylammonium fluoborate. The illumination intensity was 57 mW/cm^2 from an ELH lamp, and the beam was chopped to accentuate the difference between the light and dark currents.

The first sweep (Curve a) with the freshly polished electrode shows that there was little difference between the oxidation current when the electrode was illuminated and when it was in the dark. At a potential

FIGURE 2. OXIDATION OF FERROCENE AT POLISHED
n-TYPE SILICON IN PROPYLENE CARBONATE

of about +1.5 volts vs Ag/Ag^+ reference the large anodic current noted previously was again observed. On sweep reversal the magnitude of this current continues to increase and show a large dependence on illumination.

A second sweep to positive potentials (Curve b) revealed that the oxidation of ferrocene now occurs at a more negative potential, as was found in the acetonitrile solvent (see Figure 1). Although the total current density is decreased, the chopping of the light shows that the photocurrent is approximately 80 percent larger than the dark current at the peak of the ferrocene oxidation wave.

After a number of sweeps to potentials positive enough to cause the "etching" process to take place, several small etch pits were observed on the electrode surface. The most desirable condition for the passage of photocurrent thus appears to be after the polished surface is briefly exposed to electrochemical etching (the conditioning process which takes place).

Gallium Arsenide Cell Studies

The electrochemical behavior of a photoelectrochemical cell, comprised of a n-gallium arsenide photoelectrode, 0.08 M ferrocene with 0.1 M ferricenium tetrachloroferrate, and a platinum counter-electrode in propylene carbonate was investigated. The n-type gallium arsenide material with silicon doping was obtained from Laser Diode Laboratories, Inc., and was reported to have a resistivity of 0.0144 ohm-cm. The n-GaAs electrode was provided with an ohmic contact by rubbing the back with gallium-indium eutectic and attaching a copper wire with silver epoxy. The electrode was mounted in a glass tube with ordinary epoxy and etched via the procedure of Kohl and bard⁽⁵⁾. The cell was assembled in a dry box under an argon atmosphere, and the solution was purged with argon which had passed through a copper furnace at 350 C. A reference electrode was made from a silver wire in a propylene carbonate solution of 0.01 M AgClO_4 and 0.1 M tetrabutylammonium fluoborate, separated from the working electrode by a "thirsty glass" frit.

The current-voltage curve for a three-electrode cell, illuminated with white light at 10 mW/cm^2 from a 200 watt Xe lamp, is shown in Figure 3. The limiting current for the unstirred solution is 0.45 mA for the 0.5 cm^2 electrode area, corresponding to a limiting current density of 0.9 mA/cm^2 . While this result appears to be a respectable photocurrent density for this illumination intensity, the interpretation of this result needs some explanation. The difficulty lies in where to choose the potential at which the current corresponds to the short-circuit current of a corresponding two-electrode cell. In such a cell, the counter-electrode is held at the potential of the redox couple if only a small overpotential is required to cause current to flow at this electrode. So the external photocurrent is limited to that which corresponds to the potential difference between this level and the conduction band edge at the surface, less internal IR losses. In the potentiostated cell, on the other hand, the attainable current is limited only by the supply of photocarriers or by transfer effects in the solution.

A more realistic evaluation of cell performance can be obtained in a two-electrode experiment, in which the photopotential of the cell is "bucked" out by a voltage of equal magnitude, but of opposite polarity. As this voltage is decreased to zero the photocurrent can be recorded, and when the bucking voltage is zero the current will correspond to the short circuit current, (this experiment can also be run by starting at the short circuit current, then by increasing the bucking voltage, the open-circuit potential can be found at the point of zero current flow*). Such an experiment was performed, and the results are shown by the dashed curve in Figure 3. The open-circuit potential was 0.486 volts and the short circuit current was 0.24 mA/cm^2 . The maximum efficiency for conversion of the Xe lamp light used to electric power was 0.45 percent and the fill factor was 0.39.

* Alternatively, a conventional solar cell response experiment can be performed by varying the load resistance.

FIGURE 3. CURRENT-VOLTAGE CURVES FOR A n-GaAs/Pt CELL
(0.08 M Ferrocene; 0.1 M Ferricenium
Tetrachloroferrate in PC)

The efficiency of this cell is believed to be limited primarily by mass transfer in the solvent since no supporting electrolyte was used because it was feared that the wrong choice of anion in the supporting electrolyte might decrease the solubility of the ferricenium salt. The solubility of this salt was determined to be 0.18 molar in acetonitrile, and it appears to be at least this soluble in propylene carbonate. The relatively poor solubility of ferrocene and the large optical absorption coefficient for the ferricenium ion are factors limiting the utility of this redox couple. There is also a question concerning the stability of the ferricenium ion which we observe to decompose over a period of several hours to days in acetonitrile, as described in a later section of this report.

These considerations would seem to limit the usefulness of ferrocene to being used as a diagnostic tool (model system) in the study of semiconductor electrochemistry, unless the material is attached to the electrode surface, and serves as a mediating agent rather than redox couple.

Task 1.3: Physical Characterization of Electrode Materials

Differential capacitance curves for several silicon electrodes in a 0.1 M solution of tetrabutylammonium fluoborate in acetonitrile were obtained with a Wayne-Kerr bridge which operates at 1000 Hz. The reciprocal of the square of the space charge capacitance as a function of electrode potential is plotted in Figure 4 for several surface treatments. In these "Mott-Schottky" plots, the square symbols (Curve b) represent the results for a commercially polished, defect-free, n-type silicon electrode which was etched for 90 seconds in buffered HF. From the slope of this curve both the density of donor impurities and the value of the resistivity of the silicon can be calculated. The donor density is calculated to be approximately $5 \times 10^{16} \text{ cm}^{-3}$, and the resistivity is about 1 ohm-cm, compared to the 3 to 6 ohm-cm value claimed by the supplier. The intercept of the linear region of the curve gives a flatband potential of -0.12 volts vs Ag/Ag^+ in acetonitrile.

FIGURE 4. MOTT-SCHOTTKY PLOTS
FOR SILICON ELECTRODES

The curve for an unetched, n-type silicon sample is delineated by the triangular symbols. The difference in slope of Curve a is believed to be due to an oxide layer on the silicon surface. Extrapolation of this curve gives a flatband potential of -0.52 volts vs the Ag/Ag^+ reference half-cell.

When a silicon electrode is polished to introduce surface defects prior to measurement, as discussed previously, its differential capacitance is similar to that of a metal, and it is essentially constant as a function of applied potential. We observe, however, that when a previously polished and unetched silicon electrode was polarized to potentials positive enough for electrochemical "etching" to occur, its differential capacitance varied with changing potential, and was similar to that of an electrode chemically etched in HF. This observation is shown by the circle symbols in Figure 4. This "Mott-Schottky" plot (Curve c) has a slope identical to that of the etched electrode, and the intercept yields a flatband potential of +0.18 volts vs the Ag/Ag^+ reference. Again, it appears that the in situ conditioning process has resulted in an improvement in the performance characteristics of the electrode.

As a result of these and other experiments⁽²⁾, the flatband potential for silicon is placed between ± 0.2 volts vs an Ag/Ag^+ reference half-cell in an acetonitrile solution with tetrabutylammonium fluoborate supporting electrolyte.

Task 2.3: Determination of Degradation Mechanisms

During the electrochemical and physical characterizations of the electrode materials and cells, several important observations were made which relate to degradation or modification of electrodes and redox additives. These observations are summarized briefly below.

First, it has been found that at sufficiently high positive potentials, a reaction between the supporting electrolyte (tetrabutyl ammonium fluoborate) and the photoelectrode (n-silicon) can occur, which

may be beneficial, as discussed later. The result of this reaction is an etching of the surface, and a modification of the electrochemical behavior. This etching reaction is not associated with residual water content in the solvent. Experiments with as-received and dried acetonitrile solvent gave identical results, showing that the as-received solvent is adequate for the electrochemical studies.

Second, experiments with a redox couple of interest (ferrocene/ferricenium) showed that in acetonitrile solvent, the ferricenium ion had a limited stability, and degradation could be observed in a matter of several hours from the shape of the visible spectra obtained. In propylene carbonate solvent, the rate of degradation is less, but a brown precipitate still forms, and the color of the solution changes, whether it is illuminated or held in the dark.

No reference to the stability of the ferrocene/ferricenium redox couple in organic solvent systems has been found in the literature. The performance of n-silicon based cells incorporating this redox couple has been described⁽⁶⁾, and relatively poor optical-to-electrical energy conversion efficiencies have been obtained. Values, 1 to 4 percent are typical for low intensity, monochromatic illumination with a He-Ne laser (623.8 nm). In terms of solar-to-electrical energy conversion, the corresponding efficiencies would be much smaller.

DISCUSSION OF RESULTS

Interpretations of the nature of the photoelectrochemical etching process at silicon electrodes in organic solvents must be at present largely speculative. As mentioned earlier, the process may involve removal of residual SiO_2 , or other adsorbed or bonded oxygen; or it may involve removal of silicon; or both. If the process involves etching the roughened silicon surface, it might either tend to smooth the surface or it might tend to accentuate the irregularities; both types of etching are of course well known for silicon, and either could result in improved surface-electrolyte charge transfer. The [111] face of vacuum-cleaved silicon is copiously supplied with surface states⁽⁷⁾, mainly lying below the valence-band edge,

but extending into the lower part of the gap. These states include a small number of highly active states associated with dangling bonds at fracture steps, and a larger number associated with dangling bonds of terrace atoms. A monolayer of adsorbed oxygen eliminates all states of the former type and about 90 percent of the latter⁽⁸⁾. Some similar states, probably modified by the presence of a polar electrolyte, might occur on the photoelectrochemically etched surface, and might be involved in the reduction of hole transfer to the ferrocene by the often suggested⁽⁹⁾ (if seldom demonstrated) mechanism of improving the match between the hole injection level and the ferrocene density of available fluctuation states.

A polishing etch could provide increased numbers of states of the terrace-atom type through removal of residual isolated oxygen atoms, but it is difficult to see what the value of the coarse grinding of the surface could be. A selective etch might produce surface states associated with step-edge atoms or it might yield states associated with the surfaces of newly revealed planes. It is not known to what extent such dangling-bond surface states are related to the surface band bending at the semiconductor-vacuum interface. It seems certain, though, that this bending will be modified at the semiconductor-electrolyte interface by the formation of the Helmholtz layer. If the degree of bending is reduced, a greater proportion of the surface states are liable to find themselves in the gap.

Another possibility that should not be overlooked is that sites are produced on the silicon surface that are capable of forming some kind of bonds to the ferrocene. It appears⁽¹⁰⁾ that when silicon is cleaved within the photoelectrochemical cell, ferrocene may bond to the exposed surface without the necessity of providing bridging groups⁽¹¹⁾, and it is easy to imagine something similar could occur on surfaces revealed by photoelectrochemical etching. The bonded ferrocene provides an effective medium for charge transfer to other ferrocene ions in solution⁽¹¹⁾.

Whatever the mechanism responsible for the reaction at relatively large positive potentials, the resulting change in electrochemical behavior of the n-silicon electrode may have practical significance. In a practical silicon-based electrochemical photovoltaic cell it could be postulated that

degradation could occur because of parasitic reactions between the silicon and residual water, or water vapor and/or oxygen from air that might be present in the cell. The resulting surface oxide layer could be removed by periodically pulsing the n-silicon photoelectrode in the anodic direction to accomplish the in situ "etching" phenomenon. The useful life of such cells could be extended if this "reconditioning" technique proved to be feasible.

The development of an efficient and stable silicon-based, electrochemical photovoltaic cell is not trivial. However, silicon is attractive because of its availability, and potential for low cost production. It is obvious that its photoelectrochemical behavior, particularly in non-aqueous solvents, is not well characterized, thus further study is warranted. As a better understanding is obtained it will become more obvious whether silicon-based cells incorporating aprotic, organic solvents will provide a viable alternative to some of the other types of aqueous cells being developed elsewhere.

FUTURE WORK

Additional ohmic contacts are being prepared for single crystal, n-silicon photoelectrodes to be used for further electrochemical characterizations of solvent/supporting electrolyte/redox additive combinations. The initial results with the cuprous/cupric redox couples were sufficiently encouraging to warrant further study. Other metallic redox couples will be investigated. Several cerium salts have been found to be freely soluble in acetonitrile and propylene carbonate and the study of their electrochemical behavior has been initiated. Also solubility studies of mercury, europium, ytterbium, cobalt, and chromium salts in the solvents of interest are under way, and will be completed in the next reporting period.

The changes in behavior resulting from using propylene carbonate as a solvent, rather than acetonitrile will be observed. We plan to investigate further the photoelectrochemical etching of n-silicon electrodes,

and try to establish some working hypothesis to explain the phenomenon. We may also try etching n-silicon with some defect exposing etchants, which may give similar reactive surfaces, comparable possibly to the matte finish that has been used with gallium arsenide electrodes. Electrochemical characterizations in both acetonitrile and propylene carbonate solvents then will be made for comparison with data already obtained.

Ohmic contacts for single crystal, p-silicon electrodes are being prepared also. The surfaces of these electrodes have been subjected to different preparation techniques. These contacts will be evaluated as before by the mercury diode method, and the results obtained, along with those already reported will help provide a better understanding of the effects of surface condition on subsequent performance in electrochemical photovoltaic cells. Correlation with the results of differential capacitance measurements will also be attempted.

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