A Photoelectrochemical Solar Cell

An Undergraduate Experiment

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The beginning student's enthusiasm for chemistry can often be sparked by a creative, applicable laboratory session. Recently, we introduced a solar cell laboratory experiment in our environmental chemistry course to illustrate solid state semiconductor and electrochemical principles. The preparation and testing of a cadmium selenide photoelectrochemical solar cell (PEC), can be accomplished in a 3-4 hr laboratory session with readily available chemicals and instrumentation. Although there is some "art" in preparing thin films by chemical bath and plating techniques, very respectable cells can be produced using uncontrolled electroplating and a post deposition annealing in air.

Photoelectrochemistry is an interdisciplinary pursuit, drawing from both electrochemistry and solid state physics. It owes its existence to the fact that semiconductors form rectifying junctions with liquid electrolytes that are analogous to the solid state solar cells (7). In a regenerative photoelectrochemical cell, the semiconductor photodiode is connected through an external circuit, typically to a metallic counter electrode. Both are immersed in an electrolyte containing a dissolved redox couple (e.g., Fe(CN)₆⁻³/⁴⁻). Light absorbed by the photodiode (i.e., of energy greater than its band gap) produces minority carriers in the junction region which are drawn to the surface by the built-in field. The minority carriers are electrons for p-type semiconductors and holes for n-type semiconductors. The redox couple is chosen to have favorable thermodynamics and kinetics to react with the minority carriers and to suppress the electrolytic decomposition of the semiconductor itself. The majority carriers flow through the external circuit to the counter electrode, where they effect an oxidation or reduction reaction. If the redox couple were Fe(CN)₆⁻³/⁴⁻, oxidation of ferro to ferricyanide would occur at one electrode, while the reduction of ferrocyanide to ferricyanide would occur at the other. The maximum open circuit voltage, Vₒ, of the cell under illumination is given by the difference between the reversible potential of the redox reaction, assumed by the metal electrode, and the magnitude of the voltage drop within the bulk of the semiconductor. The latter may be strictly determined by the difference in work functions between the isolated semiconductor and the electrolyte. However, it is also known to be a strong function of the degree of charge acceptance by the semiconductor surface, either by specific adsorbance of ionic species from solution, or by electron donor/acceptor sites associated with semiconductor lattice defects or impurities known as "surface states."

The Cadmium Selenide-Aqueous Polysulfide Photoelectrochemical Cell

A photoelectrochemical solar cell generally considered to exemplify the promise of these devices is that employing CdSe as the photoelectrode, in combination with an alkaline aqueous Sₓ₋₁²⁻, Sₓ²⁻ redox electrolyte. Since CdSe is an n-type semiconductor, the minority carriers sweep to the interface on irradiation are holes, and the photoelectrode electrolyte reaction is oxidation of Sₓ₋₁²⁻ to Sₓ²⁻. The reverse reaction occurs at the counter electrode, ideally aided by a metal sulfide electrocatalyst such as CuS or CoS (2). CdS has an absorption edge determined by its band gap of 1.8 eV, slightly larger than the optimum 1.5 eV for a solar cell. Because of this and the fact that it cannot be doped p-type to form a p,n-junction, this material has not been of great interest for solid state solar cell development. Conversely, because of the apparent long-term stabilization of CdSe photoanodes against dissolution by aqueous polysulfide electrolytes, CdSe photoelectrochemical cells have been frequently studied. Of particular interest have been the effects of CdSe preparation and polycrystallinity on the conversion efficiency of light to electrical energy in these cells. Some of the more recent results are summarized in the table.

A particularly important conclusion from the data in the table is that photoelectrochemical cells employing polycrystalline CdSe are almost as efficient as the best single crystaline device. In thin-film cells, the electrodeposited CdSe performs as well as vacuum-deposited material, even though the latter has a much more homogeneous morphology when viewed under the scanning electron microscope. This morphology-independent behavior may be related to the intimacy of the liquid-solid junction. In addition, pinholes in the films are not very effective in short circuiting photoelectrochemical cells compared to solid state cells with metallic current collectors on the top surface.

Experimental

Materials
Cadmium, titanium, and brass foils
Solid state silicon solar cell for reference
Kodak side projector for light source
Milliammeter
Decade resistance box
Alligator clips and wires
Muffle furnace
Polysulfide electrolyte (1 M NaOH, 1 M Na₂S, 1 M S₈)
Cadmium sulfate 0.10 M
Selenium dioxide 0.03 M
Chromic acid cleaning solution

Preparation of the CdSe Photoelectrochemical Solar Cell

A substrate electrode cut from titanium foil (1.5 x 4.0 cm) is degreased with chromic acid, rinsed with distilled water, accurately weighed, and suspended in a CdSO₄/SO₂ electrolyte (20.00 ml of 0.10 M CdSO₄, 0.4 ml of 0.03 M SeO₂, and 5.00 ml of 1.0 N H₂SO₄). A counter electrode is cut from cadmium foil (1.5 x 4.0 cm), suspended in the electrolyte, and externally shorted to the titanium substrate using a wire with alligator clip contacts. Half reactions involved in the electrodeposition include:

\[ \text{Cd}^{2+} + 2e^- \rightarrow \text{Cd} \]
\[ \text{H}_2\text{SeO}_3 + 4H^+ + 4e^- \rightarrow \text{Se} + 3H_2O \]

The solution is stirred 40-60 min to allow adequate plating of the CdSe thin film on the titanium electrode. Increased plating time leads to thicker, better performing films. During plating, color interference
hends similar to those seen in soap bubbles form due to the varying thickness of the thin films. Final deposits are silver-gray or black in color. After plating, the titanium electrode is removed from the electrolyte, quickly rinsed with distilled water and annealed for 15 min in air in a muffle furnace set at 550°C. Upon cooling, the electrode is acid etched for approximately 3 s in 6 N HCl, followed by an immediate rinse in distilled water. The spent electrolyte is stored in bottles labeled “waste cadmium” for eventual commercial disposal or recovery.

**Measuring Solar Cell Efficiency**

A convenient light source which provides adequate illumination and simulation of the solar spectrum is a Kodak® Carousel projector lamp. The lamp’s intensity may be measured using a commercial silicon solar cell. The silicon cell is calibrated beforehand, on a clear day, using natural sunlight. At midday, the sunlight intensity may be assumed to be the solar constant (100 mW/cm² ± 20 mW/cm²), or may be measured using a pyranometer (if available). The short-circuit photocurrent of the silicon cell illuminated in full sunlight is measured, and this is related proportionately to the photocurrent obtained from the intensity of the projector lamp set at the distance and focus desired for later testing of the CdSe cell. The projector lamp’s intensity is, therefore, calculated from the equation:

$$\text{Lamp Intensity (mW/cm}^2) = \frac{\text{Photocurrent of Si cell illuminated by projector lamp}}{\text{Solar Intensity}} \times \frac{\text{Photocurrent of Si cell illuminated in full sunlight}}{\text{Area}}$$

The plated CdSe substrate serving as the photoelectrode is positioned in the transparent rectangular test cell containing a large brass strip counter electrode and the polysulfide electrolyte. The brass counter electrode acts through a thin layer of CdS which forms on its surface when immersed in polysulfide. The photoelectrode is connected directly through the milliammeter and decade resistance box to the counter electrode. It is fully illuminated by the lamp and photoelectric cell measurements of the resulting photocurrent are recorded as a function of different resistances placed on the cell. The position and focus of the projector light source should be the same as that calibrated earlier. Reactions involved in the PEC include:

$$S_2^{2-} + 2e^- \rightarrow S^{2-} + S_{2-}$$

$$xS + S_2^{2-} \rightarrow S_{x+1}^{2-}$$

**Results and Discussion**

Each student was responsible for electroplating her own CdSe thin film solar cell and collecting photoresponse data. Using Ohm’s Law, E = IR, individual current-voltage curves could be plotted from which solar power conversion efficiencies could be extracted. A typical plot is presented in Figure 1. The short circuit photocurrent, I_SC, is measured when no resistance is placed on the cell. The open circuit voltage, V_OC, corresponds to infinite resistance. The maximum solar power conversion efficiency, P_MAX, lies at some intermediate circuit load as indicated. The ratio of P_MAX to the product of I_SC and V_OC is often referred to as the “fill factor.” For a perfect solar cell this factor approaches one. The efficiency of the student’s solar cell is calculated from the relationship:

$$\text{Efficiency of PEC} = \frac{P_{\text{max}} \text{(mW)}}{\text{Lamp intensity (mW/cm}^2) \times \frac{\text{Area of CdSe deposit (cm}^2)}{100\%}}$$

**Best Reported Performances of Photoelectrochemical Cells**

<table>
<thead>
<tr>
<th>Cadmium Crystalline Form</th>
<th>Solar Intensity (mW/cm²)</th>
<th>V_OC (V)</th>
<th>I_SC (mA/cm²)</th>
<th>Efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Crystal, (111) Face</td>
<td>75</td>
<td>0.74</td>
<td>14</td>
<td>8.4</td>
<td>(3)</td>
</tr>
<tr>
<td>Pressed Ceramic Pellet</td>
<td>71</td>
<td>0.67</td>
<td>12</td>
<td>5.1</td>
<td>(4)</td>
</tr>
<tr>
<td>Electrodeposited on Ti</td>
<td>100</td>
<td>0.56</td>
<td>23.8</td>
<td>6.5</td>
<td>(5, 6)</td>
</tr>
<tr>
<td>Coevaporated Cd, Se on Ti</td>
<td>75</td>
<td>0.60</td>
<td>15.1</td>
<td>8.4</td>
<td>(7)</td>
</tr>
<tr>
<td>Spray Pyrolyzed on ITD</td>
<td>50</td>
<td>0.63</td>
<td>11.8</td>
<td>5.2</td>
<td>(8)</td>
</tr>
<tr>
<td>Chemical Bath</td>
<td>50</td>
<td>0.63</td>
<td>12.4</td>
<td>6.8</td>
<td>(9, 10)</td>
</tr>
<tr>
<td>Painted, Sintered</td>
<td>85</td>
<td>0.63</td>
<td>18.8</td>
<td>7.9</td>
<td>(11)</td>
</tr>
<tr>
<td>CdSe(100)</td>
<td>3300</td>
<td>0.63</td>
<td>20.0</td>
<td>10.2</td>
<td>(12)</td>
</tr>
<tr>
<td>CdSe(111)</td>
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</tr>
</tbody>
</table>

*a Based on CdSe and aqueous polysulfide electrolytes under solar or simulated solar radiation. All results are for the isolated photoelectrode and do not contain effects of counter electrode polarization and resistive losses.

The film thickness can be determined by a weighing of the plated substrate, calculating the surface area of the deposit, and applying the literature value for the density of CdSe.

This experiment has been favorably received by students. Typical laboratory write-ups include current-voltage plots, solar cell efficiencies, a discussion of the redox chemistry involved, and a comparison of class solar cell efficiencies as a function of thin film thickness.

**Literature Cited**