Electrosynthesis and corrosion studies on cadmium selenide

Kehar Singh & Rajesh Kumar Pathak
Department of Chemistry, Gorakhpur University, Gorakhpur (U.P.) 273 009 (India)
Received 3 December 1990; revised and accepted 21 March 1991

Electrosynthesis of cadmium selenide films from cadmium sulphate-selenium dioxide solution under different deposition potentials using titanium supports has been carried out. Current-voltage characteristics of electrodeposits have been investigated to obtain Tafel plots so as to estimate exchange current density and corrosion rates in cadmium acetate solutions of different concentrations with and without I_2/I^- redox couple. Effect of surface active cetylpyridinium chloride on corrosion characteristics has also been studied.

Cadmium selenide is a material of immense interest for capture and conversion of solar energy into other useful forms. Its band gap is 1.5 eV and it is eminently suitable for fabrication of photo-electrochemical systems endowed with reasonably high conversion efficiencies. Cadmium selenide single crystals have indeed been used to demonstrate the occurrence of efficient photoelectrochemical transformations \( \eta = 9.8\% \). Electrochemical codeposition has emerged as a simple and cost effective technique for the formation of polycrystalline cadmium selenide films. We have carried out electrosynthesis of cadmium selenide films using different deposition potentials and estimated corrosion rates by studying their current-voltage characteristics using cadmium acetate solutions of different concentrations with and without I_2/I^- redox couple. The suitability of this electrolytic system for photoelectrochemical studies involving cadmium selenide has recently been demonstrated. Attempt has also been made to explore possibilities of corrosion inhibition when surface-active cetylpyridinium chloride is added to the testing electrolytic system.

Materials and Methods
Electrosynthesis of cadmium selenide films was carried out as reported elsewhere using a three electrode set up. Electroplating solution consisted of a mixture of 0.1 M cadmium sulphate and 0.01 M selenium dioxide at pH 3. Titanium and platinum foils were used as the working and the counter-electrodes respectively. Potential of the working electrode was kept at a desired value using standard potentiostat (DB Electronics, Pune, model 1078) and the current flowing between the working and the counter-electrodes was estimated by means of a digital multimeter (HIL 2161). Analytical grade reagents were dissolved in doubly distilled water for the preparation of solutions.

Current-voltage studies were carried out using an electrochemical measurement system (EG & G PARC, USA, model 378) consisting of a potentiostat/galvanostat Model 273 and an IBM compatible Personal Computer XT.

Results and Discussion
For electrochemical codeposition to occur, it is essential that the deposition potential of the species undergoing discharge be brought to identical values. This is often done by adjustment of ionic activities. If the discharge potentials differ appreciably, electrochemical codeposition can be accomplished at potentials higher than the discharge potential of the more electropositive species. The formation of cadmium selenide may, in principle, be accomplished over a range of deposition potentials. Current-voltage data may be used to identify the optimal range. Such data for 0.1 M CdSO_4 and 0.01 M SeO_2 solutions are shown in Fig. 1. Cathodic reactions are seen to commence at \( E = -0.45 \) V vs SCE.

Cadmium selenide formation occurs through the reaction

\[
\text{Cd}^{2+} + \text{Se}^0 + 2e \rightarrow \text{CdSe}
\]  

Obviously, this is possible beyond \(-0.45\) V vs SCE till \( E = -0.75 \) V vs SCE. At more negative potentials water splitting also commences and hydrogen is formed on the surface as a result of which good quality deposit is not possible. Hence, it is preferred to operate below \( E = -0.75 \) V vs SCE. We have explored the possibility of cadmium selenide formation using deposition potentials equal to \(-0.50\) V, \(-0.60\) V, and \(-0.70\) V vs SCE.
During electrodeposition the current initially declines rapidly and approaches a time invariant value as shown for a typical case in Fig. 2. These data were used to estimate thickness, \( I \), of the deposited cadmium selenide using the relationship,

\[
I = \frac{Q \cdot E \cdot W}{FA^2 \cdot d}
\]

where,

\( Q \) = charge in coulombs, \( E \cdot W \) = equivalent weight of electroactive material, \( A \) = area of the electrode, \( d \) = density of deposited material and \( F \) = the Faraday.

For the estimation of \( Q \), area under the \( E \) vs \( t \) curve (Fig. 2) was determined extending the steady current till 60 min, the time period for which deposition was allowed. Film thickness values along with the experimental conditions under which electrodeposition was carried out are summarized in Table 1.

For investigating corrosion characteristics of electrodeposited cadmium selenide films, electrochemical system (A) was used.

\[
\text{CdSe} \left( \text{CH}_3\text{COO} \right)_2 \text{Cd or} \left( \text{CH}_3\text{COO} \right)_2 \text{Cd} + \text{I}_2/\text{I}_3 \right] \text{Pt} \quad (A)
\]

Potential of the cadmium selenide electrode with respect to reference electrode was varied and corresponding current flowing between the working and the auxiliary platinum electrodes measured to obtain Tafel plots. A typical Tafel plot obtained by polarizing the working electrode anodically and cathodically is shown in Fig. 3 along with other relevant parameters.

---

**Fig. 1**—Current-voltage behaviour in 0.1 \( M \) CdSO\(_4\) and 0.01 \( M \) SeO\(_2\) solution [scan rate = 10 mV/sec]

**Fig. 2**—Variation of current with time during electrodeposition
[Electroplating solution = 0.1 \( M \) CdSO\(_4\) + 0.01 \( M \) SeO\(_2\); deposition potential = -0.700 V vs. SCE]

**Fig. 3**—Tafel plot obtained with cadmium selenide electrodeposited prepared using deposition potential = -0.600 V vs. SCE.
Scan rate = 5 mV sec\(^{-1}\)

---

**Table 1**—Deposition conditions and film thickness values
[Electroplating solution = 0.01 \( M \) CdSO\(_4\) + 0.01 \( M \) SeO\(_2\)]

<table>
<thead>
<tr>
<th>Deposition potential (V vs SCE)</th>
<th>Deposition current</th>
<th>Deposition time (min)</th>
<th>Film thickness (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.50</td>
<td>1.900</td>
<td>0.350</td>
<td>60</td>
</tr>
<tr>
<td>-0.60</td>
<td>2.100</td>
<td>0.600</td>
<td>60</td>
</tr>
<tr>
<td>-0.70</td>
<td>2.300</td>
<td>0.500</td>
<td>60</td>
</tr>
</tbody>
</table>
The anodic and the cathodic Tafel plots are described by the equation:
\[ \eta = B \log \frac{i}{i_{corr}} \]  
\[ \eta = \text{overvoltage, } B = \text{Tafel constant; } i = \text{current at the voltage and } \eta_{corr} = \text{corrosion current.} \]
From equation (3) it follows that when \( \eta = 0 \), \( i = i_{corr} \). When no external potential is applied, i.e., \( \eta = 0 \), the open circuit potential is called corrosion potential, \( E_{corr} \). The Tafel constants \( B_A \) and \( B_C \) estimated from anodic and cathodic portions of Tafel plots along with \( E_{corr} \) and \( i_{corr} \) values for cadmium selenide films obtained using different deposition potentials are summarized in Table 2.

The values of \( B_A \), \( B_C \), \( E(i=0) \) and \( i_{corr} \) were obtained from Tafel plots using Paralac data analysis technique. It assigns weight to each data point. The weighting method used is mathematically written as:
\[ X^2 = \frac{1}{N-4} \sum (i_k - f[E_k, E(i=0), B_A, B_C, i_{corr}])^2/s_k^2 \]  
where, \( N \) = the number in the series, \( N \) = the number of data points, \( k \) = the current at the \( k \)th data point, \( f = \) the function that is being fit, \( E_k \) = the potential at the \( k \)th data point and \( s_k \) = the estimated standard deviation of the current measured at the \( k \)th point.

The above equation states that \( X^2 \) is an average value of the square of the relative standard deviation, averaged over all the data points considered. \( X^2 = 0 \) indicates perfect fit. A value as high as 50 is not unusual and indicates an acceptable degree of deviation.

Electrochemically, estimation of corrosion rate is based on a knowledge of corrosion current. The corrosion current is related to the weight of the electroactive material as,
\[ W = i_{corr} \cdot t \cdot (E \cdot w)/F \]  
so that, corrosion rate (g/sec) = \( W/t \)
\[ = \frac{i_{corr}(E \cdot W)}{F} \]  
where \( W = \text{weight of the electroactive material, } t = \text{time, } F = \text{the Faraday and } E \cdot W = \text{equivalent weight of the electroactive material.} \]
Equation (6) may alternatively be written as:
\[ \text{Corrosion rate (cm/sec) = } \frac{i_{corr}(E \cdot W)}{F \cdot d \cdot A} \]  
where \( A \) is the cross-sectional area of the corroding species and \( d \), its density. More commonly, corrosion rate expressed in milli inches per year (mpy) is expressed as,
\[ \text{Corrosion rate (mpy) = } 0.13 \frac{i_{corr}(E \cdot W)}{d} \]  
The metric and time conversion factor is 0.13. Equation (8) has been used for the estimation of corrosion rates (Table 2) using corrosion current values obtained from Tafel plots. Corrosion rates of cadmium selenide electrodeposits obtained using different deposition potentials are given in Table 2. Their values for cadmium acetate solutions of different concentrations are included in Fig. 4.

An examination of the results presented in Table 2 clearly shows that the corrosion rate value increases when \( \text{I}_2/\text{I}_3^- \) redox couple is used along with cadmium acetate. Corrosion of cadmium selenide is known to occur as:
\[ \text{CdSe} + 2h^+ \rightarrow \text{Cd}^{2+} + \text{Se}^0 \]  
In the presence of the \( \text{I}_2/\text{I}_3^- \) redox couple, observed additional corrosion may occur due to the reaction.

| Table 2 — Tafel constants \( (B_A \) and \( B_C \)), and corrosion parameters for CdSe/0.1 M CdSO\(_4 \)+ 0.01 M SeO\(_2 \) system |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Potential = -0.5 V vs SCE | Potential = -0.6 V vs SCE | Potential = -0.7 V vs SCE |
| \( B_A \) (mV) | Solution I | Solution II | Solution I | Solution II | Solution I | Solution II |
| 198.20 | 153.15 | 240.84 | 370.02 | 96.1 | 209.37 |
| \( B_C \) (mV) | 169.95 | 285.17 | 170.08 | 176.07 | 103.95 | 327.63 |
| \( E_{corr} \) (mV) | 2.28 | 331.35 | -0.56 | 180.05 | -366.63 | 168.36 |
| \( i_{corr} \) (\( \mu A/cm^2 \)) | 0.08 | 0.44 | 0.76 | 1.58 | 1.38 | 1.53 |
| Corrosion rate (mpy) | 0.1610 | 0.9096 | 1.5742 | 3.2951 | 2.8768 | 3.1809 |

Solution I = 1 M (CH\(_3\)COO)\(_2\)Cd; pH = 6
Solution II = 1 M (CH\(_3\)COO)\(_2\)Cd + 0.1 M KI + 0.5 M Ml\(_2\); pH = 6
mpy = milli inches per year
CdSe + 2I⁻ → CdI₂ + Se⁰ + 2e  \[\text{Eq. 10}\]

It is worth noting that the corrosion rates are lowest with cadmium selenide formed at deposition potential of 0.50V vs SCE. It appears that with increase in potential, electrodeposits endowed with increased surface roughness and enhanced susceptibility to corrosion are formed.

The cadmium selenide corrosion rate also depends on the concentration of cadmium acetate solution; it decreases with concentration and is lowest at 0.80 M. This is expected because of possibility of suppression of the corrosion (Eq. 9) when Cd²⁺ concentration is increased. Increase in corrosion rate when 1 M cadmium acetate solution is used is somewhat intriguing.

Surface active species present in an electrolyte solution are known to accumulate in the interfacial region as a result of which ability of an electrode to withstand corrosion is expected to improve. With this objective in mind, polarization resistance measurements using different concentrations of cetylpyridinium chloride were carried out for the estimation of corrosion rates. A typical polarization curve is shown in Fig. 5. Polarization resistance, \(R_p\), is defined as,

\[R_p = \frac{\Delta E}{\Delta i}\]  \[\text{Eq. 11}\]

where \(\Delta E/\Delta i\) is the slope of the linear region of \(E\) vs \(i\) curve. Stern and Geary have deduced the follow-
dowed with somewhat pronounced corrosion (Table 2). Contrary to expected lowering of corrosion rate, it increased in the presence of the surfactant, progressively increasing with increase in surfactant concentration. Such anomalous corrosion behaviour in the presence of Cl⁻ ions has been observed by some workers 12.

Acknowledgement

The authors are grateful to the Head, Chemistry Department, Gorakhpur University, Gorakhpur for research facilities under the UGC COSIST Programme and financial assistance to one of them (RKP).

References