Electrodeposition of Cobalt Selenide Thin Films: An Electrochemical Quartz Crystal Microgravimetry Study

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The mechanism of electrodeposition of cobalt selenide (CoSe) thin films was investigated by the combined application of linear sweep voltammetry (LSV) and electrochemical quartz crystal microgravimetry (EQCM) on Pt-coated quartz electrodes. Cobalt selenide films were electrodeposited on the Pt surface from 0.1 M Na2SO4 electrolyte solution containing 5 mM SeO2 and 5 mM Co(CH3COO)2 by linear sweep voltammetry. Four cathodic waves were observed during the linear scans and the reactions corresponding to these waves were investigated with LSV and EQCM. Combined stripping voltammetry and EQCM showed that CoSe was electrodeposited via two routes: (1) Underpotential deposition of Se followed by deposition of cobalt as CoSe; and (2) Reaction of Co(II) with electrogenerated Se(−II) to result in CoSe. Compositional analyses revealed that the electrodeposited films contained CoSe and free Se, depending on the deposition potential. However, no cobalt was found in these films because of chemical (galvanic) instability of the cobalt film in the deposition bath.

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Transition metal chalcogenides, comprised of earth-abundant elements, have served as effective alternatives for expensive, noble metal catalysts for the hydrogen evolution reaction (HER), and the oxygen evolution reaction (OER). Especially, cobalt selenides have attracted much attention due to their favorable attributes such as good electrical conductivity, optimal band gap (~1.5 eV) in terms of match with the solar spectrum, and a high optical absorption coefficient. Thus they have been used as counter electrodes in photoelectrochemical cells and in dye-sensitized solar cells, as electrocatalysts for HER1–8 and OER, as anode material in lithium-ion batteries, and as a visible-light absorber in photovoltaic solar cells.10

The phase diagram of the Co-Se system11 reveals two homogeneous and stable compounds at room temperature: CoSe2 and CoSe. Two other possible compositions (Co3O4 and Co2Se3) have not yet been conclusively established.11 Cobalt selenides have been synthesized by several routes including chemical bath deposition,12,13 solvothermal method,14 mechanical alloying,15 and electrodeposition.2,4,6,7,10,16 Of these variants, synthetic options, electrodeposition offers many advantages17 such as cost-effectiveness, simplicity, easy scale-up, the use of relatively mild conditions, and the fact that (volatile) organometallic chemicals are not needed (as in techniques such as molecular beam epitaxy and atomic layer deposition). In addition, the composition and structure of electrodeposited films can be controlled by controlling pH, electrolyte composition, or deposition potential.

In this work, we present a detailed study of the electrodeposition mechanism of cobalt selenide (CoSe) using combined linear sweep voltammetry and electrochemical quartz crystal microgravimetry (EQCM). We are only aware of one prior study on the electrodeposition mechanism for CoSe on fluorine-doped tin oxide (FTO) electrode using cyclic voltammetry.16 On the other hand, the addition of a complementary mass-change probe such as EQCM to a voltammetry-based study, offers considerable advantage in a mechanistic sense as we demonstrate below. Compositional analysis of the electrodeposited films using combined stripping voltammetry and EQCM, is finally demonstrated.

Experimental

Cobalt acetate tetrahydrate, selenium dioxide, and sodium sulfate were from Sigma-Aldrich, and used without further purification. For voltammetry and EQCM, an EG&G Princeton Applied Research 263A instrument equipped with Power Suite electrochemistry software, a Seiko EG&G model QCA 922 instrument and an oscillator module (QCA 922–10), was used. A single compartment, three-electrode cell setup was used for electrochemical experiments at room temperature and comprised of an AT-cut, Pt-coated quartz crystal (geometric area, 0.2 cm2) working electrode, a Pt counter electrode, and an Ag/AgCl/3 M NaCl reference electrode. All potentials below are quoted with respect to this reference electrode. For voltammetry, the potential scan rate was 20 mV/s. The cleanliness of the Pt working electrode surface was checked by cyclic voltammetry in 0.5 M H2SO4 by cycling potential between 0.8 V and −0.6 V until the voltammetric and EQCM frequency signals were stable. The electrolytes were degassed with high-purity nitrogen prior to the electrochemical measurements and nitrogen blanket was used during the measurements.

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 DISCOVER diffractometer with Cu Ka radiation source. Film morphology and composition were obtained on a field emission scanning electron microscope (JEOL Model 6700F) equipped with an energy-dispersive X-ray emission analysis (EDX) probe.

Results and Discussion

Figure 1 contains a linear sweep voltammetry (LSV) scan and corresponding frequency changes (as monitored by EQCM) of a Pt-coated quartz electrode in 0.1 M Na2SO4 electrolyte containing 5 mM SeO2 and 5 mM Co(CH3COO)2. The pH of the electrolyte was 2.4. The voltammogram clearly shows four cathodic waves at −0.53, −0.68, −0.81, and −0.89 V and substantial current flow beyond −1.3 V due to proton reduction (i.e., HER). During the cathodic scan, frequency decrease (mass increase) started at ~−0.4 V, coinciding with the first cathodic wave and continuing until ~−1.5 V. No frequency (i.e., mass) change was observed at the linear scans after ~−1.5 V. Unlike the cyclic voltammograms reported for the FTO electrode in LiCl solutions containing SeO2 and Co(CH3COO)2 by previous workers,16 Figure 1 shows a more complex wave morphology, which will be assigned and explained in detail below.

To probe reactions occurring at each cathodic wave in Figure 1, experiments were performed using combined linear sweep voltammetry and EQCM at the Pt electrode in electrolytes containing only selenium or cobalt species. Figure 2A shows an LSV scan and corresponding frequency changes for a Pt-EQCM electrode in 0.1 M Na2SO4 electrolyte containing 5 mM Co(CH3COO)2. The cathodic wave at ~−0.87 V can be assigned to cobalt deposition, which is consistent with the frequency decrease (mass gain). Comparison of this cathodic wave with Wave d in Figure 1 clearly revealed that Wave 207.241.231.81 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
Figure 1. Combined cathodic linear sweep voltammetry (LSV) (——) and electrochemical quartz crystal microgravimetry (EQCM) (- - - - -) scan for a Pt-coated quartz electrode in 0.1 M Na2SO4 electrolyte containing 5 mM SeO2 and 5 mM Co(CH3COO)2.

d stemmed from cobalt reduction. As shown in Figure 1, no further decrease in frequency was observed after \( \sim -1.5 \) V.

It is well known that the electrochemistry of selenium is complicated due to several factors including underpotential deposition, coupled chemical reactions, stepwise reduction of Se(IV) to Se(0) and to Se(-II) as well as the 6-electron pathway of Se(IV) to Se(-II). \(^{18}\)

Since Wave d in Figure 1 was found to be due to cobalt reduction, it is reasonable to attribute the other three Waves a–c to the electrochemistry of Se(IV). To assign these waves, linear sweep cathodic voltammetry was combined with EQCM at a Pt electrode using 0.1 M Na2SO4 containing only 10 mM SeO2. In Figure 2B, the first wave at \( \sim -0.57 \) V was associated with mass gain and the wave at \( \sim -0.82 \) V accompanied with mass decrease. As discussed in the literature, the wave at \( \sim -0.57 \) V is due to a combination of Reactions 1 and 2: \(^{18}\)

\[
\begin{align*}
    \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{e}^- &= \text{Se} + 3\text{H}_2\text{O} \quad [1] \\
    \text{H}_2\text{SeO}_3 + 6\text{H}^+ + 6\text{e}^- &= \text{H}_2\text{Se} + 3\text{H}_2\text{O} \quad [2]
\end{align*}
\]

Reaction 2 can be combined with the chemical Reaction 3 to result in Se(0) deposition, which is manifest from the frequency decrease during the wave at \( -0.57 \) V.

\[
2\text{H}_2\text{Se} + \text{H}_2\text{SeO}_3 = 3\text{Se} + 3\text{H}_2\text{O} \quad [3]
\]

Wave a in Figure 1 is now assigned to the deposition of Se(0) by Reaction 1 as well as Reaction 2 combined with Reaction 3. Another wave at \( \sim -0.82 \) V wave is due to the reduction of Se(0) to selenide via Reaction 4, which is manifest from the mass decrease and cathodic current:

\[
\text{Se} + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{Se} \quad [4]
\]

A slight mass increase was observed at \( \sim -1.2 \) V due to the Se(0) re-deposition via Reaction 3 and Reaction 4. At the end of a cathodic scan, the EQCM frequency does not return to the initial value, which implies incomplete stripping of Se(0). This trend is ascribed to the presence of Se(IV) in the electrolyte. When the electrolyte contained no Se(IV), complete stripping of Se was achieved at the end of a cathodic scan (see below). From the potential and frequency change, Wave c in Figure 1 is now assigned to the reduction of Se(0) to selenide. Another evidence that Wave c in Figure 1 is due to reduction of Se(0) is contained in Figure 2C.

The stripping voltammogram along with frequency change was obtained using a Se-modified electrode in 0.1 M Na2SO4 electrolyte containing 5 mM SeO2 and 5 mM Co(CH3COO)2. During the electrodeposition, a potential of \( -0.6 \) V was held until the EQCM frequency changed to \( \sim 700 \) Hz. The stripping peak at \( \sim -0.80 \) V accompanied with monotonic mass decrease can be assigned to the reduction of Se(0) to selenide. Unlike the scan in Figure 2B, the frequency returned to the initial value at the scan termination, diagnosing complete stripping of the electrodeposited selenium layers. [This contrast with the trend above.] Therefore, the waves at \( \sim -0.8 \) V in Figures 1 (wave c), 2B and 2C all originated from the electroreduction of selenium to selenide (Reaction 4).
measuring the number of electrons transferred (n). The n value is calculated from the slope of the charge-frequency plot by combining the Sauerbrey equation and Faraday’s law.22,23 The n value was found to be ~2, which corroborates the notion that the peak at ~−1.03 V is due to the electroreduction of CoSe to Co + Se2−.

In order to probe the origin of Wave b in Figure 1, a Pt electrode was modified with a CoSe film by scanning the electrode potential to −0.6 V in 0.1 M Na2SO4 electrolyte containing 5 mM Co(CH3COO)2 and 5 mM SeO2. Then, a LSV scan with EQCM was obtained at the Pt-EQCM electrode modified with cobalt selenide film in 0.1 M Na2SO4 containing 5 mM Co(CH3COO)2 (Figure 4A). As shown in the figure, a single major cathodic wave at ~−0.89 V was accompanied with monotonic mass increase, which pointed to cobalt deposition.

An interesting feature was observed in the voltammogram obtained at the same electrode in 0.1 M Na2SO4 containing 5 mM Se2O3 (Figure 4B). The voltammogram showed current increase with mass increase, unlike the voltammogram obtained with bare Pt electrode in 0.1 M Na2SO4 containing 10 mM SeO2 (Figure 2B). The cathodic wave at ~−0.68 V with mass decrease is clearly due to the reduction of newly-deposited selenium on the surface to selenide during the cathodic scan. This is manifest from the difference in stripping potential of selenium in Figure 2B (~−0.82 V, selenium to selenide) and in Figure 3A (~−1.03 V, cobalt selenide to cobalt and selenide). To enhance the wave prominence, selenium layers were deposited by applying ~−0.1 V at the cobalt selenide film-modified electrode in 0.1 M Na2SO4 containing 5 mM Se2O3. Selenium stripping in 0.1 M Na2SO4 blank electrolyte now resulted in an amplified wave signal at ~−0.63 V with mass decrease (Figure 4C). In other words, the waves at ~−0.68 V in Figure 4B and at ~−0.63 V in Figure 4C are both due to the reduction of selenium to selenide on the cobalt selenide film surface. The other waves at more negative potentials in Figure 4C are due to the electroreduction of free selenium to selenide and CoSe to Co + Se2−, respectively.

To further examine whether Wave b was due to the reduction of selenium on the Se or CoSe surface, a Se2-modified Pt electrode was prepared at ~−0.5 V in 0.1 M Na2SO4 containing 5 mM SeO2. Since the cobalt selenide films used in Figure 4 can be composed of free Se and CoSe, a CoSe-modified electrode was also prepared at ~−0.7 V in 0.1 M Na2SO4 electrolyte containing 5 mM Co(CH3COO)2 and 5 mM SeO2, followed by complete stripping of selenium at ~−0.8 V in 0.1 M Na2SO4 blank electrolyte. As shown in Figure 5A, Se reduction on the Se layers revealed two cathodic waves at ~−0.54 and ~−0.88 V due to Reactions 1 and 4, respectively, which are slightly different from Wave b in Figure 1.

The LSV scan morphology and frequency changes in Figure 5A are very similar to those in Figure 2B. Finally, another voltammogram accompanied with mass changes was obtained for the CoSe-modified electrode in 0.1 M Na2SO4 containing 5 mM SeO2 (Figure 5B). Current and mass increase from the beginning of the cathodic scan are very similar to the features in Figure 4B. In addition, one distinct wave at ~−0.64 V is well matched with Wave b in Figure 1, which clearly proved that this wave is assignable to reduction of newly-deposited selenium (to selenide) on the CoSe surface. Summarizing the data in Figures 2–5, Waves a, c, and d are attributable to reduction of Se(IV) to Se(II) and Co2+ to Co, respectively on the Pt surface, while Wave b arises from the further reduction of deposited Se(0) to Se(−II) on the CoSe surface.

**Electrodeposition Mechanism and Film Compositional Aspects**

As discussed earlier, Wave a in Figure 1 involves the underpotential deposition of selenium (Reaction 1). However, as in the case of many metal halogenides (e.g., CdSe), induced reduction of the metal ion, i.e., cobalt ions in this case, is also involved here resulting in the formation of cobalt selenide (Reaction 5):

\[
\text{Se} + \text{Co}^{2+} + 2\text{e}^- = \text{CoSe}
\]
Figure 4. Combined LSV-EQCM scans for the cobalt selenide film-modified Pt electrode in 0.1 M Na$_2$SO$_4$ containing (A) 5 mM Co(CH$_3$COO)$_2$ and (B) 5 mM SeO$_2$. (C) The same trace was obtained for the Se-deposited cobalt selenide films in 0.1 M Na$_2$SO$_4$ electrolyte. Selenium layers were deposited on the cobalt selenide films by applying $-0.1$ V in 0.1 M Na$_2$SO$_4$ electrolyte containing 5 mM SeO$_2$.

The reduction current in 0.1 M Na$_2$SO$_4$ containing 5 mM Co(CH$_3$COO)$_2$ and 5 mM SeO$_2$ was larger than that in 0.1 M Na$_2$SO$_4$ electrolyte containing 5 mM SeO$_2$, pointing to the involvement of cobalt reduction via Reaction 5 and/or Reaction 6:

$$\text{H}_2\text{SeO}_3 + \text{Co}^{2+} + 4\text{H}^+ + 6e^- = \text{CoSe} + 3\text{H}_2\text{O} \quad [6]$$

Electrodeposition at $-0.5$ V in 0.1 M Na$_2$SO$_4$ solutions containing 5 mM Co(CH$_3$COO)$_2$ and 5 mM SeO$_2$ (peak potential of wave a) resulted in films containing free selenium as well as cobalt selenide, even though the deposition potential was too positive for cobalt deposition. Clearly, underpotential deposition of Co is involved here, and is driven by the free energy of compound formation with the pre-deposited Se.

Figure 6A shows the composition of cobalt selenide films, electrodeposited at $-0.5$ V using 0.1 M Na$_2$SO$_4$ containing 5 mM Co(CH$_3$COO)$_2$ and 5 mM SeO$_2$. The combined LSV-EQCM data for the 0.1 M Na$_2$SO$_4$ blank electrolyte clearly demonstrated that electrodeposited CoSe films at $-0.5$ V contained free Se (wave at $\sim-0.78$ V) and CoSe (wave at $\sim-1.04$ V). At a deposition potential of $-0.7$ V (a potential beyond Waves b and c in Figure 1), CoSe was electrosynthesized with free selenium via Reactions 3 and 6. This was confirmed by reduction waves in the voltammogram with mass changes for the electrodeposited films in 0.1 M Na$_2$SO$_4$ blank electrolyte (Figure 6B). Two reduction waves at $\sim-0.72$ V and $\sim-1.03$ V are due to reductions of selenium to selenide and CoSe to Co$^+$ and Se$^{2-}$, respectively.

Interestingly enough, these electrodeposited cobalt selenide films contained no free cobalt regardless of the deposition potential as long as films were in touch with the deposition electrolyte for enough time. This trend is attributable to the instability of cobalt films in acidic electrolytes and the spontaneous corrosion of cobalt by more noble species such as Se(IV). Figure 7A shows the stability of cobalt films in contact with 0.1 M Na$_2$SO$_4$ electrolyte whose pH was adjusted to that of the electrodeposition solution case. As shown in the figure,
the electrodeposited cobalt film gradually dissolved and frequency returned to the original value within 5 min. On the other hand, when the cobalt film was in the electroplating solution, cobalt dissolution was complete in less than 3 min demonstrating the effect of Se(IV) species. Considering standard reduction potentials, Se(IV) can oxidize cobalt to Co$^{2+}$:

$$\text{Co}^{2+} + 2e^- = \text{Co} \quad E^o = -0.277\text{V}$$

$$\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4e^- = \text{Se} + 3\text{H}_2\text{O} \quad E^o = 0.739\text{V}$$

Therefore, cobalt films are more easily oxidized in the deposition solution than in a blank solution with the same pH.

In situ composition analysis of electrodeposited cobalt selenide films revealed that free cobalt was removed immediately after electrodeposition as shown in Figure 7B. In the figure, the initial mass gain was due to film deposition at $-0.7\text{V}$. After deposition, the film was in the deposition solution without applied bias potential (i.e., at open circuit) and spontaneous mass loss was observed for the reasons discussed above (see also Figure 7A). Next, the solution was changed to 0.1 M Na$_2$SO$_4$ blank electrolyte and free selenium was cathodically stripped at $-0.8\text{V}$, followed by the stripping of Se in CoSe and Co in CoSe at $-1.3\text{V}$ and $+2.0\text{V}$, respectively. The content of free Se in the electrosynthesized film was determined by the frequency changes at $-0.8\text{V}$. The EQCM frequency changes at $-1.3\text{V}$ (Se in CoSe, 900 Hz) and $+2.0\text{V}$ (700 Hz, Co in CoSe) were in good agreement with the atomic mass ratio (Co: Se = 1:1.3). Clearly, these electrodeposited films contained no free cobalt and the compound stoichiometry was close to 1:1 as expected for CoSe.

Figure 8 displays the XRD pattern obtained from the electrodeposited CoSe films on a SnO$_2$ coated glass substrate. One major peak at 31.94° clearly confirms the presence of CoSe. Other peaks are from the underlying FTO electrode support. No other peaks from metallic cobalt and selenium were observed.

Figure 9 contains a scanning electron micrograph of the electrodeposited CoSe film. The films were prepared by the procedure described in Figure 8. The as-deposited films showed a smooth and uniform surface with well-defined grain boundaries and the electrode surface was well covered with cobalt selenide films. The side view clearly showed well-distinguished layers comprising of the top CoSe layer, the (~700 nm), SnO$_2$ substrate layer, and the bottom glass support.

Conclusions

This study demonstrated the application of combined linear sweep voltammetry and electrochemical quartz crystal microgravimetry for studying the CoSe electrodeposition system. Electrodeposition involved selenium deposition first followed by the induced (underpotential) deposition of cobalt to result in the formation of CoSe. On the other hand, CoSe can also be electrodeposited by the reaction
Figure 8. XRD pattern for a CoSe film prepared on the FTO electrode. The film was electrosynthesized at $-0.7 \text{ V}$ for 20 min in 0.1 M Na$_2$SO$_4$ containing 5 mM Co(CH$_3$COO)$_2$ and 5 mM SeO$_2$.

Figure 9. SEM images of electrodeposited CoSe thin films. (A) top view and (B) side view. XRD pattern for a CoSe film prepared on the FTO electrode. The film was electrosynthesized by the procedure described in Figure 8.

of Co$^{2+}$ with electroreduced Se$^{2-}$ at more negative potentials. The electrochemical behavior of selenium on the Pt surface was different from that at the pre-deposited CoSe film surface. The electrodeposited cobalt selenide films contained no free cobalt due to its instability in acidic electrolytes and due to galvanic corrosion instigated by the more noble Se(IV) species. A method for in situ compositional analysis of electrosynthesized cobalt selenide films using combined stripping voltammetry and EQCM was finally demonstrated. A newly developed method for compositional analysis was elaborated.

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