Compositional Analysis of Electrodeposited Cobalt Selenide Thin Films Using Continuous Flow Electrochemical Quartz Crystal Microgravimetry

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In this study, the composition of electrochemically deposited cobalt selenide thin films was analyzed by electrochemical quartz crystal microgravimetry (EQCM) in a continuous flow mode. First, cobalt selenide films were electrodeposited on a Pt-EQCM electrode using a 0.1 M Na2SO4 electrolyte solution containing Co and Se precursor species at different potentials. A combination of sequential stripping and EQCM frequency monitoring protocol enabled mapping of the Co, free Se, and CoSe content of the electrodeposited films. It was found that the composition of cobalt selenide film was very sensitive to the electrodeposition potential. The targeted CoSe content was maximum at −0.7 V and the free Co content was minimum at this potential. On the other hand, the free Se content decreased from ~45% at −0.6 V to nearly 0% at −0.9 V. The film composition as established by the continuous flow analysis mode stood in stark contrast with the static (batch) mode where no free Co was observed in the films. Factors in these compositional differences as well as in the EQCM electrode geometry (face-down vs. face-up) are finally discussed.

The Co-Se compound system potentially offers a rich variety of compounds: CoSe, Co3Se4, Co2Se3, and CoS2; and stoichiometries progressing from 1:1 to 1:2, although the existence of the middle two compositions has not been conclusively established yet.1 Cobalt selenides have applicability as counter-electrodes in dye-sensitized solar cells,2,3 as electrocatalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER),4,5,6 as anode material in lithium-ion batteries,6 as a glucose sensor.7 They have been synthesized by several routes including chemical bath deposition,8 solvothermal method,9 mechanical alloying,10 and electrodeposition.11,12 Among them, electrodeposition has multiple advantages14 including process simplicity, mild conditions in terms of synthesis temperature, and amenability to large area deposition. However, co-deposition or contamination of the target material (in this case, CoSe) with unwanted phases (for example, free Co and free Se) is often a problem with electrodeposition.1,14–16

On the other hand, this compositional variability handicap can be turned into an advantage in that properties and morphology that are dependent on the composition of electrodeposited thin films can be tuned for a given application. To cite one example, electrodeposited cobalt selenide films showed different catalytic activity as a counter electrode in DSSC depending on the Co:Se ratio in the films.13 Additionally, details of the electrodeposition mechanism can be deduced from the film composition electrochemically synthesized at specific deposition potentials or different electrolytes. Therefore, development of a facile in situ methodology for the compositional analysis is both fundamentally and practically important. Unlike spectroscopic methods that yield only total species content, the approach presented below is chemical-selective. In other words, the methodology presented below can differentiate between free Se, free Co and CoSe in the electrodeposited films based on the mass changes occurring during the stripping steps.

In this report, the feasibility of compositional analysis of cobalt selenide thin films electrodeposited at different potentials using a continuous flow-EQCM approach, is demonstrated. To our knowledge, the present study constitutes the first example of in situ compositional analysis of electrodeposited cobalt selenide thin films. A previous report described the composition of cobalt selenide films electrochemically synthesized at various potentials using energy-dispersive X-ray analysis or EDX.12 However, EDX yields only total species contents and differentiation of the CoSe content from any free Se and free Co deposited was not addressed. The flow-EQCM approach described below also has advantages over static or batch analysis counterparts such as complete control of potential during the change of electrolyte solution as well as during deposition and stripping. The EQCM technique, unlike the amperometric or coulometric procedures, is free from interferences of side reactions such as hydrogen evolution because this technique uses frequency (mass) changes rather than current as a response.

Experimental

The chemicals Co(CH3COO)2·H2O, SeO2, Na2SO4 were from Sigma-Aldrich, and used without further purification. An EG&G Princeton Applied Research 263A instrument equipped with PowerSuite electrochemistry software, a Seiko EG&G model QCA 917 instrument and an oscillator module (QCA 917-11), was used. A single compartment, three-electrode electrochemical cell setup was used for batch type (static) 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 a Ag/AgCl/3 M NaCl reference electrode. All potentials below are quoted with respect to this reference electrode. For voltammetry combined with microgravimetry in a static cell, the potential scan rate was 25 mV/s. The electrolytes were degassed with high-purity nitrogen prior to the electrochemical measurements and nitrogen blanket was used during the measurements.

Details of the continuous flow-EQCM setup are given elsewhere.16,17 Briefly, solution to the flow-EQCM system was delivered by a Gilson Minipuls 3 peristaltic pump at a nominal flow rate of 0.50 mL/min.

Results and Discussion

In the companion report,1 we presented study on the electrodeposition mechanism of cobalt selenide investigated by EQCM combined with voltammetry. Also, we reported that the electrodeposited films contained no free cobalt because of the instability of cobalt films in acidic electrolytes and the spontaneous oxidation of cobalt by the more noble Se(IV) species. These features render compositional analysis difficult by a static analysis approach. The data contained in Figure 1A demonstrate the instability of electrodeposited cobalt films in a stream of 0.1 M Na2SO4 blank electrolyte with pH of 2.4. After initial electrodeposition of cobalt at −0.9 V in 0.1 M Na2SO4 containing 10 mM of Co(CH3COO)2, the Co film was poissed in the blank electrolyte flow at open circuit potential. As shown in the figure,
the electrodeposited cobalt film in contact with acidic electrolyte was gradually corroded as evidenced by an increase of frequency, at times longer than ~100 s.

It was also found that electrodeposited cobalt films were not stable in electrolytes containing Se(IV) species due to the galvanic reaction. Voltammetry (data not shown) revealed that cobalt can be oxidized (stripped) even at a potential of 0.0 V, a potential of −0.80 V was found to be ~4.1 and ~2.2 during the deposition and stripping steps, respectively. The values clearly correspond to the following reactions for deposition and stripping of selenium:

Deposition: \[ \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{e}^- = \text{Se}^0 + 3\text{H}_2\text{O} \]  

Stripping: \[ \text{Se}^0 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{Se} \]

Figure 2 confirms that electrodeposited cobalt can be replaced with Se by a spontaneous galvanic reaction in electrolytes used for electrodeposition of cobalt selenide. Considering standard reduction potentials, Se(IV) can oxidize cobalt to \( \text{Co}^{2+} \):

\[ \text{Co}^{2+} + 2\text{e}^- = \text{Co} \quad E^\circ = -0.277 \text{ V} \]

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

Cobalt film was electrodeposited by the process as in Figure 1 and soaked in deposition solution (0.1 M Na$_2$SO$_4$ containing 5 mM of Co(CH$_3$COO)$_2$ and 5 mM SeO$_2$) to result in deposition of Se by the galvanic reaction. A voltammogram obtained with a static cell containing 0.1 M Na$_2$SO$_4$ blank electrolyte clearly revealed a cathodic peak at −0.80 V with frequency increase due to the reduction of Se to Se$^2^-$. Figure 3 demonstrates efficiency and applicability of continuous flow-EQCM over multiple cycles both for Se deposition/stripping (Figure 3A) and Co deposition/stripping (Figure 3B). After deposition of selenium at −0.5 V using flow of 0.1 M Na$_2$SO$_4$ electrolyte containing 10 mM SeO$_2$, complete stripping was achieved at −0.9 V in a 0.1 M Na$_2$SO$_4$ blank electrolyte by deploying the slider valve (Figure 3A). Charge and frequency were sampled during the deposition and stripping steps and the number of electrons transferred \( n \) was determined by the combining the Sauerbrey equation with Faraday’s law. For the calculation, the background charge and frequency were also sampled and subtracted from the values obtained during the deposition and stripping steps. Thus calculated \( n \) values were found to be ~4.1 and ~2.2 during the deposition and stripping steps, respectively. The values clearly correspond to the following reactions for deposition and stripping of selenium:

Deposition: \[ \text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{e}^- = \text{Se}^0 + 3\text{H}_2\text{O} \]

Stripping: \[ \text{Se}^0 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{Se} \]
Figure 3. EQCM frequency changes during the electrodeposition and stripping steps. (A) Selenium deposition at $-0.5 \text{ V}$ in a 0.1 M Na$_2$SO$_4$ solution containing 10 mM SeO$_2$ and stripping at $-0.9 \text{ V}$ in a 0.1 M Na$_2$SO$_4$ solution. (B) Cobalt deposition at $-0.9 \text{ V}$ in a 0.1 M Na$_2$SO$_4$ solution containing 10 mM Co(CH$_3$COO)$_2$ and stripping at $+2.0 \text{ V}$ in a 0.1 M Na$_2$SO$_4$ solution. Solution flow rate: 0.50 mL/min.

Figure 4. Combined linear cathodic sweep voltammetry (LSV) (black) and EQCM (red) scans in 0.1 M Na$_2$SO$_4$ solution (A) for as-electrodeposited cobalt selenide films and (B) for the same electrode as in panel (A) but after complete stripping of free Se at $-0.9 \text{ V}$ in a 0.1 M Na$_2$SO$_4$ solution. The cobalt selenide film was electrodeposited at $-0.7 \text{ V}$ in 0.1 M Na$_2$SO$_4$ containing 5 mM Co(CH$_3$COO)$_2$ and 5 mM SeO$_2$. Scan rate: 25 mV/s.

from the voltammogram, which implies that a potential of $-0.9 \text{ V}$ is enough for the determination of free Se (Figure 4B). Therefore, the data in Figure 4 facilitate the choice of potentials at $-0.9 \text{ V}$ and $-1.3 \text{ V}$ respectively for the complete stripping of free Se and Se in CoSe. The measured EQCM frequency change at $-1.3 \text{ V}$ was used for the determination of CoSe content in the films based on the assumption of 1:1 compound stoichiometry.

Figures 5 contains EQCM frequency changes during the electrodeposition and stripping stages carried out using continuous flow-EQCM at two different deposition potentials, (A) $-0.5 \text{ V}$ and (B) $-0.7 \text{ V}$. Compositional analysis of cobalt selenide films was based on the EQCM frequency changes during the stripping step at the designated potentials. First, cobalt selenide film was electrodeposited at the designated potentials in 0.1 M Na$_2$SO$_4$ containing 5 mM SeO$_2$ and 5 mM Co(CH$_3$COO)$_2$. The electrolyte was then changed to 0.1 M Na$_2$SO$_4$ blank under deposition potential control until frequency was stabilized. After deposition was complete, a stripping potential of $-0.9 \text{ V}$ was applied to the electrode and free Se was determined from the frequency change. After complete stripping of free Se (manifest from a constant frequency), a potential of $-1.3 \text{ V}$ was applied to the electrode for the reduction of Se in CoSe to Co + Se$^{2-}$ and the content of CoSe was determined based on the assumption of 1:1 CoSe stoichiometry. Finally, the total Co content (free Co and Co in CoSe) was determined from anodic stripping at $+2.0 \text{ V}$ and the content of free Co was determined from the difference in frequency changes between the contents of total Co and Co in CoSe. As shown in the figure, the frequency of the EQCM electrode returned to the initial value after application of $+2.0 \text{ V}$ to the electrode, which implied complete stripping of the electrodeposited material.

Closer inspection of the data in Figures 5 and 6 clearly reveal that compositions of cobalt selenide films are very sensitive to the deposition potential. For example, films electrosynthesized at $-0.5 \text{ V}$ contain $\approx 42$ (mass) % of free Se, $\approx 37\%$ of free Co and only $\approx 20\%$ of CoSe (Figure 6). However, films deposited at $-0.7 \text{ V}$ contain more than 80% of the target material, CoSe and only a few % of free Co. Table I and Figure 6 summarize compositional variations of electrodeposited films as a function of deposition potential in the $-0.5 \text{ V} \sim -0.9 \text{ V}$ range. All quantitative data were based on the frequency changes observed during the stripping step and reproducibility was checked by running five replicates (Table I).

Interestingly, the present results from continuous flow-EQCM approach contrast with previous results using the “batch” experiments$^1$ in which electrodeposited films contain no free cobalt regardless of deposition potential. In a batch process, cobalt selenide films are electrosynthesized at various potentials and the films were in the deposition solution without applied bias potential (i.e., at open circuit). Co-deposited free cobalt was removed immediately after electrodeposition due to the instability of cobalt films in acidic electrolytes and the spontaneous corrosion by more noble species such as Se(IV) (see Figure 1). However, in the flow approach, the deposition potential
Co(CH$_3$COO)$_2$ and 5 mM SeO$_2$. Composition of films were consecutively analyzed at −0.7 V for free Se, −0.8 V for CoSe and −0.9 V for total Co (free Co + Co in CoSe) in the flow of 0.1 M Na$_2$SO$_4$ blank electrolyte. Solution flow rate: 0.50 mL/min.

**Figure 5.** EQCM frequency (mass) changes during the electrodeposition and stripping steps. During the deposition step, (A) −0.5 V and (B) −0.7 V were applied to the EQCM electrode in 0.1 M Na$_2$SO$_4$ containing 5 mM Co(CH$_3$COO)$_2$ and 5 mM SeO$_2$. Composition of films were consecutively analyzed at −0.9 V for free Se, −1.3 V for CoSe and −2.0 V for total Co (free Co + Co in CoSe) in the flow of 0.1 M Na$_2$SO$_4$ blank electrolyte. Solution flow rate: 0.50 mL/min.

**Figure 6.** Composition (mass %) of Co-Se films electrodeposited at different potentials. Numbers in parentheses are standard deviations from five replicates.

| Deposition potential (V) | Free Se (mass %) | CoSe (mass %) | Free Co (mass %) |
|-------------------------|-----------------|---------------|-----------------|
| −0.5                    | 42.5 (±3.1)     | 19.8 (±1.3)   | 37.7 (±3.1)     |
| −0.6                    | 45.6 (±1.5)     | 28.8 (±0.6)   | 25.9 (±2.2)     |
| −0.7                    | 14.9 (±1.8)     | 83.0 (±1.0)   | 2.08 (±1.3)     |
| −0.8                    | 5.18 (±1.7)     | 76.4 (±0.2)   | 18.4 (±1.8)     |
| −0.9                    | 0               | 0             | 100             |

is held until deposition is complete and while switching to a 0.1 M Na$_2$SO$_4$ blank electrolyte. After that, stripping potentials were successively applied to the electrode in a blank electrolyte. Therefore, free Co, if any, can be maintained in the electrodeposited cobalt selenide films. The results in Figure 6 revealed that electrodeposited cobalt selenide films contain free cobalt regardless of deposition potential from −2.08% at −0.7 V to ∼100% at −0.9 V.

It is well known that CoSe can be electrodeposited in two routes.$^{1,12}$ The first route is via the deposition of selenium followed by the induced deposition of cobalt, Reaction 3. The second route is the reaction of electrogenerated Se$^{2-}$ with Co$^{2+}$, Reaction 4.

\[
\text{Se} + \text{Co}^{2+} + 2e^- = \text{CoSe}
\]  

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

At the deposition potentials of −0.5 V and −0.6 V, deposition of Se followed by the induced deposition of Co results in the formation of CoSe with free Co and free Se. This mechanism is well discussed in previous reports.$^{1,12}$ On the other hand, films deposited at −0.7 V and −0.8 V contained 83.0% and 76.4% of CoSe (Figure 6). Clearly, the combined effect of induced deposition and the reaction of electrogenerated Se$^{2-}$ with Co$^{2+}$ was beneficial in these cases. This trend is also in agreement with the observation that Se is more easily reduced on the CoSe surface than a Pt electrode.$^1$ Electrogeneration of Se$^{2-}$ on the CoSe at −0.7 V made possible the content of CoSe to be maximum at −0.7 V. At a more negative potential of −0.9 V, cobalt reduction was dominant and electrodeposited films contained ∼100% of cobalt (Figure 6).

Since electrogenerated Se$^{2-}$ plays an important role in the formation of CoSe, especially at −0.7 and −0.8 V, the effect of Se$^{2-}$ on the formation of CoSe was investigated using the EQCM working electrode oriented face down.$^{11}$ Figure 7 contains data for the compositional analysis of cobalt selenide films electrodeposited at −0.7 V with (A) a face down electrode and (B) a face up electrode at higher flow rate (2.5 mL/min.). As shown in Figure 7A, cobalt selenide film deposited with face-down geometry contains free Co and free Se with no CoSe. This result is strikingly different from the results with face-up geometry in which the film contains more than ∼80% of CoSe (see Table I and Figure 6). This is because the electrogenerated Se$^{2-}$ species were washed out before reaction with Co$^{3+}$ could proceed to a significant extent. This trend is consistent with the earlier report$^{18}$ that Se deposition by Reaction 5 is negligible at an electrode face down in 0.5 M Na$_2$SO$_4$ with 4 mM H$_2$SeO$_3$.

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

Further, the CoSe film content was decreased to ∼19.2% (Figure 7B) when electrodeposition was performed at higher flow rate (2.5 mL/min.) even with the face-up geometry. Taken as a whole, the results in Figure 7 underline that the reaction of electrogenerated Se$^{2-}$ with Co$^{3+}$ is very critical for the formation of CoSe in the film.

**Conclusions**

This study demonstrated the application of continuous flow-EQCM approach for the compositional analysis of electrodeposited
cobalt selenide thin films. The results showed that the target material, CoSe, was synthesized dominantly at $-0.7$ and $-0.8$ V by the combination of induced deposition and reaction of electrogenerated Se$^{2-}$ with Co$^{2+}$ species. At more positive deposition potentials, induced deposition played a main role for the synthesis of CoSe. On the other hand, free cobalt was the main component in the film at a deposition potential of $-0.9$ V. The flow-EQCM approach provided more reliable results than a static approach on the electrodeposited film composition in that problems associated with the stability of co-deposited cobalt could be circumvented. Finally, it is worth emphasizing again that the electroanalysis methodology presented in this report is chemical state-selective in that free Se, free Co and CoSe in electrodeposited films can be differentiated.

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**References**

1. H.-W. Jee, K.-J. Paeng, N. Myung, and K. Rajeshwar, *J. Electrochem. Soc.*, 164, D861 (2017).
2. Z. Jin, M. Zhang, M. Wang, C. Feng, and Z.-S. Wang, *J. Power Sources*, 378, 475 (2018).
3. S. Zhou, Q. Jiang, J. Yang, W. Chu, W. Li, X. Li, Y. Hou, and J. Hou, *Electrochem. Acta*, 220, 169 (2016).
4. X. Xu, P. Du, Z. Chen, and M. Huang, *J. Mater. Chem. A*, 4, 10933 (2016).
5. J. Masud, A. T. Swesi, W. P. R. Liyanage, and M. Nath, *ACS Appl. Mater. Interfaces*, 8, 17292 (2016).
6. H. Hu, J. Zhang, B. Guan, and X. W. Lou, *Angew. Chem. Int. Ed.*, 55, 9514 (2016).
7. M. C. D. Cooray, X. Zhang, Y. Zhang, S. J. Langford, A. M. Bond, and J. Zhang, *J. Mater. Chem. A*, 5, 19289 (2017).
8. M. L. Gaur, P. P. Hanksare, K. M. Gadakar, I. S. Mulla, and V. M. Bhuse, *New J. Chem.*, 38, 255 (2014).
9. Z. Wang, Q. Sha, F. Zhang, J. Pu, and W. Zhang, *CrystEngComm.*, 15, 5928 (2013).
10. M. Achimuthovicova, N. Danau, E. Dutkova, and A. Zorkovska, *Appl. Phys. A*, 123, 154 (2017).
11. A. I. Carim, F. H. Saadi, M. P. Soriaga, and N. S. Lewis, *J. Mater. Chem. A*, 2, 13835 (2014).
12. F. Liu, B. Wang, Y. Lai, J. Li, Z. Zhang, and Y. Liu, *J. Electrochem. Soc.*, 157, D523 (2010).
13. Y. Lai, F. Liu, J. Yang, B. Wang, J. Li, and Y. Liu, *Appl. Phys. Express*, 4, 071201 (2011).
14. K. Rajeshwar, *Adv. Mater.*, 4, 23 (1992).
15. N. Myung, C. Wei, and K. Rajeshwar, *Anal. Chem.*, 64, 2701 (1992).
16. S. Ham, S. Jeon, U. Lee, M. Park, K.-J. Paeng, N. Myung, and K. Rajeshwar, *Anal. Chem.*, 80, 6724 (2008).
17. N. Myung, J. H. Jun, H. B. Ku, H.-K. Chung, and K. Rajeshwar, *Microchem. J.*, 62, 15 (1999).
18. C. Wei, N. Myung, and K. Rajeshwar, *J. Electroanal. Chem.*, 375, 109 (1994).
19. A. J. Bard, R. Parsons, and J. Jordan, *Standard Potentials in Aqueous Solution*, Marcel Dekker: New York, 1985.