# 12TH WORKSHOP ON SURFACE ENGINEERING

28.06.2023 to 30.06.2023, J. Selye University, Slovakia

# Electrodeposition of cobalt selenide nanostructures from deep eutectic solvent

Mikołaj Kozak [a,b], Agnieszka Brzózka [a], Grzegorz Sulka [a]

[a] Jagiellonian University, Faculty of Chemistry, Department of Physical Chemistry and Electrochemistry, Gronostajowa 2, 30-387 Krakow, Poland
[b] Jagiellonian University, Doctoral School of Exact and Natural Sciences, Łojasiewicza 11, 30-348 Krakow, Poland

## SUMMARY

*Co-electrodeposition of cobalt and selenium from deep eutectic solvent (DES) can be an effective method of obtaining cobalt selenide materials. Electrodeposition with potential pulses allowed obtaining compact structures of thin films deposited on graphite and nanowires with controlled compostion.*

## INTRODUCTION

Cobalt selenide is a compound examined for many applications, especially those electrochemical such as electrode material for batteries, supercapacitors, or water electrolysis [1,2,3]. In presented research we developed a technique of cobalt selenide electrodeposition from a deep eutectic solvent solution. We synthesized two structures of this material: thin films deposited on graphite foil and nanowires deposited into pores of anodic aluminum oxide (AAO).

### Experimental

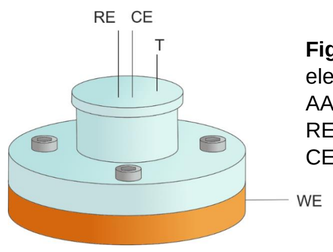


**Fig. 1** Scheme of teflon cell for used for performing electrodeposition. WE – working electrode (graphite or AAO) put on brass base, which ensures electric contact; RE – pseudoreference electrode – platinum wire; CE – counter electrode – platinum wire; T – thermometer.

- Electrolyte: 0.1 M $CoCl_2$ + 0.1 M $SeO_2$ in deep eutectic solvent (ethylene glycol + choline chloride in a 2:1 molar ratio)
- Electrodeposition was performed in teflon cell (Fig. 1) in three electrode system. The solution was stirred and heated to 80 ° C.
- Constant potential electrodeposition was performed with five different potentials, chosen basing on cyclic volatammogram: -0.8 V; -0.9 V; -1.0 V; -1.3 V and -1.5 V. Electroreduction was conducted for 10 min.
- To obtain structures with a more controlled composition and a better morphology, electrodeposition with potential pulses was performed. The pulse 'on' potential was -1.0 V, $t_{on}$=1 ms, three different „off" potentials were tested: -0.17 V (OCP), -0.50 V and -0.75 V, $t_{off}$=5 ms. Electroreduction was carried out for 60 min, which correspond to total time of pulse „on" equal to 10 min.
- To obtain stoichiometric composition ($CoSe_2$), concentration of $SeO_2$ in bath was decreased to 0.05 M.
- Nanowires were electrodeposited under conditions optimized for thin films ($E_{on}$=-1.0 V, $t_{on}$=1 ms; $E_{off}$=-0.75 V, $t_{off}$=5 ms, 0.1 M $CoCl_2$ + 0.05 M $SeO_2$).

## RESULTS

### Constant potential electrodeposition

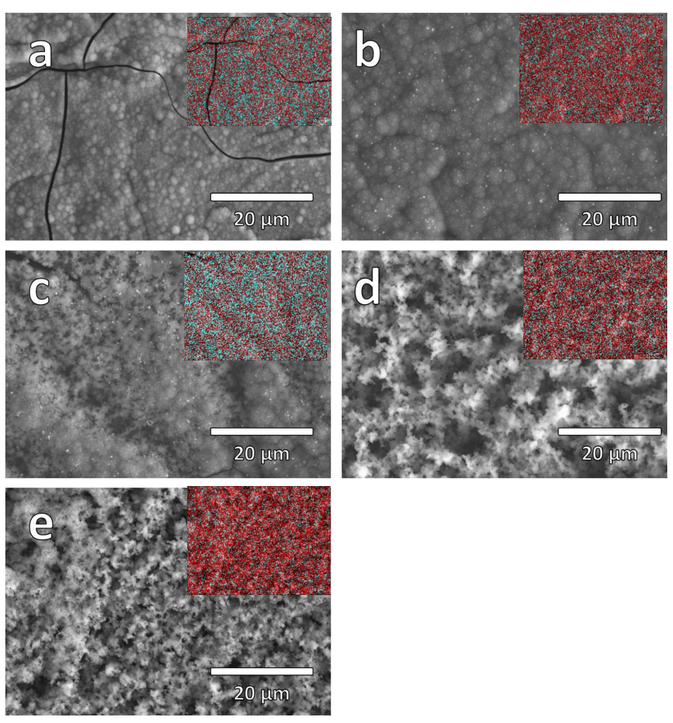


**Fig. 2** SEM images of Co-Se electrodeposited on graphite with different values od constant potential : (a) -0.8 V; (b) -0.9 V; (c) -1.0 V; (d) -1.3 V; (e) -1.5 V. On EDX maps cobalt is marked in red (K line) and selenium in blue (K line).

**Table 1** Compositions of samples electrodeposited with constant potential.

| E [V] | Co [%] | Se [%] | formula |
|---|---|---|---|
| -0.8 | 23.8±1.4 | 76.2±1.4 | $Co_{0.31}Se$ |
| -0.9 | 39.2±1.0 | 60.8±1.0 | $Co_{0.64}Se$ |
| -1.0 | 42.7±3.6 | 57.3±3.6 | $Co_{0.75}Se$ |
| -1.3 | 60.6±3.4 | 39.4±3.4 | $CoSe_{0.65}$ |
| -1.5 | 58.9±0.9 | 41.2±0.9 | $CoSe_{0.70}$ |

### Electrodeposition with potential pulses

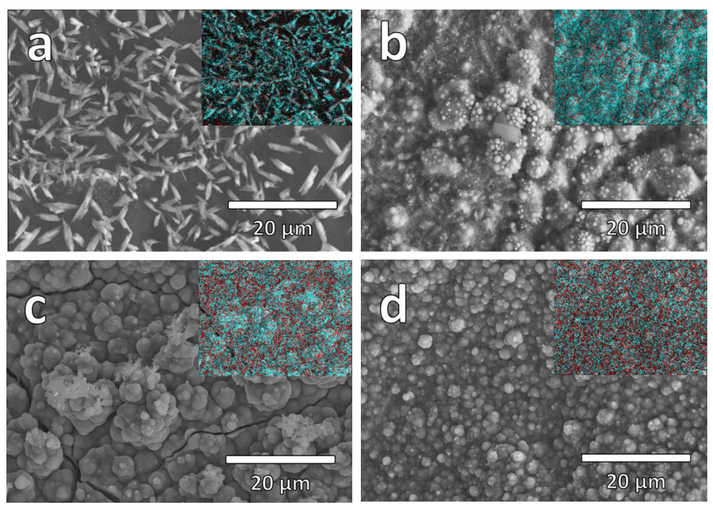


**Fig. 3** SEM images and EDX maps of Co-Se electrodeposited on graphite. Potential of pulse „on" $E_{on}$=-1.0 V and different „off" potentials: a) $E_{off}$ -0.17 V; b) $E_{off}$ =-0.50 V; c) $E_{off}$ -0.75 V; d) $E_{off}$ =-0.75 V ($SeO_2$ concentration decreased to 0.05 M). On EDX maps cobalt is marked in red (K line) and selenium in blue (K line).

**Table 2** Compositions of samples electrodeposited with potential pulses

| $E_{off}$ | Co [%] | Se [%] | formula |
|---|---|---|---|
| -0.17 V | 2.3±1.4 | 97.7±1.4 | $Co_{0.02}Se$ |
| -0.50 V | 1.3±0.3 | 98.7±0.3 | $Co_{0.01}Se$ |
| -0.75 V | 23.1±1.8 | 76.9±1.8 | $Co_{0.30}Se$ |
| -0.75 V* | 31.2±0.3 | 68.8±0.3 | $Co_{0.45}Se$ |

*$SeO_2$ concentration decreased to 0.05 M

### Nanowires

Composition: 38.9±4.7% Co 61.1±4.7% Se; formula: $Co_{0.54}Se$

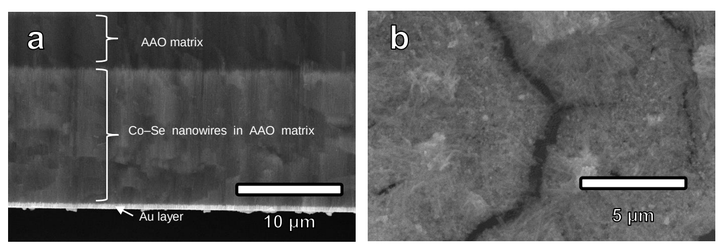


**Fig. 4** SEM images of Co-Se nanowires a) cross-section of AAO membrane with nanowires b) nanowires after etching of membrane.

## CONCLUSIONS

- Electrodeposition with potential pulses allows to obtain more compact structures and to better control the composition.
- Optimal conditions are: pulse "on": E=-1.0 V, t=1 ms; pulse "off": E=-0.75 V, t=5 ms, from bath containing 0.1 M $CoCl_2$ and 0.05 M $SeO_2$.
- Conditions of thin films synthesis can be directly applied to nanowires synthesis.
- Synthesized nanowires have average diameter of 55 nm and length of 11.6 µm.

## LITERATURE

[1] Nithya, V.D. Recent Advances in $CoSe_2$ Electrocatalysts for Hydrogen Evolution Reaction. *International Journal of Hydrogen Energy* 2021, *46*, 36080–36102

[2] Masud, J.; Swesi, A.T.; Liyanage, W.P.; Nath, M. Cobalt Selenide Nanostructures: An Efficient Bifunctional Catalyst with High Current Density at Low Coverage. *ACS applied materials & interfaces* 2016, *8*, 17292–17302.

[3] Zhang, X.; Gong, J.; Zhang, K.; Zhu, W.; Li, J.-C.; Ding, Q. All-Solid-State Asymmetric Supercapacitor Based on Porous Cobalt Selenide Thin Films. *Journal of Alloys and Compounds* 2019, *772*, 25–32.

## ACKNOWLEDGEMENTS

Authors acknowledge financial support of the National Science Centre, Poland (Project no. 2017/26/M/ST5/00715).