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Influence of synthesis conditions on morphology and composition of electrochemically deposited Ni_xSe_y films

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SUMMARY

Electrodeposition is a versatile synthesis method and offers many advantages for preparing electrotalytic materials. In case of the Ni-Se system, where compounds with varying stoichiometries exist, the influence of deposition parameters on the morphology and composition should be investigated. Here, the properties of Ni_xSe_y deposits obtained from a non-aqueous, ethaline-based bath are examined with respect to deposition conditions.

INTRODUCTION

Nickel selenides belong to a group of compounds considered for use as water splitting electrocatalysts, due to their favourable catalytic activity – towards both hydrogen and oxygen evolution reactions (HER and OER, respectively) – as well as good conductivity and stability. [1,2] Among available Ni_xSe_y synthesis methods, electrodeposition offers several advantages for electrocatalytic materials. Firstly, it enables direct preparation of the material on a conductive support, eliminating the need for additional binders and current collectors. Additionally, the morphology and phase composition of the deposits can be controlled through the manipulation of deposition parameters, such as the deposition mode used, applied current or potential values, time, temperature, and bath composition.

In recent years, deep eutectic solvents (DESs) have been increasingly used in electrodeposition, due to e.g. extended potential windows, ease of preparation and use, or relatively low toxicity [3,4]. Their another advantage is the possiblity to prevent or diminish hydrogen co-evolution, which might occur during the deposition of the element/compound of interest in aqueous solutions.

SYNTHESIS

electrodeposition

- three-electrode cell; working electrode: graphite foil or carbon fiber paper (CFP); counter electrode: Pt, quasi-reference electrode: Pt
- deposition bath: 0.1 M $NiCl_2$ + 0.1 M SeO_2 solution in ethaline DES
  - ethaline = choline chloride + ethylene glycol, 1:2 molar ratio
- deposition parameters:
  - constant potential regime: -0.75 V, -1.00 V or -1.25 V; time of deposition = 10 min
  - pulsed potential regime: „on” pulse = -1.00 V, 1 ms; „off” pulse = -0.50 V or -0.75 V, 5 ms; total duration of „on” pulses = 10 min
  - 70°C

mean Ni, Se percentages in samples were calculated from EDS measurements (relative at% values)

RESULTS

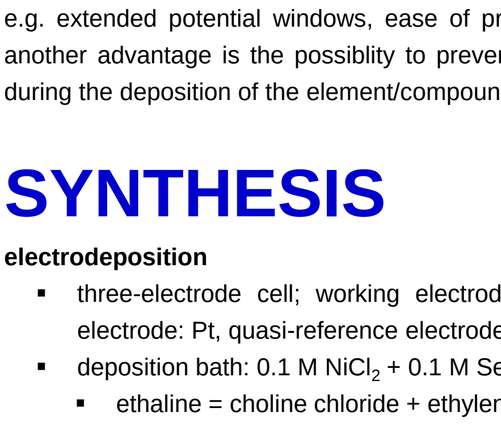

Fig. 1. Cyclic voltammograms recorded for 0.1 M $NiCl_2$ (Ni), 0.1 M SeO_2 (Se), and 0.1 M $NiCl_2$ + 0.1 M SeO_2 (NiSe 1:1) solutions in ethaline.
Working electrode: glassy carbon, counter and quasi-reference electrodes: Pt; scan rate 20 mV/s; 70°C.

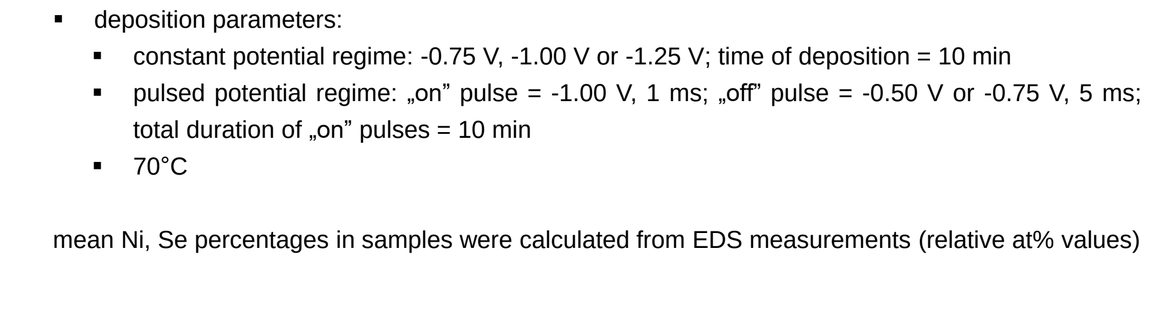

Fig. 2. SEM microphotographs of Ni_xSe_y films electrodeposited on graphite at various constant applied potentials.

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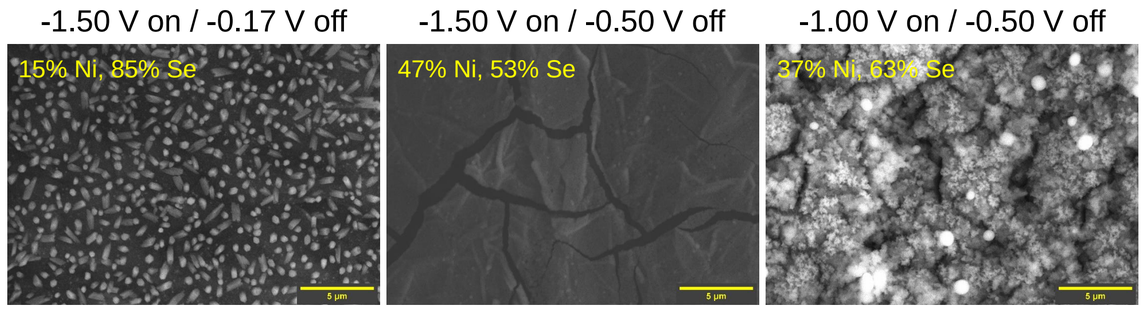
RESULTS



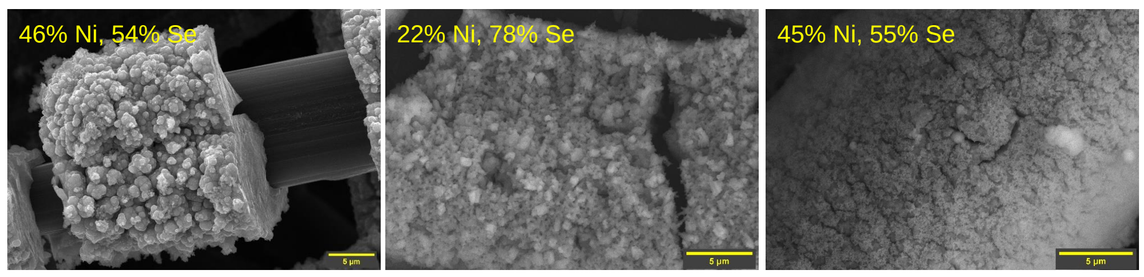


Fig. 3. SEM microphotographs of Ni_xSe_y films electrodeposited on graphite and CFP under constant or pulsed potential regime.

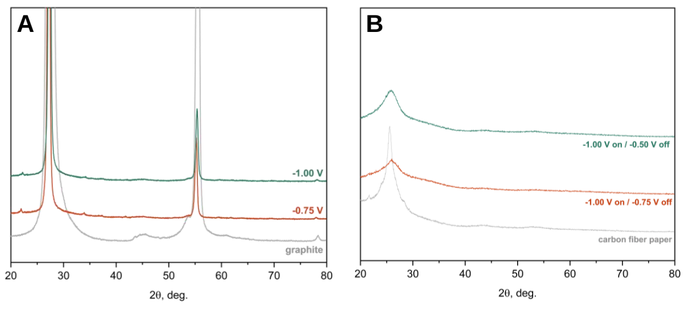


Fig. 4. Diffractograms of Ni_xSe_y films electrodeposited under (A) constant or (B) pulsed potential regime.

constant potential deposition

- deposition results in grainy, compact films, with grain sizes growing when the applied potential becomes more negative
- deposit obtained at -1.25 V is non-uniform (as shown in Fig. 2), and detaches easier from the substrate
- Ni content relative to Se increases with increasing deposition potential
- deposits seem to be amorphous, although some weak deposit-related peaks can be seen in the diffractograms

pulsed potential deposition

- deposition results in compact films, which are less grainy than those electrodeposited at similar values of applied constant potential
- during „off” pulses Ni can be leached out of the deposit; as such, Ni content relative to Se increases when the applied „off” pulse potential becomes more negative
- pulse deposits are most likely amorphous; no distinct deposit-related peaks can be seen in the diffractograms

LITERATURE

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