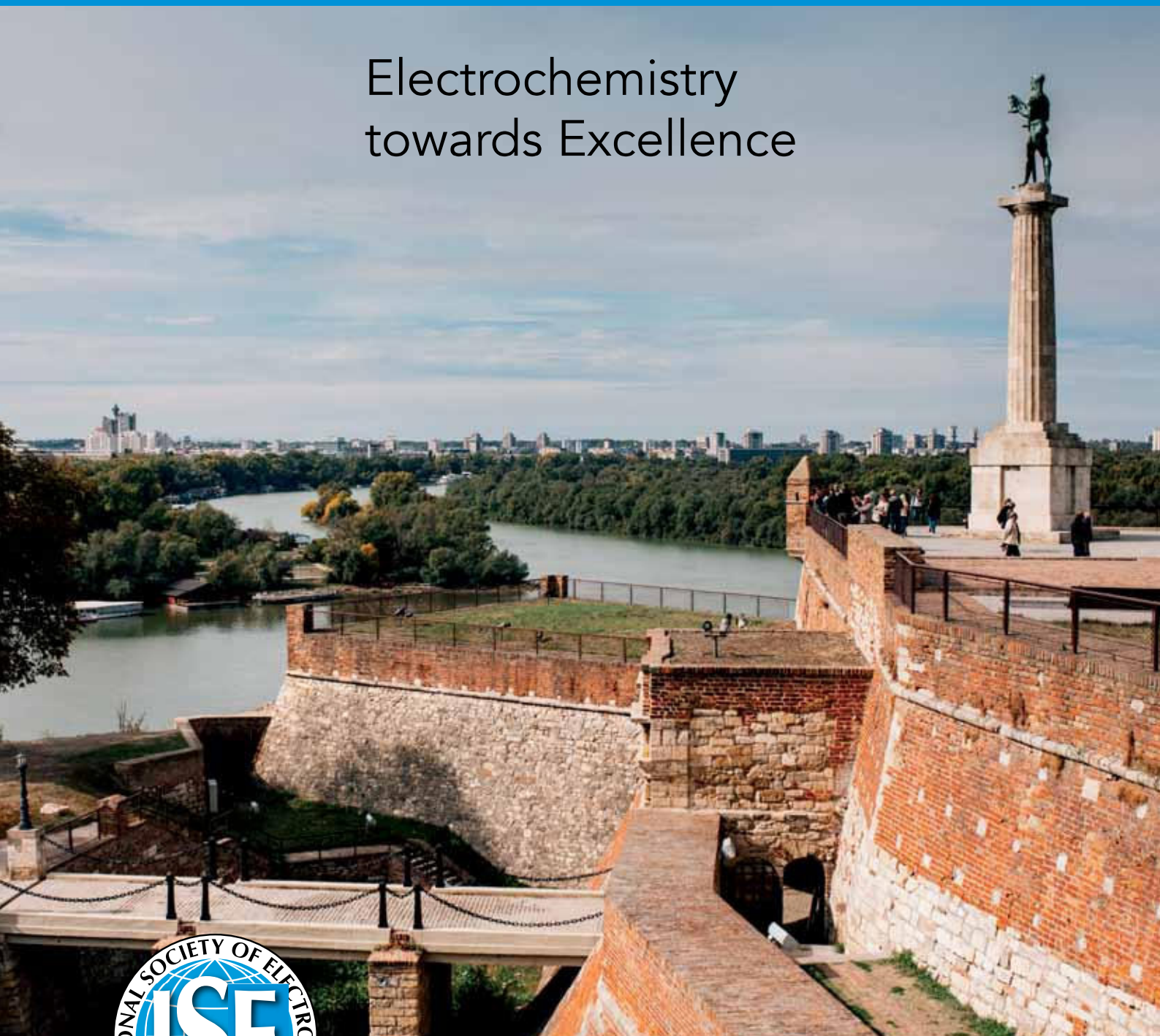


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Electrodeposition of compact Ag-Ni alloys and their performances as cathode towards nitrate reduction

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Bimetallic alloys are attracting much interest for the production of efficient and cheap materials, applicable to many areas. In this context, Ag-Ni alloys are promising for applications in electric/magnetic devices and (electro)catalysis [1]. Ag and Ni have both face-centered cubic (fcc) structure, however due to large difference in atomic radii, they do not exhibit solubility at equilibrium in the solid state. Electrodeposition may generate materials of structure or composition far from thermodynamic equilibrium, made stable by their (very) slow rearrangement at room temperature [2]. However, the deposition of Ag-Ni films is complicated by a fairly large difference in standard reduction potentials, respectively 0.799 V for Ag and -0.25 V for Ni (vs NHE). Cyanide baths were used in the past to deposit Ag and Ag-based alloys, for their strong complexing action of Ag^+ ions, leading to deposition of compact films, but nowadays less dangerous solutions are preferred, both for safety and environmental concerns. Ag-Ni thin films were already electrodeposited from baths containing thiourea as complexing agent, obtaining quite compact films but also undesired sulfur inclusions up to 20% [3].

We propose here the electrodeposition of Ag-Ni alloys from concentrated chloride baths, already used in the past for deposition of Ag-Pt and Ag-Pd alloys [4]. Concentrated chloride media may dissolve various metal ions and, in the specific case, the Ag-chloride complexes $[\text{Ag}(\text{Cl})_n]^{(1-n)-}$ are more stable than the Ni ones, bringing closer the reduction potentials and promoting co-electrodeposition.

Linear sweep voltammeteries of Ag-Ni electrodeposition performed in 10 M chloride baths indicate that alloy formation occurs under transport-limited reduction of silver complexes, so that films of desired composition may be obtained by regulating the deposition current j_{dep} . The obtained films have good compactness, with globular morphology (Fig.1, left); moreover, microanalysis indicates that they are free from foreign species. XRD spectra indicate the presence of two crystalline phases, one Ag- rich and the other Ni-rich (only for Ni >50 at%) with minimal inclusions (few atoms %) of the minority species. Tests of nitrate reduction, based on linear sweep voltammeteries (Fig. 1, right) and constant potential electrolyses, were performed on an alloy of approximate composition $\text{Ag}_{30}\text{Ni}_{70}$, with a significant yet limited Ag content. The main observations from these tests are: a) lower overvoltages for nitrate reduction with respect to pure Ni; b) marked increase of reduction current with respect to both Ag and Ni, in a broad potential region; c) better selectivity to NH_3 production and lower H_2 evolution.

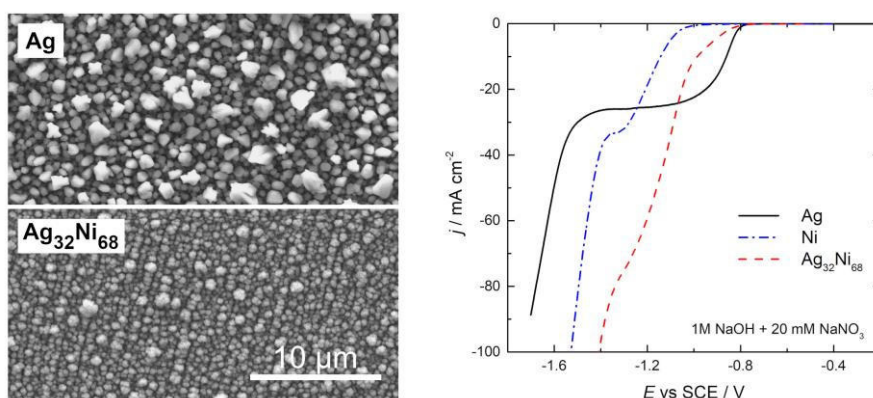


Fig. 1: SEM images of Ag and $\text{Ag}_{32}\text{Ni}_{68}$ samples from conc. chloride medium (left), and LSV of NO_3^- reduction on Ag, Ni and $\text{Ag}_{32}\text{Ni}_{68}$ cathodes in 1 M NaOH (right).

References

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