Initial Stages of Deposition of Ultrathin Overlayers of Ni, Co and Fe on Au {111} in DMSO

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The mechanism of the initial stages of electrodeposition of magnetic metals is important for the preparation of novel nanostructured surfaces. In the present study the formation of ultrathin overlayer of magnetic metals on Au {111} electrodes in DMSO solutions was studied by electrochemistry and XPS. The use of a non-aqueous electrolyte enables to observe clearly the onset and sequential stages of the deposition process, masked by concurrent hydrogen evolution in aqueous environments.[1]

Linear scan voltammetry of Fe, Co and Ni on Au{111} shows a pattern typical of systems where a UPD layer is formed prior to OPD (Figure 1). In the negative scan the onset of UPD is manifested as a well-defined cathodic peak, followed by a broad potential region (ca. 200 mV) where UPD persists. With Fe UPD a second, poorly-defined wave is observed following the first cathodic peak. The onset of OPD shows the usual sharp current rise, with a nucleation loop obtained in the case of Ni deposition. Well separated stripping peaks of the OPD and UPD layers, respectively, are observed on the reverse scans. Nearly identical UPD stripping traces are obtained for UPD layers of the three metals formed under potentiodynamic conditions or at a constant potential applied in the OPD region (shown in Figure 1 for Co as an example). Large differences between the potentials of UPD deposition and stripping are observed, i.e., ~0.5 V (Fe), ~0.7 V (Co), 0.9-1.0 V (Ni).

In order to investigate the UPD-OPD transition, evolution of the anodic voltammetric profile (corresponding to metal overlayer stripping) following deposition at a constant negative potential was studied (Figure 2). Current traces for sequential deposition/stripping of Fe (Figure 2a) and Co (not shown) were significantly different from those of Ni (Figure 2b). Although the kinetics of the OPD process become faster upon sequential deposition/stripping of Fe and Co, the main peak for the UPD layer dissolution remains essentially unaltered (Figure 2a; the same is observed for Co). In contrast, sequential Ni deposition/stripping results in rapid change in both the potential of the UPD stripping peak and the coulometric charge for the UPD layer oxidation (Figure 2b). The electrochemical and XPS data are consistent with the formation of a surface alloy during the deposition of a Ni underpotential overlayer.

XPS spectra of Au electrodes with a Ni overlayer, emersed from the solution under potential control, show the presence of a strongly adsorbed layer comprising either DMSO or products of its interaction with the electrode. The structure of the S 2p line shows the presence of thiolate-type adsorbates (binding energy, ca. 162 eV) for samples emersed at underpotentials. For electrodes emersed at overpotentials (onset of bulk Ni formation), oxidized sulfur (binding energy, 167-169 eV) was also present in the adsorbed layer. This can be attributed to catalytic decomposition of the solvent by 3D Ni clusters formed at overpotentials.

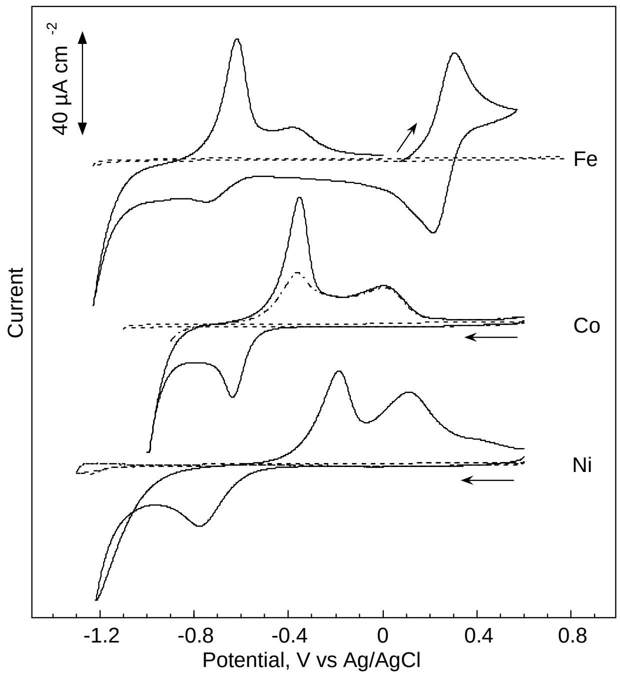

Figure 1. Deposition and stripping of Fe, Co and Ni UPD and OPD layers on Au{111} electrode. Solid lines: linear scan voltammetry; dashed-dotted line: stripping of Co deposited for 20 sec at –0.9 V; dashed lines: background in supporting electrolyte. Deposition solutions: 1 mM Me(ClO_4)$_2$ in DMSO. Scan rate: Fe, 50 mV sec^{-1}; Co and Ni, 20 mV sec^{-1}.

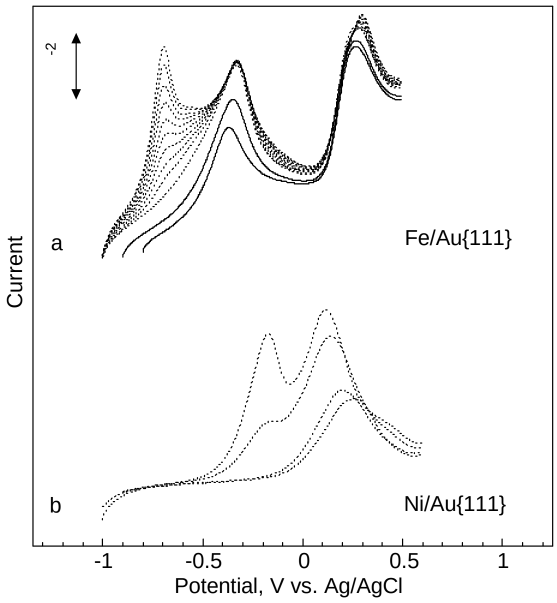

Figure 2. Anodic stripping of Fe and Ni deposited at a constant potential. Solid lines: deposition at underpotentials; dashed lines: deposition at overpotentials. Solution composition: (a) 0.3 mM $Fe(ClO_4)_3$ in DMSO; (b) 1 mM $Ni(ClO_4)_2$ in DMSO. Deposition potentials and times: (a) –0.8 V, –0.9 V, –1.0 V (10 cycles), all for 60 sec; (b) –0.9 V, –1.0 V, all for 80 sec. Scan rate: 20 mV sec^{-1}.

[1] A. Vaskevich and I. Rubinstein, *J. Electroanal. Chem.* **491** (2000) 87.