

NICKEL UNDERPOTENTIAL DEPOSITION ON WELL DEFINED PLATINUM (110) SURFACE

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The possibility of nickel underpotential deposition (upd) onto well defined platinum surfaces has been evaluated in different acidic media using cyclic voltammetry. Nickel upd on polycrystalline platinum electrodes has already been studied by El-Shafei [1]. The main conclusions of his work were that, in acidic medium: (1) Ni upd takes place in the hydrogen adsorption-desorption region (2) the electrosorption valence is 2 and (3) the Ni upd coverage depends on the surface structure (orientation) of the platinum electrode, Ni upd being more favoured on the Pt(110) surfaces. However, his work did not consider the use of single crystals to assert the last point. Thus the goal of the present study is to verify El-Shafei's assumption towards Ni upd on platinum single crystals.

For the sake of comparison, the study was at first attempted on a poly-oriented single crystal sphere of platinum. The results on such surface tend to confirm El-Shafei's: preferential Ni upd takes place on the Pt(110). From this basis, the experiments were undertaken on Pt(110) for various media, namely sulphuric and perchloric acid, sodium sulphate (pH = 4.5) and sodium hydrogenphosphate (pH 5.5). The parameters studied for Ni upd onto platinum were the nickel source (either NiSO₄ or NiCl₂) and concentration (10⁻² or 10⁻³ M), as well as voltammetry parameters (scan rate, lower potential limit and deposition time at low potential). For clarity, only results in 0.1 M sulphuric acid are presented in this abstract.

Voltammetry on Pt(110) in 0.1 M H₂SO₄ exhibit the classical pattern, and reveal that the platinum surface is reconstructed in the (2x1) configuration, leading to 222 μC cm⁻² of platinum for hydrogen desorption peak coulometry [2]. The voltammograms on this surface will serve as benchmark to assert the possibility for Ni upd onto Pt(110). Figure 1 exhibits typical voltammograms for Pt(110) in presence of NiSO₄. It shows the conventional peak (labelled I and I') for H-desorption at -0.14 V/SCE and another peak (II) at -0.19 V/SCE that we believe to be related to the desorption of Ni upd. Peak (II) grows both when the lower potential limit decreases at fixed scan rate (figure 1) and also when the time at the lower limit increases. Also, its potential varies with the scan rate, which probably signs its upd-character, Ni_{upd}/Pt(110). Unfortunately, no adsorption (deposition) peak (II') is related to peak (II). We believe that Ni deposition occurs while H₂ evolves onto Pt(110), hiding Ni deposition signal. Also, Ni²⁺ has a very large solvation sphere (6 H₂O) rendering its decomplexation necessary prior adsorption and explaining the rather slow adsorption kinetics. It also explains the sharp increase for peak (II) coulometry when the lower potential limit (and thus deposition time) varies to the more cathodic potentials. The Ni upd dissolution peak never reaches a

full monolayer, which is normal since $E_{Ni^{2+}/Ni}^{\circ} = -0.47$ V/SCE, a potential never attained herein.

To assert the presence of Ni_{upd}/Pt(110), CO-stripping experiments have been undertaken. They consisted of 5 minutes under CO atmosphere, followed by 20 minutes under nitrogen flush to remove any traces of CO, the electrode being held at -0.25 V/SCE during the whole treatment, prior the voltammetry experiments. Figure 2 exhibits the remarkable effect of the Ni submonolayer. For both media (with or without Ni) peak (b) signs the irreversible CO-oxidation. The second cycle (not shown for clarity) exhibit the normal pattern for Pt(110) with or without NiSO₄ in solution. More strikingly, there is a sharp difference between the scan for Ni_{upd}/Pt(110) and the benchmark scan for Pt(110), as peak (a) only appears in presence of NiSO₄ in solution. We believe this peak (a) is related to the oxidation of CO at the Pt-Ni sites, directly followed by Ni dissolution. More experiments would be required to assert this latter point.

The results for other media (perchloric, sodium sulphate at various concentrations), and experimental conditions will be given in the talk.

REFERENCES

- [1] A. A. El-Shafei, J. Electroanal. Chem., **447** (1998) 81
- [2] P. N. Ross, Surface Science, **102** (1981) 463

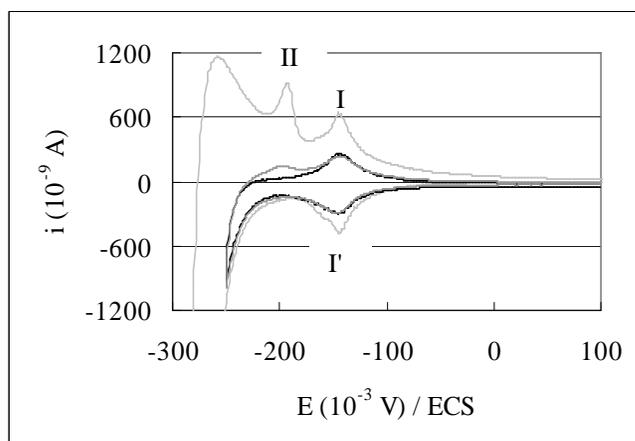


Figure 1: influence of the lower potential limit for voltammograms on Pt(110) ($\phi = 0.35$ cm) in 0.1 M H₂SO₄ at $2 \cdot 10^{-3}$ V s⁻¹ without (black) or with (grey) 10^{-3} M NiSO₄ in solution.

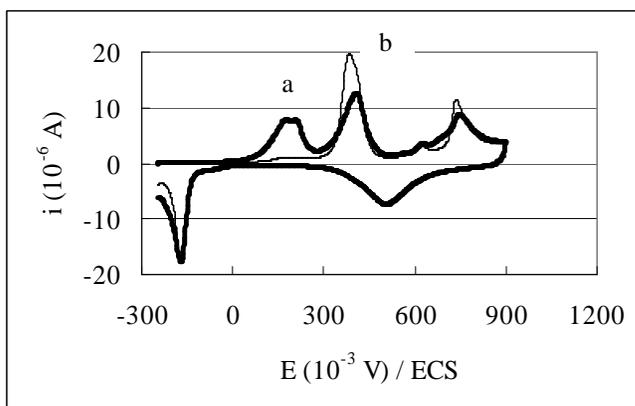


Figure 2: CO-stripping voltammograms for Pt(110) ($\phi = 0.35$ cm) in 0.1 M H₂SO₄ at $2 \cdot 10^{-3}$ V s⁻¹ without (thin black) or with (wide black) 10^{-2} M NiSO₄ in solution.