

# Photoemission and electrochemical studies of nickel deposits on hypo-d-electronic metal electrodes.

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## Introduction

It has long been appreciated that of submonolayer and monolayer metal deposits on foreign metallic substrates may possess special physical and electrochemical properties compared to the pure metal constituents. The formation of a metal monolayer at potentials more positive than the reversible Nernst potential, the so-called underpotential deposition (UPD), offers a unique possibility to form metal monolayer deposits and to vary their coverage by the applied potential.

Supported nickel catalysts, obtained by different chemical and electrochemical procedures are used in several electroanalytical applications. The main advantages of the dispersed nickel catalyst over other metals or bare nickel electrodes are related to their electrochemical stability and resistance to poisoning [1].

## Results and discussion

The hypo-hyper-d-electronic metal combinations, has already been proved to affect the electrocatalytic properties of pure metal electrodes upon hydrogen electrode reaction (HER) [2]. In the light of this observation, nickel (a hyper-d-electronic metal) electrodeposition on a series of hypo-d-electronic metals (such as vanadium, molybdenum and tungsten) was investigated using combined photoelectron spectroscopy and electrochemical studies. In this work we focused mainly on the influence of Ni adatoms on the metal electrode on the hydrogen evolution reaction, as well as an attempt was made to combine those findings with modifications observed in nickel electronic states detected by means of photoemission experiments.

The deposition of Ni on electrodes surface was carried out potentiostatically in an electrolyte solution containing 0.1 M NiSO<sub>4</sub> (pH = 5.9). Electrochemical measurements were performed at room temperature in a conventional three-electrode electrochemical cell with a SCE reference electrode and a Pt-wire counter electrode. After electrochemical experiments the samples were thoroughly rinsed in Millipore water, dried in a nitrogen stream and immediately transferred into the UHV chamber for analysis.

After the preparation of nickel deposits on hypo-d-metal electrodes the samples were characterized *ex situ* using photoelectron spectroscopy. This allowed for the determination of nickel amount on the electrode surface, as well as its chemical state. In figure 1 we present the Ni/V XPS intensity ratio as a function of applied potential. This ratio represents nickel coverage on the surface. On the basis of the values of Ni/V ratio, the total Ni uptake in potential region between -0.40 and -0.77 V is low but detectable and is not influenced by potential. The calculated nickel coverage in this region was always below 1 ML. When going to more negative potentials the Ni uptake increases rapidly and forms multilayer deposits. Those findings clearly show the UPD of Ni on V in the

range of -0.40 and -0.77 V.

The aforementioned experimental results are combined with voltametric electrochemical hydrogen evolution measurements on these bimetallic electrode surfaces. Current-potential curves of Ni-V surfaces (Figure 2), show higher evolution rate and adsorption capacity for the electrodeposited Ni electrode on V as compared to that of Ni and V separately.

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## References

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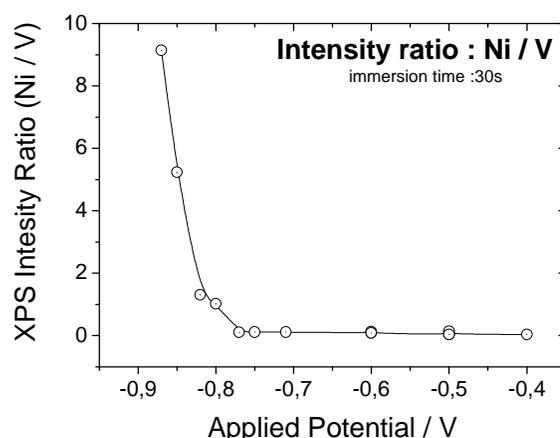


Figure 1 Ni/V XPS intensity ratio as a function of applied potential.

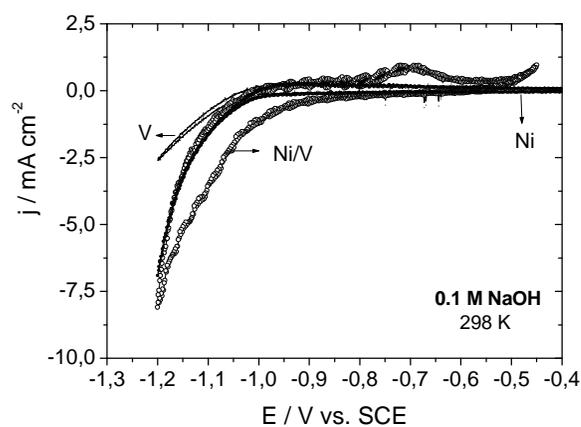


Figure 2. Cyclic voltammograms (1<sup>st</sup> cycle) for Ni, V and Ni/V electrodes into 0.1 M NaOH. Scan rate : 50 mVs<sup>-1</sup>.