

Electrochemical properties of Ni-P electrode materials modified with nickel oxide and cobalt

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This study was undertaken in order to obtain the amorphous Ni-P layers, containing additional components as nickel oxide and cobalt powders. The choice of these materials was made on the base of the knowledge of the properties of these components in hydrogen evolution reaction. The purpose of this work was to determine surface morphology of Ni-P+NiO+Co composite layers and to evaluate their suitability as electrode materials for hydrogen evolution reaction in alkaline solution. In order to attain improvements in electrochemical properties of Ni-P+NiO+Co composite layers, they were modified by thermal and chemical treatment. Microscopic and electrochemical studies were used to characterise the layers.

The electrodeposition process was conducted under galvanostatic conditions at the current density 0.20 A cm⁻², at the temperature 293 K with intensive stirring. Thermal treatment was conducted at the temperature of 500°C in argon atmosphere, in order to attain crystallisation of amorphous matrix. Chemical treatment consisted in leaching of nickel oxide in 1 M CH₃COOH, in order to attain large surface area. All obtained layers show good adhesion to the substrate and no internal stresses which could cause cracking or delamination. Microscopic studies revealed that the chemical treatment of Ni-P+NiO+Co layer enlarges real surface area of the layer.

Behaviour of obtained layers was investigated in the process of hydrogen evolution reaction (HER) from 5 M KOH using classical methods (voltammetry, steady-state polarisation) and electrochemical impedance spectroscopy. For the hydrogen evolution process the potentiodynamic and steady-state polarization curves showed that the chemical treatment of Ni-P+NiO+Co layer produced an increase in the current density and decrease the hydrogen evolution overpotential, in comparison with the values observed for Ni-P+NiO+Co and Ni-P+NiO+Co after thermal treatment. All Tafel curves were characterised by one slope in the whole potential range studied. Increased activity of Ni-P+NiO+Co after chemical treatment composite layers

may be attributed to the increase of the real surface area.

The complex impedances were analysed using a modified version of the complex nonlinear least-squares fitting program (CNLS) [1]. It has been found that the ac impedance behaviour of obtained layers may be well described using the one-CPE electrode models (Fig.1). Using the obtained parameters (R_{ct} , R_s , T , ϕ), the double-layer capacitances were determined. Assuming that the average double-layer capacitance of a smooth metal surface is 20 $\mu\text{F}\cdot\text{cm}^{-2}$ [2], the surface roughness was determined. The largest roughness was observed for Ni-P+NiO+Co after chemical treatment. Nonlinear least-squares approximation of current and charge-transfer resistance led to determination of the kinetic parameters (Tab.1). An increase of electrochemical activity of Ni-P+NiO+Co after chemical treatment is probably connected with increase of the real surface area.

It was found that chemical modifications of Ni-P+NiO+Co composite layers produced materials which could be used for industrial hydrogen evolution process.

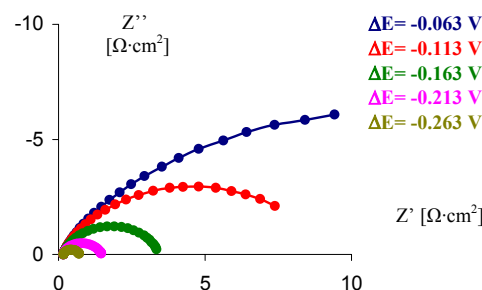


Fig.1. Complex-plane plots obtained on Ni-P+NiO+Co after chemical treatment layer in 5 M KOH.

Table 1. Kinetic parameters of HER obtained from steady state and ac impedance experiments in 5 M KOH on obtained layers.

Electrode	$k_{av} \times 10^9 (\text{mol cm}^{-2} \text{s}^{-1})$	α
Ni-P+NiO+Co	3.04	0.35
Ni-P+NiO+Co after thermal treatment	1.56	0.53
Ni-P+NiO+Co after chemical treatment	3.35	0.45

Reference

1. J. R. Macdonald, *Impedance Spectroscopy*, John Wiley & Sons, New York (1987).
2. R. Karimi - Shervedani, A. Lasia, *J. Appl. Electrochem.*, 29 (1999) 982.