

# Study of the hydrogen evolution reaction on Ni-P+titanium oxides electrodes in alkaline solutions

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## Introduction

Hydrogen evolution reaction (HER) has been studied extensively in electrochemistry due to its importance in different fields such as energy storage, fuel cells, and last but not least corrosion [1,2]. It is a relatively complicated process involving several reaction steps. Apart from the transport of  $H^+$  ions to the electrode and  $H_2$  from the electrode to the bulk electrolyte, there are still three reaction steps involved belonging to two reaction paths, the Volmer-Tafel and the Volmer-Heyrovský mechanism. Determination of the kinetic parameters of the HER is usually carried out by simultaneous approximation of the *dc* current and the parameters obtained from the electrochemical impedance spectroscopy (EIS) by adjusting the rate constants.

The present study was undertaken in order to obtain the composite layers in a Ni-P system containing  $TiO_2$  and Ti components. Stereoscopic microscopy, surface analysis, X-ray diffractometry, Auger spectroscopy, and absorption spectroscopy, were used for physical and chemical characterization of the layers.

Electrolytic activity towards the HER was studied on electrodeposited Ni-P+ $TiO_2$ +Ti layers before and after heating. The mechanism of the HER on obtained Ni-P+titanium oxides electrodes was studied in 5 M KOH at 25°C, and the kinetic parameters were determined using steady-state polarization and EIS techniques.

## Results and discussion

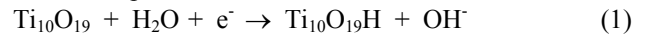
Composite Ni-P+ $TiO_2$ +Ti layers were prepared by simultaneous electrodeposition of nickel with titanium dioxide and titanium from a solution in which  $TiO_2$  and Ti particles were suspended by stirring. The electrodeposition was carried out under galvanostatic conditions at a room temperature. Deposited Ni-P+ $TiO_2$ +Ti layers were heated at 400°C, 500°C, and at 800°C for 10 h under a flow of argon.

Obtained layers exhibit an amorphous structure of Ni-P matrix in which the crystalline  $TiO_2$  and Ti are embedded. On the Ni-P+ $TiO_2$ +Ti layer surface, the non-stoichiometric oxide,  $Ti_{10}O_{19}$ , and intermetallic compounds, NiTi, formed on a boundary of the  $TiO_2$  or Ti grains, and the nickel matrix during the electrodeposition, are additionally present. The heat-treatment in argon of such layers leads to the Ni-P matrix crystallization and non-stoichiometric titanium oxides as well as NiTi formation.

Electrolytic activity towards the HER was studied on such electrode materials before and after heat-treatment. In order to explain the electrochemical behaviour of the electrode materials, electrical equivalent circuits containing: (i) the constant-phase element (CPE), (ii) the porous electrode impedance, and (iii) two-CPE elements, were compared and verified. It has been found that the *ac* impedance behaviour of the Ni-P+titanium oxides electrodes may be well described using the two-CPE electrode model. The HER mechanism was determined on the basis of the dependence of both the current density *j* registered in the steady-state measurements and the parameter *A* being the inverse of the charge-transfer

resistance determined by EIS, on the overpotential  $\eta$  [1,2]. It was established that the HER on all investigated electrodes in 5 M KOH at 25°C proceeds via the Volmer-Heyrovský reaction mechanism, which should include the participation of non-stoichiometric titanium oxides. It could be described by the following equation:

Volmer step:



Heyrovský step:



An increase in activity occurs after heating of the Ni-P+ $TiO_2$ +Ti layer, which is connected with  $TiO_2$  reduction and formation of non-stoichiometric titanium oxides:  $Ti_{10}O_{19}$  (400°C),  $Ti_7O_{13}$  (500°C) and  $Ti_4O_7$  (800°C) (Tab.1). It has been postulated that the increase in electrochemical activity can be connected with properties of these oxides and a facility for H reduction/adsorption on their surface as well as the presence of NiTi intermetallics having an ability to cumulate the hydrogen in its crystal lattice, as compared with the Ni-P+ $TiO_2$ +Ti.

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Table 1. Average rate constants of the HER obtained from steady-state and *ac* impedance experiments in 5 M KOH at 25°C on the Ni-P+ $TiO_2$ +Ti electrode before and after heat-treatment.

Electrode	$\bar{k}_{av}$ (mol cm <sup>-2</sup> s <sup>-1</sup> )
Ni-P+ $TiO_2$ +Ti	$(6.09 \pm 0.04) \times 10^{-9}$
Ni-P+ $TiO_2$ + $Ti_{10}O_{19}$ (400°C)	$(1.98 \pm 0.14) \times 10^{-8}$
Ni-P+ $TiO_2$ + $Ti_7O_{13}$ (500°C)	$(5.69 \pm 0.05) \times 10^{-9}$
Ni-P+ $TiO_2$ + $Ti_4O_7$ (800°C)	$(3.88 \pm 0.05) \times 10^{-9}$

## Reference

- 1 A. Lasia in *Modern Aspects of Electrochemistry*, B.E. Conway and R.E. White, Edts, Kluwer/Plenum, New York, 2002, vol. 35, p. 1.
- 2 A. Lasia in *Modern Aspects of Electrochemistry*, B.E. Conway, J.Bockris, and R.E. White, Edts., Kluwer Academic/Plenum Publishers, New York, 1999, Vol. 32, p.143.

Fig. 1. Dependence of the inverse of charge-transfer resistance,  $A = 1/R_{ct}$ , on overpotential,  $\eta$ , for the HER in 5 M KOH at 25°C on the Ni-P+ $TiO_2$ +Ti electrode: directly after deposition (○) and after heating in argon at 400°C (□), at 500°C (△), and at 800°C (■).

