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Otrzymano (Received) 10.12.2009

IN SITU ELECTROCHEMICAL METHODS FOR PRODUCTION AND POROSITY CHARACTERIZATION OF COMPOSITE Ni-P+TiO₂ CATALYST COATINGS

The present work deals with the development of new electrochemical ways to improve the electrode material activity towards hydrogen evolution reaction (HER). An *in situ* composite electrodeposition technique has been proposed to prepare the porous Ni-P+TiO₂ coatings. Production of this catalyst material was carried out by simultaneous codeposition of amorphous nickel with titanium dioxide (anatase) powder on a copper substrate from the bath in which TiO₂ particles were held in suspension by magnetic stirring. The electrodeposition of the Ni-P+TiO₂ coatings was carried out under galvanostatic conditions at room temperature from the plating bath containing nickel sulfate, ammonium chloride, sodium hypophosphite, sodium acetate, boric acid, and an addition of TiO₂ powder.

The chemical and physical characteristics of the obtained deposits have been discussed. Surface morphology was carried out using a scanning electron microscopy (SEM). Structural investigations were conducted by X-ray diffraction method (XRD). The chemical composition of the coatings was determined by means of atomic absorption spectroscopy (AAS). The *in situ* method of electrochemical impedance spectroscopy (EIS) was applied to the porosity studies of the coatings. For comparison, the Ni-P and Ni coatings were also obtained and investigated in the same manner.

The SEM observations of the surface morphology revealed that the composite Ni-P+TiO₂ coatings exhibit the presence of TiO₂ particles (diameter of particle below 40 μm) uniformly embedded into the amorphous nickel matrix. The structural investigations of the deposits exhibit the composite structure with an amorphous nickel matrix into which the solid crystalline TiO₂ particles are embedded. The optimum production conditions of the porous coatings containing 30.3 wt.% of TiO₂ micro-particles, were proposed. Such electrochemical codeposition method may be a good alternative in the field of composite large-surface electrodes for HER. The pore geometry was determined by impedance modeling and to explain the impedance behavior of the electrode materials, three electrical equivalent circuits containing: (i) the constant-phase element (CPE), (ii) two-CPE elements and (iii) the finite length porous model, were compared and verified. The electrochemical impedance behavior of the composite Ni-P+TiO₂ electrode may be well described using the two-CPE model related to the presence of pear-like shape pores with the diameter of 0.37 Ω cm² on the surface, and a simple CPE model for the Ni-P and Ni electrodes containing the flat pores. It has been found that *in situ* electrochemical methods can be successfully applied for both production and characterization of the large-surface composite coatings with a high performance towards HER.

Keywords: composite coatings, impedance, electrodeposition, Ni-P+TiO₂, porosity

METODY ELEKTROCHEMICZNE *IN SITU* DO OTRZYMYWANIA I CHARAKTERYZOWANIA POROWATOŚCI KATALITYCZNYCH WARSTW KOMPOZYTOWYCH Ni-P+TiO₂

Warstwy kompozytowe Ni-P+TiO₂ otrzymywano techniką *in situ* współosadzania amorficznego niklu i proszku TiO₂ na podłożu miedzi z kąpiel, w której cząstki tlenku tytanu (<40 μm) utrzymywano w zawiesinie, stosując mieszanie magnetyczne. Elektroosadzanie prowadzono galvanostaticznie w temperaturze pokojowej. W celach porównawczych otrzymano w tych samych warunkach warstwy Ni-P i Ni. W pracy zanalizowano charakterystykę fizykochemiczną osadzanych warstw. Obserwacje morfologii powierzchni warstw wykazują, że cząstki TiO₂ są jednorodnie rozmieszczone w osnowie Ni-P. Badania strukturalne potwierdzają strukturę kompozytu o osnowie amorficznego niklu, w której zabudowane są krystaliczne cząstki stałe TiO₂ w ilości 30,3% wag. Charakterystyka porowatości powierzchni warstw zrealizowana została techniką *in situ*, stosując elektrochemiczną spektroskopię impedancji. Badania impedancyjne ujawniły obecność porów w kształcie gruszki o średnicy 0,37 Ω cm² na powierzchni warstw Ni-P+TiO₂ oraz płtych porów w przypadku warstw Ni-P i Ni. Stwierdzono, że modyfikacja amorficznej osnowy Ni-P poprzez zabudowanie do niej krystalicznego składnika kompozytu w postaci proszku TiO₂ w zaproponowanych optymalnych warunkach prowadzi do otrzymania materiału kompozytowego o silnie rozwiniętej powierzchni, który może stanowić obiecującą alternatywę w obszarze materiałów elektrodowych dla reakcji wydzielania wodoru.

Słowa kluczowe: warstwy kompozytowe, impedancja, elektroosadzanie, Ni-P + TiO₂, porowatość

INTRODUCTION

The technological area most affected by advances in electrocatalysis is electrochemical energy conversion, especially fuel cells for which hydrogen is potential fuel [1-3]. Hydrogen can be produced on a large scale

through raw materials and processes which are economically profitable. Water electrolysis is one of the most utilizable industrial processes for hydrogen production today, and is expected to become even more important in the future. The three major technologies currently under consideration for electrolytic hydrogen production are classified as alkaline, polymer membrane and ceramic oxide electrolyte [2]. A principal focus of modern electrochemistry in hydrogen production by electrolysis is to develop novel electrode materials that exhibit good electrochemical stability and show interesting activity for hydrogen evolution reaction (HER) [1-6]. It is also desirable to produce these materials as inexpensive, abundantly available, tailored to meet the needs of catalysis and nonpolluting. Scheme of the standard and new electrode materials used for HER in alkaline media is shown in Figure 1a.

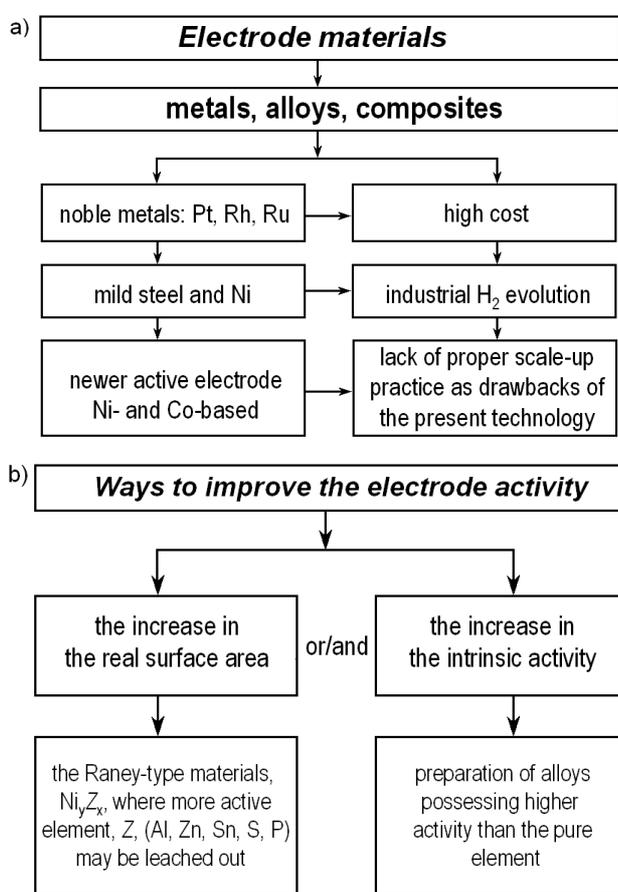


Fig. 1. Scheme of most active electrode materials for HER in alkaline media (a) and ways to improve the electrode activity (b)

Rys. 1. Schemat najaktywniejszych materiałów elektrodowych do elektrolitycznego wydzielenia wodoru w środowisku alkalicznym (a) i sposoby poprawy aktywności elektrod (b)

Most active and simultaneously expensive metals for HER are Pt-group metals (Pt, Rh, Ru, Ir) followed by transition metals (Au, Ni, Co, Fe, Cu). However, for noble metals fast deactivation is often observed due to adsorption or electrodeposition of impurities [2]. For this reason, in the industrial elec-

trolysis conditions mild steel and Ni are mostly used. Nickel and Ni-based electrodes are among the best materials for water electrolysis in alkaline media because of their relatively high activity and chemical stability and lower cost as compared to Pt-metals. Alloying various metals often leads to an increase in electrocatalytic activity. Many efforts have been also made towards development newer active electrodes based on Ni and Co. Such multicomponent and multiphase catalyst materials with modified structure become more popular as they exhibit higher activity in HER in comparison with pure metals. Composite coatings belong to the specific type of modified electrode materials consisting of a crystalline or amorphous matrix and the other solid phase dispersed within it [1-5]. Such materials can be obtained by chemical, thermal or electrolytic methods [2]. The kind of matrix and the type of embedded solid particles determine the properties of the composite material. Due to the interaction between the matrix and dispersed substance a complex with properties different from the component's features is created. This might be a reason for the occurrence of synergetic effect of the substrate in the course of HER.

Progress in the science of the electrode reactions is achieved by various high performance electrocatalysts development to enhance the rates of the half reactions that comprise the fuel cell. Ways to improve the electrode activity are: (i) to increase the real surface area to achieve porous electrodes or/and (ii) to increase the intrinsic activity (Fig. 1b). The latter case leads to preparation of alloys possessing higher activity than the pure element. In recent years, electrodeposition in aqueous solution has been identified to be a technologically feasible and economically superior technique for the production of such large-surface area electrodes where an increase in the real surface area leads to increase in catalytic activity. The major existing techniques employed in electrodeposition for porous electrodes production include high current density deposition, reactive deposition, electrodeposition-activation processes and composite electrodeposition [2-5]. The latter technique can increase the electrode surface through an *in situ* codeposition of metal or/and metal oxide micro-particles in a metal matrix.

Good knowledge of the porous electrode theory permits for the construction of the electrodes with optimal utilization of the active electrode material. The porous electrode model was first developed for dc conditions [7] and later applied to the electrochemical impedance spectroscopy (EIS) studies. The EIS is an *in situ* method in which small sinusoidal perturbation of the potential or the current is applied and the ac response is measured, from which the complex impedance is obtained at different frequencies. It is sensitive to the interfacial processes (e.g. reaction mechanism, adsorption), the surface geometry (planar, spherical,

cylindrical, porosity) and the mass transfer (semi-infinite or finite length diffusion, forced mass transfer). Reviews on impedance with a theory of the EIS including a general discussion of porous materials [1, 8] and the applications to the reactions involving hydrogen [2, 3, 9], are available. Understanding of the theoretical basis of the impedance is essential in comprehension of the theory of porous electrodes. Recently, a simple cylindrical porous electrode model was presented [1] in the absence and in the presence of the concentration gradient. The fractal model and the constant phase element (CPE) were also discussed as they are often related to the electrode roughness.

In this paper, an environmentally friendly electroplating process of composite Ni-P+TiO₂ coatings was developed. The main aim was to report on these porous deposits production technology, and their physical and chemical characterization including modeling of impedance of porous electrodes. The choice of the matrix type and the component was based on earlier tests of their individual activity during HER [5].

EXPERIMENTAL DETAILS

Scheme of the experimental set-up used for electrodeposition is shown in Figure 2. Composite Ni-P+TiO₂ coatings were electrodeposited from a Ni-plating bath of composition given in Table 1. Ultrapure water (Millipore, 18.2 MΩ cm) and chemicals of analytical grade (Merck, POCh Gliwice), were used for the bath preparation. TiO₂ powder (anatase, Loba Feinchemie, 99%, diameter of particle below 40 μm) was added and maintained in suspension by magnetic stirring at 300 rpm. Sedimentation of TiO₂ powder was not observed. The constant current electrodeposition was carried out on a Cu substrate (1.0 cm²) at $j = 250 \text{ mA cm}^{-2}$, at room temperature. Details of the deposition conditions are listed in Table 1. The substrate pretreatment has been described previously [5]. The mass increment of depo-

sits was measured and estimated on the basis of the mass difference before and after electrodeposition. For comparison, the Ni-P and Ni coatings were also obtained under the same conditions from the appropriate baths.

TABLE 1. Bath composition and electrodeposition conditions for the composite Ni-P+TiO₂ coatings.

TABELA 1. Skład kąpiel i warunki elektroosadzania warstw kompozytowych Ni-P+TiO₂

Type of the coating	Ni-P+TiO ₂
Bath composition	NiSO ₄ ·7H ₂ O – 51 g dm ⁻³ + NH ₄ Cl – 10.7 g dm ⁻³ + NaH ₂ PO ₂ ·H ₂ O – 29 g dm ⁻³ + CH ₃ COONa – 10 g dm ⁻³ + H ₃ BO ₃ – 8 g dm ⁻³
TiO ₂ (anatase) powder	99 g dm ⁻³ (<40 μm)
pH	4.8
Temperature	293 K
Deposition current density	250 mA cm ⁻²
Substrate	Polycrystalline copper
Magnetic stirring, <i>r</i>	300 rpm
Weight of the coating	0.18 g cm ⁻²
Thickness of the coating	150 μm
Adhesion	Very good
Colour of the coating	Mat-grey, white velvet-like tarnish on the surface

Quantitative chemical analysis of the coatings was determined by means of atomic absorption spectroscopy (AAS) using a Perkin-Elmer spectrometer. The element content was determined as described in details in Ref. [5]. Surface morphology was investigated using a scanning electron microscope (SEM, Hitachi S-4200, Japan). The thickness of the coatings was estimated by SEM to be approximately 150, 25 and 20 μm for the Ni-P+TiO₂, Ni-P and Ni coatings, respectively. Structural investigations were carried out by X-ray diffraction (XRD) method using a Philips diffractometer and Cu_{Kα} radiation. The electrochemical measurements of the tested electrodes were carried out using three-electrode electrochemical cell at 293 K in 5 M KOH solution with 10 g dm⁻³ of C₁₀H₁₄O₈N₂Na₂·2H₂O. Such

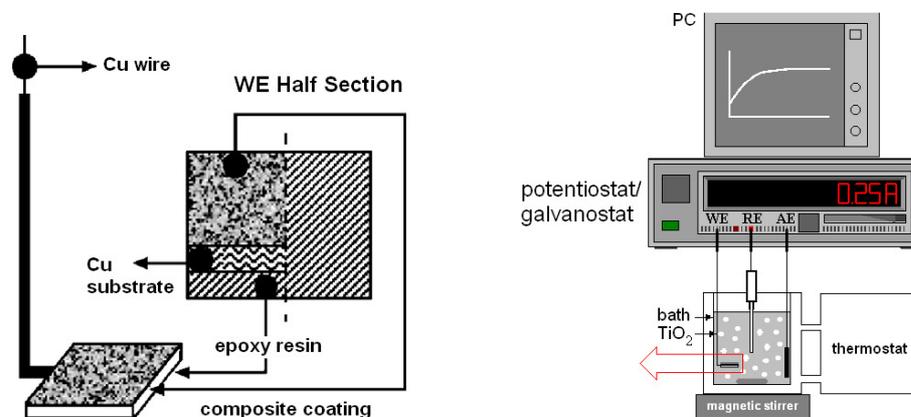


Fig. 2. Set-up for electrodeposition with an electrochemical cell (right): a Pt auxiliary electrode (AE), saturated calomel electrode as reference electrode (RE), the working electrode (WE), agitation of the electrolyte containing TiO₂ powder using magnetic stirrer, and thermostated water, and WE details (left)

Rys. 2. Stanowisko do elektroosadzania z naczynkiem elektrochemicznym (z prawej): przeciwelektroda Pt (AE), nasycona elektroda kalomelowa jako elektroda odniesienia (RE), elektroda pracująca (WE), mieszanie elektrolitu zawierającego proszek TiO₂ za pomocą mieszadła magnetycznego i termostatowana woda oraz szczegóły WE (z lewej)

a complexing agent was added to avoid the electrode deactivation through cathode poisoning [5, 6]. A Pt grid AE of 1 dm² and the external Hg/HgO/5 M KOH RE connected to the cell through the bridge filled with 5 M KOH and a Luggin capillary, were used. Oxygen was removed by bubbling argon. The EIS studies were carried out using an Autolab 20 Potentiostat/ Galvanostat and Frequency Response Analyser (Eco Chemie B.V., Netherlands) in the frequency range of 10 kHz to 100 mHz. Ten frequencies per decade were scanned using a sinusoidal signal of 5 mV peak-to-peak. The complex impedances were analysed using a modified version of the complex non-linear least-squares fitting program (CNLS) of Macdonald et al. [8].

RESULTS AND DISCUSSION

The surface morphology of as-deposited Ni, Ni-P and Ni-P+TiO₂ coatings are shown in Figure 3a, b and c, respectively. All deposits show a good adhesion to the substrate and no internal stresses resulting in cracks or defoliation from the Cu plate. One can see that surface morphology of smooth polycrystalline Ni (Fig. 3a) is developed in the first step by an addition of phosphorus what leads to amorphous nickel formation (Fig. 3b). Further modification of the Ni-P system by embedding of TiO₂ particles into the metallic matrix results in porous Ni-P+TiO₂ material production (Fig. 3c).

The Ni and Ni-P coatings show silvery-grey colour. Composite Ni-P+TiO₂ coating has a mat-grey, rough metallic surface with grains of embedded TiO₂ powder visible as white velvet-like tarnish on the surface.

The appropriate XRD patterns are also displayed in Figure 3. The corresponding elements are indicated at

the top of each diffraction line. The XRD pattern of the Ni-P+TiO₂ coating (Fig. 3c) shows that the structure of this type of deposit exhibits a matrix in the range of 2 θ angles corresponding to the amorphous matrix of the Ni-P deposit (Fig. 3b). There is no diffraction line coming from polycrystalline Ni (Fig. 3a). The composite structure of the Ni-P+TiO₂ coating additionally differs from the Ni-P deposit in the presence of crystalline TiO₂ phase. This means that during *in situ* composite electrodeposition method a spherical crystalline particle could be embedded into the Ni-P phase matrix under optimized conditions. Such codeposition of insoluble particles with amorphous Ni occurs as the result of a two-step adsorption process. Initially, solvated particles come into contact with the substrate and are loosely adsorbed. The potential difference existing at the metal/solution interface then results in a field-assisted strong adsorption of some of the particles followed by incorporation into the growing film. The AAS results show that the Ni-P+TiO₂ deposit obtained in this way contain (wt.%): 52.2 Ni, 17.5 P and 30.3 TiO₂ while the Ni-P coating electrodeposited under the same conditions 71.2 Ni and 28.8 P.

To characterize the porosity of the obtained coatings during HER, the *in situ* EIS method was used. Keiser et al. [10] have studied by EIS different pore shapes displayed in Figure 4a. At high frequencies (HF), on the complex plane plots, they display a line at 45° for cylindrical pores, more than 45° for the groove shape pores or a form resembling a partially or fully developed semicircle. Such a well developed semicircle is clearly visible for pear-shape pores, curve 4. Similar simulations were later continued for the pear-shape and spherical or bispherical pores (Fig. 4b) [5, 6]. It is clear

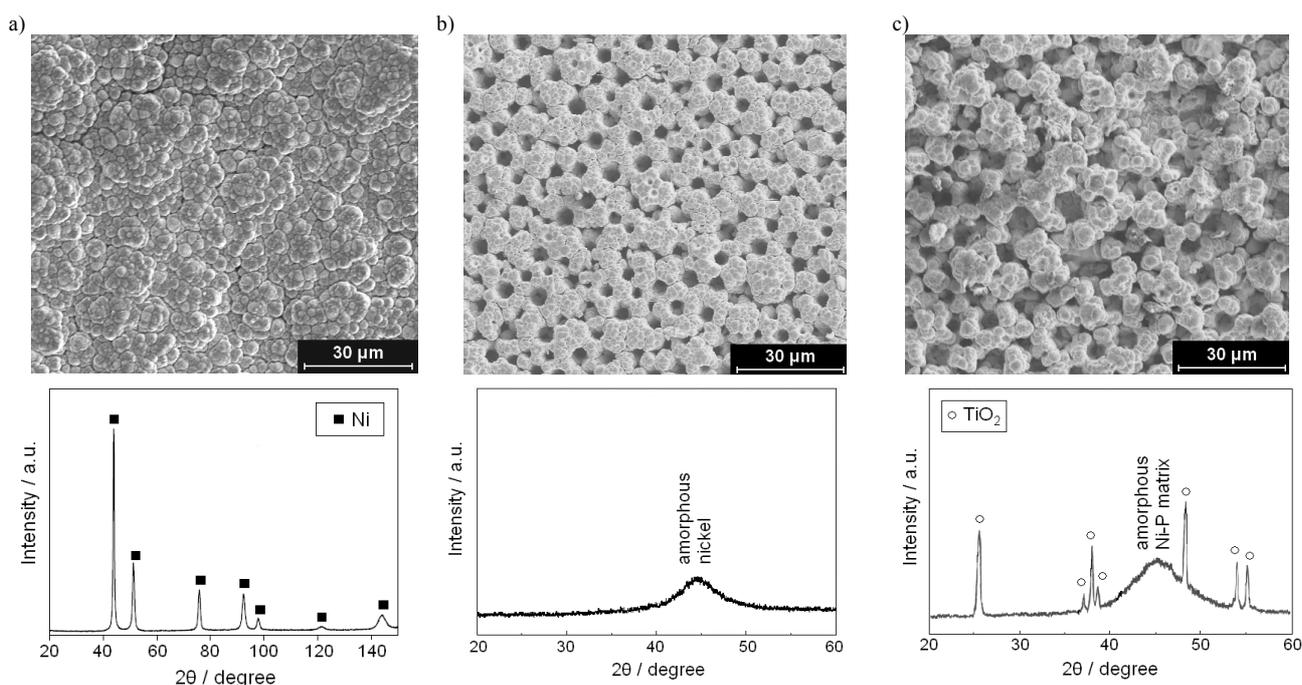


Fig. 3. Surface morphology and XRD pattern of the as-plated coatings: a) Ni, b) Ni-P, c) Ni-P+TiO₂

Rys. 3. Morfologia powierzchni i dyfraktogram warstw po osadzeniu: a) Ni, b) Ni-P, c) Ni-P+TiO₂

that the shape of impedance curves depends not only on the pore geometry but also on the size of the opening. For the bispherical pores, the effects of each sphere can be observed at different frequencies; at HF the ac signal penetrates only to the first sphere and at lower frequencies (LF) it penetrates up to the second (deeper) sphere displaying two 1/2 overlapping semicircles [6]. Impedance of other arbitrary noncylindrical pores was also simulated using division into small cylinders and matrix calculation [1].

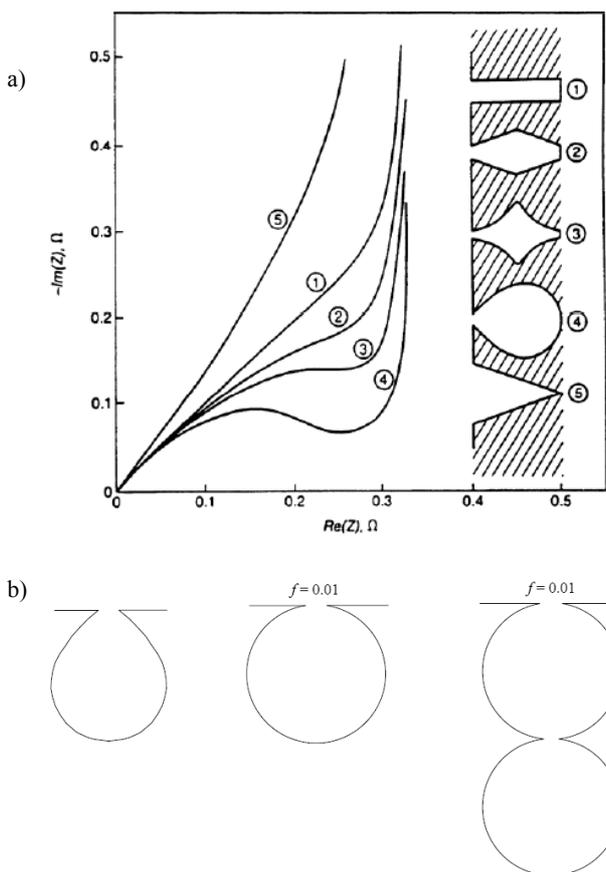


Fig. 4. Impedance spectra for different pore shapes [10] (a) and pore shapes used in the simulation of impedances [6] (b)

Rys. 4. Widmo impedancji dla porów o różnych kształtach [10] (a) i kształty porów użytych do symulacji impedancji [6] (b)

Formation of HF semicircle related to the pore geometry was observed experimentally on the composite Ni-P+TiO₂ electrode (Fig. 5a). This electrode displayed ac behavior characteristic of the porous and rough electrode. In Figure 5a two semicircles are visible on the complex-plane plot, where the diameter of the first semicircle was constant in the whole range of studied overpotentials for HER. These impedances were modeled using three porous models assuming the presence of flat (CPE model), pear-shape (two-CPE model) and cylindrical pores (finite length porous model), described by electrical equivalent circuits shown in Figure 6. Details of the theory for these models were presented previously [1-3, 5, 6, 8, 9].

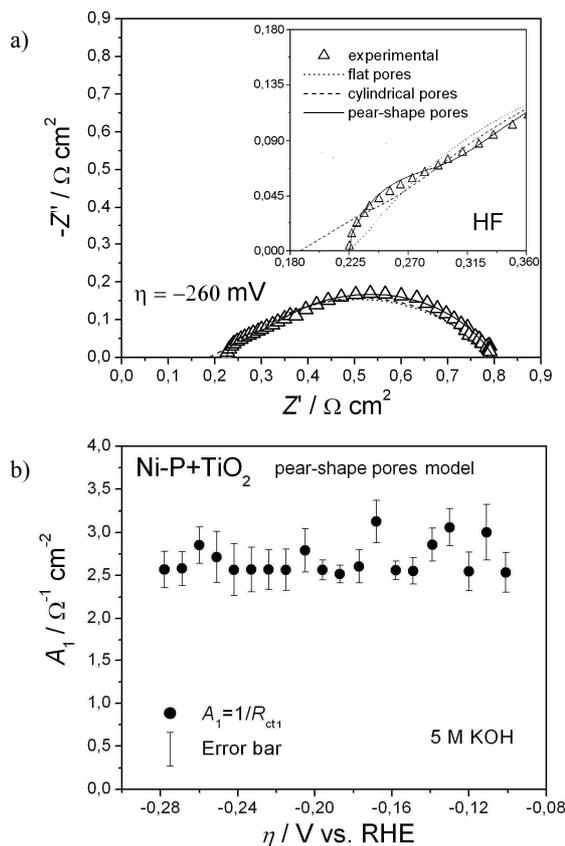


Fig. 5. Complex-plane plot obtained on the Ni-P+TiO₂ electrode at $\eta = -260$ mV during HER in 5 M KOH, at 25°C, fitted to different models shown in Figure 6 in the whole range of frequencies and at high-frequency range (the inset) (a); A_1 parameter as a result of fitting in dependence on overpotential (b)

Rys. 5. Krzywa impedancji otrzymana na elektrodzie Ni-P+TiO₂ przy $\eta = -260$ mV w procesie elektrowydziałania wodoru w 5 M KOH w 25°C, fitowana modelami pokazanymi na rysunku 6 w całym zakresie częstotliwości i przy wysokich częstotliwościach (powiększenie) (a); parametr A_1 jako wynik fitowania w zależności od nadpotencjału (b)

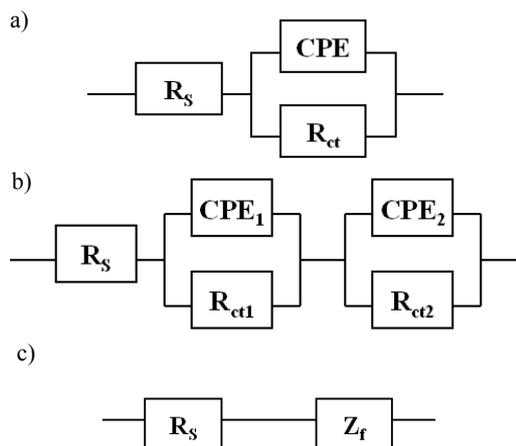


Fig. 6. Electrical equivalent circuits used for HER: a) CPE, b) two-CPE, c) finite length porous models

Rys. 6. Elektryczne obwody zastępcze dla HER: a) model CPE, b) model dwa-CPE, c) model porów o skończonej długości

The best fit for experimental data of the Ni-P+TiO₂ electrode was achieved using the two-CPE model consisting of the solution resistance and a connection of

two parallel R -CPE elements in series, the HF R -CPE element is related to the porosity while the LF element to the kinetics of HER (Fig. 6b). The two-CPE model produces two semicircles on the impedance spectra, where the HF semicircle is related to the surface porosity, and the LF semicircle is due to the charge-transfer process of HER. From the HF part parameters like R_s , $A_1 = 1/R_{ct1}$, T_1 and ϕ_1 could be determined, and from the LF part, connected with the faradaic process, parameters as $A = 1/R_{ct2}$, T and ϕ were found [1, 5, 6, 8]. The average value of parameter A_1 of $2.69 \pm 0.21 \Omega^{-1} \text{ cm}^{-2}$ was determined (Fig. 5b). This indicates that at this electrode, pores of the pear-like shape are present during the continuous hydrogen gas evolution reaction with the constant diameter of $0.37 \Omega \text{ cm}^2$. The ac data obtained on the comparative Ni-P and Ni electrodes showed only one semicircle in the whole frequency range. This behavior is similar to that found for smooth electrodes covered with flat pores (Fig. 6a). Other parameters for all tested electrodes were determined and discussed previously [5]. Based on these results, the activity and the kinetics of HER on the composite Ni-P+TiO₂ electrode and smooth Ni-P as well as Ni electrodes was compared in Table 2.

TABLE 2. Activity and kinetics of HER obtained from Tafel plots and EIS tests at $\eta = -205 \text{ mV}$ in 5 M KOH at 25°C on the Ni-P+TiO₂, Ni-P and Ni electrodes; j_0 - exchange current density, k_{global} - global rate constant of HER and R_f - roughness factor

TABELA 2. Aktywność i kinetyka HER otrzymana z krzywych Tafela i pomiarów EIS przy $\eta = -205 \text{ mV}$ w 5 M KOH w 25°C na elektrodzie Ni-P+TiO₂, Ni-P i Ni; j_0 - gęstość prądu wymiany, k_{global} - globalna stała szybkości HER i R_f - współczynnik chropowatości

Electrode	Shape of a single pore determined by EIS	Activity j_0 , A cm^{-2}	Kinetic parameter of HER k_{global} , $\text{mol s}^{-1} \text{ cm}^{-2}$	R_f	Ref.
Ni-P+TiO ₂	pear-shape	1.43×10^{-3}	$7.0 \pm 0.1 \times 10^{-9}$	950	[5]
Ni-P	flat	1.88×10^{-4}	$9.6 \pm 1.3 \times 10^{-10}$	317	[5]
Ni	flat	6.35×10^{-5}	$4.8 \pm 0.6 \times 10^{-10}$	92	[4]

One can see that impedance modeling for various shapes of a single pore allows for the *in situ* electrochemical characterization of the surface porosity. Knowledge of the pore shape leads to determination of the HER kinetics and surface roughness, and real catalytic activity of electrodes can be known what is of key importance in tailoring of new high-performance electrode materials.

CONCLUSIONS

- The composite Ni-P+TiO₂ coatings can be prepared by *in situ* codeposition of amorphous Ni-P with titanium dioxide powder under proposed electrochemical conditions. Such a deposit con-

tain (wt.%): 52.2 Ni, 17.5 P and 30.3 TiO₂, and it exhibit a composite structure consisting of the metallic Ni-P matrix in which the crystalline TiO₂ (anatase) particles are embedded.

- Modification of smooth polycrystalline Ni by amorphization and embedding of TiO₂ micro-particles into the Ni-P matrix results in the inexpensive/efficient/fast production of the large-surface Ni-P+TiO₂ coatings being an attractive candidate for electrode materials in hydrogen evolution reaction.
- The porosity characterization of such electrodes can be realized by *in situ* EIS measurements which revealed the presence of pear-like shape pores with the diameter of $0.37 \Omega \text{ cm}^2$ on the surface of the composite Ni-P+TiO₂ electrode, and flat pores in the case of Ni-P and Ni electrodes.

Acknowledgement

The author wishes to express its special thanks to Prof. Antoni Budniok (University of Silesia, Poland) and Prof. Andrzej Lasia (Université de Sherbrooke, Québec, Canada) for the collaboration undertaken within the bilateral scientific and technological co-operation agreement in the field of electrochemistry in the areas of new materials for water electrolysis and the studies of the mechanism and kinetics of hydrogen adsorption, absorption and evolution.

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