

Magdalena Popczyk

University of Silesia, Institute of Materials Science, Bankowa 12, 40-007 Katowice, Poland

Corresponding author. E-mail: magdalena.popczyk@us.edu.pl

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ELECTROLYTIC PRODUCTION AND CHARACTERIZATION OF NICKEL COMPOSITE AND ALLOY COATINGS CONTAINING TUNGSTEN

Ni+W composite coating was obtained by electrodeposition from the following electrolyte (concentrations in g dm^{-3}): $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ - 84, H_3BO_3 - 8, CH_3COONa - 10, $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$ - 30, NH_4Cl - 10 + 50 g dm^{-3} of tungsten powder ($< 150 \mu\text{m}$, Aldrich). Ni-W alloy coating was obtained by electrodeposition from the following electrolyte (concentrations in g dm^{-3}): $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ - 13, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ - 68, NH_4Cl - 50, $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$ - 200. Ni+W and Ni-W coatings were prepared under the galvanostatic conditions in such manner, that the coatings contain the same quantity of tungsten. The surface morphology of the coatings was studied using a scanning microscope (JEOL JSM - 6480). Chemical composition of obtained coatings was determined by the X-ray fluorescence spectroscopy (XRF) with a special attachment to the X-ray generator TUR-M62 with flat LiF crystal. The surface of the Ni-W alloy coating is relatively regular of an island character and the surface of the Ni+W composite coating is covered by a well visible velvet-like dark grey tarnish. This composite coating has a matt, rough surface with visible grains of incorporated powder. Introduction of tungsten powder into the nickel matrix causes obtained composite coating of very developed and rough surface. Ni+W and Ni-W coatings contain almost identical quantity of tungsten and therefore was determined influence of manner of tungsten introducing to the nickel matrix on electrochemical properties of these coatings. The electrochemical activity of these coatings was studied in the process of hydrogen evolution reaction (HER) from 5 M KOH solution using steady-state polarization and electrochemical impedance spectroscopy (EIS) methods. Approximations of the experimental impedances permitted determinations of the following parameters: R_{ct} , R_s , T , ϕ and in consequence the surface roughness factor R_f was estimated. It was assumed, that surface roughness factor, is connected with the value of electrochemical active surface. The values of R_f , obtained for the Ni+W composite coating are higher, than that for the Ni-W alloy coating. The reason of this could be increase of real surface area for the Ni+W composite coating. Basing on the results of EIS measurements the rate constants of the HER were determined. It was found that Ni+W composite coating is characterized by enhanced electrochemical activity towards hydrogen evolution as compared with Ni-W alloy coating. An increase in the electrochemical activity may be attributed both to the synergetic effect of tungsten dispersed in the nickel matrix and to the increase in the real surface area resulting from the composite character of coating. Thus obtained composite coating may be useful in application as electrode material for the hydrogen evolution reaction.

Keywords: composite and alloy coatings, hydrogen evolution reaction (HER), electrochemical impedance spectroscopy (EIS)

ELEKTROLITYCZNE OTRZYMYWANIE I CHARAKTERYSTYKA KOMPOZYTOWYCH I STOPOWYCH POWŁOK NIKLOWYCH ZAWIERAJĄCYCH WOLFRAM

Powłokę kompozytową Ni+W otrzymano poprzez elektroosadzanie z kąpeli o następującym składzie (g dm^{-3}): $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ - 84, H_3BO_3 - 8, CH_3COONa - 10, $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$ - 30, NH_4Cl - 10 + 50 g dm^{-3} proszku wolframu ($< 150 \mu\text{m}$, Aldrich). Powłokę stopową Ni-W otrzymano poprzez elektroosadzanie z kąpeli o następującym składzie (g dm^{-3}): $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ - 13, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ - 68, NH_4Cl - 50, $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$ - 200. Powłoki te otrzymano w warunkach galwanostacyjnych, w taki sposób, aby zawierały taką samą ilość wolframu. Morfologię powierzchni otrzymanych powłok określono metodą mikroskopii skaningowej. Badania składu chemicznego wykonano metodą fluorescencji rentgenowskiej. Charakterystykę aktywności elektrochemicznej w procesie wydzielania wodoru w środowisku alkalicznym (5 M KOH) prowadzono metodą stacjonarnych krzywych polaryzacji oraz metodą elektrochemicznej spektroskopii impedancyjnej. Stwierdzono, że powłoka kompozytowa Ni+W charakteryzuje się podwyższoną aktywnością elektrochemiczną w procesie wydzielania wodoru w porównaniu do powłoki stopowej Ni-W. Wzrost aktywności elektrochemicznej może wynikać zarówno z efektu oddziaływania wolframu zdyspergowanego w osnowie niklowej, jak i ze wzrostu rozwinięcia powierzchni. Tak otrzymana powłoka kompozytowa może być zastosowana jako materiał elektrodowy w procesie wydzielania wodoru.

Słowa kluczowe: powłoki kompozytowe i stopowe, proces wydzielania wodoru, elektrochemiczna spektroskopia impedancyjna

INTRODUCTION

Many transition metals have been characterized as hydrogen electrodes. Among them, nickel and nickel-based alloys have a high catalytic activity [1-5]. In order

to improve the utilization of nickel materials and to enhance their electrocatalytic activity, various modifications could be applied, such as the use of composites or

alloys instead of pure elements and other modifications to obtain electrodes with very developed, rough or porous electrode surface [3, 4, 6-11]. Tungsten as component of coatings seems to be interesting on account of its electrochemical properties. In such cathode material, tungsten plays a role of activator in the hydrogen evolution reaction [8-11].

This study was undertaken in order to obtain the nickel coatings, containing the same quantity of an additional component of tungsten, as an embedded phase (Ni+W) and as an alloying component (Ni-W). The purpose of this work was to evaluate effectiveness of these coatings as electrode materials for hydrogen evolution in an alkaline solution.

EXPERIMENTAL

Ni+W composite coating was obtained by electro-deposition from the following electrolyte (concentrations in g dm^{-3}): $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ - 84, H_3BO_3 - 8, CH_3COONa - 10, $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$ - 30, NH_4Cl - 10 + 50 g dm^{-3} of tungsten powder ($< 150 \mu\text{m}$, Aldrich). Ni-W alloy coating was obtained by electrodeposition from the following electrolyte (concentrations in g dm^{-3}): $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ - 13, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ - 68, NH_4Cl - 50, $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$ - 200. Distilled water and 'analytical grade' reagents were used for preparation of the electrolyte. Composite coating was electrodeposited under the galvanostatic conditions, at the current density $j_{\text{dep.}} = 0.100 \text{ A cm}^{-2}$ and alloy coating was electrodeposited under the same conditions, but at the current density $j_{\text{dep.}} = 0.200 \text{ A cm}^{-2}$. A platinum mesh served as an auxiliary electrode. The coatings were deposited on the steel plate (St3S) of the geometric surface area of 1 cm^2 and were used as working electrodes. The surface morphology of the coatings was studied using a scanning microscope (JEOL JSM - 6480). Chemical composition of obtained coatings was determined by the X-ray fluorescence spectroscopy (XRF) with a special attachment to the X-ray generator TUR-M62 with flat LiF crystal. Investigations of electrolytic hydrogen evolution on the prepared coatings were conducted in a three-electrode cell, using steady-state polarization and electrochemical impedance spectroscopy (EIS) methods. These measurements were carried out in 5 M KOH solution, at the temperature of 293 K, using Autolab[®] electrochemical system. The auxiliary electrode was a platinum mesh and the reference electrode was of the type Hg/HgO/5 M KOH. The EIS measurements were performed approximately after 24 h of the HER at the constant current density, $j = 0.320 \text{ A cm}^{-2}$. For each coating, three cycles were recorded. Each cycle consisted of 30 minutes of galvanostatic electrolysis at $j = 0.320 \text{ A cm}^{-2}$ and 43 minutes of curve recording using galvanostatic polarization (45 s per point) ranging from 0.320 A cm^{-2} to $0.1 \mu\text{A cm}^{-2}$. At the steady-state, the electrode potentials were corrected for iR_s drop determined by EIS. In the EIS measurements the amplitude of ac signal was

equal 0.005 V. A frequency range from 10 kHz to 0.1 Hz was covered with 10 points per decade. The real and imaginary components of the complex plane plots were analysed using a modified version of a complex non-linear least-squares fitting program (CNLS) [3, 4] from which the experimental parameters of an electrical equivalent circuit were determined. Assuming that the average double-layer capacitance of a smooth metal surface is $20 \mu\text{F cm}^{-2}$ [12], the surface roughness factor was determined. Kinetics of hydrogen evolution process was determined on basis of the dependences of both the $1/R_{\text{ct}}$ (inverse the charge-transfer resistance) and the total current density j , on overpotential ΔE . The rate constants (k_1 , k_{-1} , k_2 , k_{-2}) were evaluated using the NLS method [3, 4].

RESULTS AND DISCUSSION

Ni+W and Ni-W coatings show good adhesion to the steel substrate. The surface of the Ni-W alloy coating is relatively regular of an island character and the surface of the Ni+W composite coating is covered by a well visible velvet-like dark grey tarnish. This composite coating have a matt, rough surface with visible grains of incorporated powder (Fig. 1a, b). Introduction of tungsten powder into the nickel matrix causes obtained composite coating of very developed and rough surface. Ni+W and Ni-W coatings contain almost identical quantity of tungsten (Tab. 1) and therefore was determined influence of manner of tungsten introducing to the nickel matrix on electrochemical properties of these coatings.

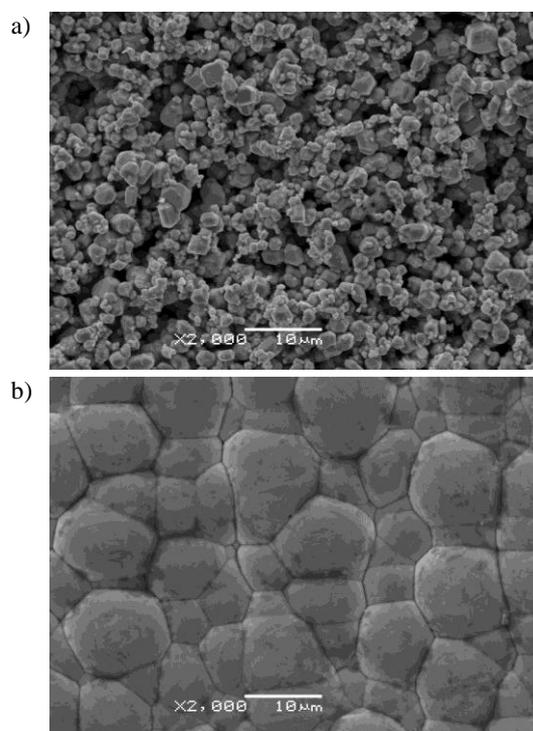


Fig. 1. Surface morphology of Ni+W composite coating (a) and Ni-W alloy coating (b)

Rys. 1. Morfologia powierzchni powłoki kompozytowej Ni+W (a) i powłoki stopowej Ni-W (b)

TABLE 1. Chemical composition of obtained coatings
TABELA 1. Skład chemiczny otrzymanych powłok

Type of coating	Ni, wt. %	W, wt. %
Ni+W	57.7	42.3
Ni-W	56.9	43.1

The electrochemical activity of thus obtained coatings was studied in the process of hydrogen evolution from 5 M KOH solution. The steady-state polarization curves obtained on different electrodes are presented in Figure 2, and the kinetic parameters are presented in Table 2. On the bases of steady-state of the hydrogen evolution, the rate of this process was estimated depending on the type of coatings. The value of hydrogen evolution overpotential at the current density of -100 mA cm^{-2} , ΔE_{100} , is smaller for the Ni+W composite coating than for the Ni-W alloy coating and the value of the exchange current density, j_0 , is higher. As was shown in [6] the value of ΔE_{100} is distinctly higher and value j_0 is distinctly smaller for the nickel coating in comparison with obtained coatings. It means that for obtained coatings the increase in the rate of hydrogen evolution in comparison with nickel coating was observed. For the comparative contents of tungsten in the Ni+W composite coating, significant change of ΔE_{100} and j_0 values was observed (Tab. 2). The reason for the increased activity of Ni+W composite coating for the hydrogen evolution may be connected with the increased surface area.

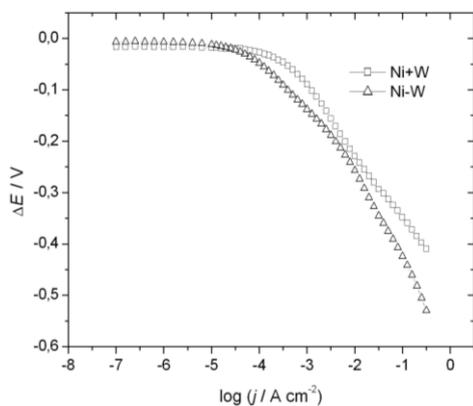


Fig. 2. Dependences of $\Delta E = f(\log j)$ for the hydrogen evolution reaction on Ni+W and Ni-W coatings

Rys. 2. Zależności $\Delta E = f(\log j)$ dla procesu wydzielania wodoru na powłokach Ni+W i Ni-W

TABLE 2. Kinetic parameters of the HER

TABELA 2. Parametry kinetyczne procesu wydzielania wodoru

Type of coating	j_0 A cm^{-2}	ΔE_{100} V
Ni+W	$1.80 \cdot 10^{-4}$	-0.347
Ni-W	$7.52 \cdot 10^{-5}$	-0.424

On solid electrodes ac impedance plots deviate from the classical Randles' equivalent circuit. The typical model for the HER on solid electrodes contained a con-

stant phase element (CPE) instead of the double-layer capacitance.

The presence of the CPE was initially attributed to the surface roughness or porosity (geometric factors) [13], however, it was found experimentally that these factors were unrelated. Recent studies attribute it to the atomic scale inhomogeneities, see [14] and references therein. It is well known that adding small amount of adsorbing ions causes immediate appearance of the CPE. Moreover, on the porous surfaces the de Levie's porous model [15] should be used. It assumes that the electrode materials composed of cylindrical pores of radius r and length l . As it was shown earlier [16] for short and wide pores l^2/r is very small and only one semicircle on the complex plane plot was observed.

Impedance measurements displayed one depressed semicircle on the complex plane plots at all overpotentials. Examples of such plots are presented in Figure 3. Using the complex nonlinear least-squares (CNLS) fitting program the real, Z' , and imaginary, Z'' , components of the electrode impedance could be analysed [16]. The values of real and impedance components are smaller for the Ni+W composite coating than for the Ni-W alloy coating. This means that Ni+W composite coating is characterized by enhanced electrochemical activity for HER compared to Ni-W alloy coating.

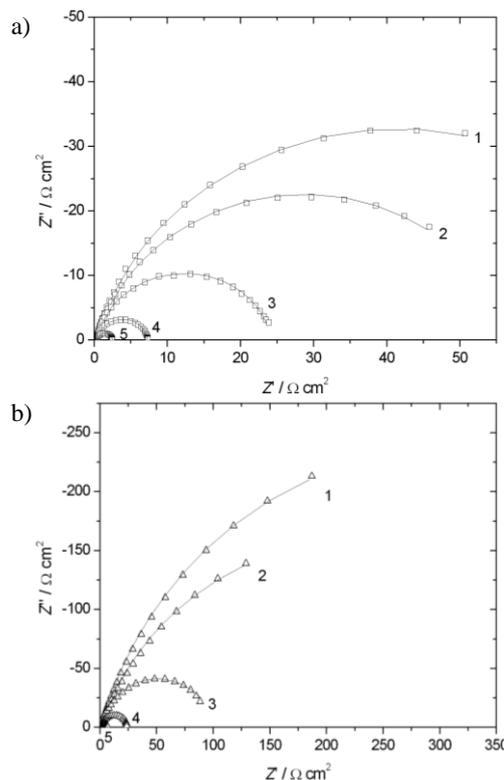


Fig. 3. Dependences of $Z'' = f(Z')$ for the Ni+W composite coating (a) and for the Ni-W alloy coating (b), at the $\Delta E = 0.070 \text{ V}$ (1), $\Delta E = 0.120 \text{ V}$ (2), $\Delta E = 0.170 \text{ V}$ (3), $\Delta E = 0.220 \text{ V}$ (4), $\Delta E = 0.270 \text{ V}$ (5), (\square , Δ - experimental points, — - approximation line)

Rys. 3. Zależności $Z'' = f(Z')$ dla powłoki kompozytowej Ni+W (a) oraz dla powłoki stopowej Ni-W (b), przy nadpotencjałach $\Delta E = 0.070 \text{ V}$ (1), $\Delta E = 0.120 \text{ V}$ (2), $\Delta E = 0.170 \text{ V}$ (3), $\Delta E = 0.220 \text{ V}$ (4), $\Delta E = 0.270 \text{ V}$ (5), (\square , Δ - punkty doświadczalne, — - linia aproksymacji)

It has been found that the ac impedance behaviour may be well described by the one-CPE electrode model. This model consists of the solution resistance, R_s , in series with the parallel connection of the CPE element and charge-transfer resistance, R_{ct} . The Nyquist plots, presented in Figure 3, show a good agreement between the experimental points and approximations. From these plots also results, that values of charge-transfer resistance, R_{ct} , are lower for the Ni+W composite coating than for the Ni-W alloy coating.

CNLS approximations of the experimental impedances permitted determinations of the following parameters: R_{ct} , R_s , T , ϕ , where T is the capacity parameter and ϕ is the CPE angle, $Z_{CPE} = 1/[(j\omega)^\phi T]$. The double-layer capacitance, C_{dl} , was estimates as:

$$T = C_{dl}^\phi (1/R_s + 1/R_{ct})^{1-\phi}$$

and in consequence, surface roughness factor $R_f = C_{dl} / (20 \mu\text{F cm}^{-2})$ was estimated [12]. Relations between R_f and ΔE are presented in Figure 4. It was assumed, that surface roughness factor, R_f , is connected with the value of electrochemical active surface. For the Ni+W composite coating the electrochemical active surface decreases with negative overpotentials, probably because of filling the smaller pores with evolving hydrogen. The values of R_f , obtained for the Ni+W composite coating are higher, than that for the Ni-W alloy coating. The reason of this could be increase of real surface area for the Ni+W composite coating.

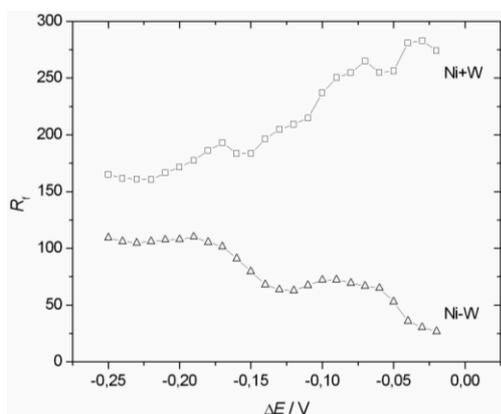


Fig. 4. Dependences of $R_f = f(\Delta E)$ for the Ni+W and Ni-W coatings
Rys. 4. Zależności $R_f = f(\Delta E)$ dla powłok Ni+W i Ni-W

An approximation of the values of $1/R_{ct}$ in function of ΔE and j in function of ΔE was carried out by adjusting the rate constants k_1 , k_{-1} , k_2 , k_{-2} [3, 4] and are presented in Table 3. Values of k_1 , k_{-1} , k_2 and k_{-2} for the Ni+W composite coating are higher than for the Ni-W alloy coating which points at the synergetic effect of tungsten with nickel matrix. Main contribution to the improvement of catalytic properties of Ni+W coating toward HER arises from the increase of the real surface area but tungsten particles can be covered with nickel

and some catalytic effect in points of contact of these two metals also cannot be excluded.

TABLE 3. The rate constants of the HER

TABELA 3. Stałe szybkości procesu wydzielania wodoru

Type of coating	k_1 mol cm ⁻² s ⁻¹	k_{-1} mol cm ⁻² s ⁻¹	k_2 mol cm ⁻² s ⁻¹	k_{-2} mol cm ⁻² s ⁻¹
Ni+W	$9.35 \cdot 10^{-10}$	$1.43 \cdot 10^{-8}$	$1.15 \cdot 10^{-11}$	$7.52 \cdot 10^{-13}$
Ni-W	$6.27 \cdot 10^{-11}$	$2.54 \cdot 10^{-9}$	$3.09 \cdot 10^{-12}$	$7.63 \cdot 10^{-14}$

CONCLUSION

Ni+W and Ni-W coatings could be obtained by electrolytic deposition of crystalline nickel with tungsten - as an alloying component and as an embedded phase. It was found that Ni+W composite coating is characterized by enhanced electrochemical activity towards hydrogen evolution as compared with Ni-W alloy coating. An increase in the electrochemical activity may be attributed both to the synergetic effect of tungsten dispersed in the nickel matrix and to the increase in the real surface area resulting from the composite character of coating. Thus obtained composite coating may be useful in application as electrode materials for the hydrogen evolution reaction in comparison with Ni-W alloy coating.

REFERENCES

- [1] Paseka I., Evolution of hydrogen and its sorption on remarkable active amorphous smooth Ni-P(x) electrodes, *Electrochim. Acta* 1995, 40(11), 1633-1640.
- [2] Paseka I., Vielicka J., Hydrogen evolution and hydrogen sorption on amorphous smooth Me-P(x) (Me = Ni, Co and Fe-Ni) electrodes, *Electrochim. Acta* 1997, 42(2), 237-242.
- [3] Karimi-Shervedani R., Lasia A., Kinetics of hydrogen evolution reaction on nickel-zinc-phosphorous electrodes, *J. Electrochem. Soc.* 1997, 144(8), 2652-2657.
- [4] Karimi-Shervedani R., Lasia A., Study of the hydrogen evolution reaction on Ni-Mo-P electrodes in alkaline solutions, *J. Electrochem. Soc.* 1998, 145(7), 2219-2225.
- [5] Karimi-Shervedani R., Lasia A., Studies of the hydrogen evolution reaction on Ni-P electrodes, *J. Electrochem. Soc.* 1997, 144(2), 511-519.
- [6] Panek J., Serek A., Budniok A., Rówiński E., Łągiewka E., Ni+Ti composite layers as cathode materials for electrolytic hydrogen evolution, *Int. J. Hydrogen Energy* 2003, 28, 169-175.
- [7] Popczyk M., Budniok A., Lasia A., Electrochemical properties of Ni-P electrode materials modified with nickel oxide and metallic cobalt powders, *Int. J. Hydrogen Energy* 2005, 30, 265-271.
- [8] Popczyk M., Serek A., Budniok A., Production and properties of composite layers based on an Ni-P amorphous matrix, *Nanotechnology* 2003, 14, 341-346.
- [9] Popczyk M., Budniok A., Electrochemical properties of Ni-P electrode materials modified with tungsten, *Archiwum Nauki o Materiałach (Archives of Material Science)* 2001, 22(4), 261-269.

- [10] Popczyk M., Budniok A., Elektrolityczne otrzymywanie i charakterystyka warstw kompozytowych Ni-P+W i Ni-P+NiO+W w środowisku alkalicznym, *Kompozyty (Composites)* 2003, 3(6), 17-22.
- [11] Popczyk M., The hydrogen evolution reaction on electrolytic Ni+W+Si and Ni+W+Mo+Si composite coatings, *Physics and Chemistry of Solid State* 2007, 8(4), 767-770.
- [12] Shervedani R.K., Lasia A., Evaluation of the surface roughness of microporous Ni-Zn-P electrodes by *in situ* methods, *J. Appl. Electrochem* 1999, 29, 979-986.
- [13] Lasia A., (in:) Conway B.E., White R.E., *Modern Aspects of Electrochemistry*, Kluwer/Plenum, New York 2002.
- [14] Kerner Z., Pajkossy T., On the origin of capacitance dispersion of rough electrodes, *Electrochim. Acta* 2000, 46(2-3), 207-211.
- [15] de Levie R., (in:) Delahay P., Tobias C.W., *Advances in Electrochemistry and Electrochemical Engineering*, Wiley, New York 1967.
- [16] Lasia A., Nature of the two semi-circles observed on the complex plane plots on porous electrodes in the presence of a concentration gradient, *J. Electroanal. Chem.* 2001, 500, 30-35.