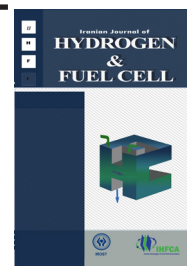Iranian Journal of Hydrogen & Fuel Cell

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Effect of temperature on kinetics of the hydrogen evolution reaction on Ni-P-C cathodes in alkaline solution

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Article Information

Abstract

The kinetics of hydrogen evolution reaction (HER) was studied in 1M NaOH solution at various temperatures (298 to 358 K) on Ni-P-C (composite electrodes). The electrochemical efficiency of the electrodes has been evaluated on the basis of electrochemical data obtained from the steady-state polarization Tafel curves, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) in 1M NaOH solution at 298, 323, 348 and 358 K. The HER rate constants were estimated using Tafel-impedance data assuming the Volmer-Heyrovský path at various temperatures. The k_2 values were smaller than those obtained for hydrogen adsorption rate constants (k_1) at all temperatures. The average values of k_2, which characterize the apparent activity of the electrodes for the HER on the Ni-P-C cathodes, are increased by factors of 4.0, 3.7 and 3.5 from temperatures of 298 to 323 K, 323 to 348 K and 348 to 358 K, respectively. Microstructure and composition of the investigated electrodes were studied using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The kinetic parameters showed that the temperature plays an important role on increase of the activities of Ni-P-C composite cathodes toward the HER.

1. Introduction

Hydrogen evolution reaction (HER) is one of the most studied electrochemical reactions, and an extensive amount of work has been performed in this field. The HER has received wide attention because;

(i) hydrogen is one of the most energy carriers and alternative to fossil fuels. Gaseous hydrogen can be easily produced by water electrolysis, and can be used as a non polluting fuel directly in internal combustion engines or converted to electricity in fuel cells, (ii) the HER is important for such processes as

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water electrolysis in chlorine production, and (iii) electrocatalytic HER supplies hydrogen of very high purity for food and medicine industries [1-3]. The HER is important from a technological viewpoint for such processes as water electrolysis and chlorine production. For these applications materials with low hydrogen overpotential are needed. The activity of a material to the HER is governed by its intrinsic activity and real surface area [4-6]. The noble metals, such as platinum and ruthenium, are the most active materials, but for industrial applications these metals are very expensive [7]. Among more studied transition metals, like Fe, Co, and Ni, only Ni is stable in concentrated alkaline solutions at hydrogen equilibrium potential [8,9]. However, nickel suffers from low electrocatalytic performance and does not resist well to intermittent electrolysis [10-12]. Nickel based electrodes having a non-metallic element, such as phosphorous and carbon, have been developed for hydrogen evolution reaction (HER) due to their high electrocatalytic activity [13-16]. In the previous work [17] we reported the electrocatalytic activities of a Ni-P-C composite electrode toward the HER, where the activities were improved mainly by increasing the intrinsic activity induced by carbon embedded in the Ni-P matrix. The kinetic of the HER on a nickel-phosphorous-carbon (Ni-P-C) composite electrode at room temperature was reported. The increased activity for the Ni-P-C electrode was mostly due to the synergetic effect of carbon. Also, the Ni-P-C electrode was physically, chemically, and electrochemically stable. In the current study the effect of temperature was studied on the kinetic of the HER at Ni-P-C composite electrodes in alkaline solution using steady-state polarization Tafel curves, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) techniques, and the HER rate constants was determined at different temperatures.

2. Experimental procedures

2.1. Electrode preparation

The electrodeposition of Ni-P-C cathodes for the

HER were performed in a three-step method (details described in [17]): first, a layer of Ni was deposited on a copper substrate with an area of 0.229 cm^2 from bath A (Table 1), then Ni-P was coated on Ni from bath B, and finally deposition of carbon with nickel and phosphorous was performed from bath C.

Table 1. Composition and operating conditions of the plating baths.

Constituents and operating conditions of plating baths	Bath		
	A	B	C
$NiSO_4.7H_2O$ (M)	1.14	1.14	1.14
$NiCl_2.6H_2O$ (M)	0.19	0.19	0.19
H_3BO_3 (M)	0.49	0.49	0.49
$Na_3C_6H_5O_7 \cdot 2H_2O$ (M)	0.12	0.12	0.12
$NaH_2PO_2.H_2O$ (M)	-	0.14	0.14
L-Lysine (M)	-	-	0.06
Applied current (mA cm^{-2})	22	22	13
Time (min)	30	45	45
Temperature (K)	298	298	298

2.2. Electrochemical measurements

The steady state polarization Tafel curves and EIS measurements were used to investigate the electrocatalytic activities of the Ni-P-C composite electrodes in 1 M NaOH. In all experiments the working electrode (Ni-P-C) and counter electrode (Pt plate with area 25 cm^2) compartments were thermostated at 298, 323, 348 and 358 K, while the reference electrode (Hg/HgO/1 M NaOH) was held at room temperature. In order to obtain the stationary conditions necessary for impedance measurements, the working electrodes were polarized at 100 mA for 1 h in 1 M NaOH at each temperature. Hence, the investigated electrodes were cycled galvanostatically to obtain Tafel curves; each cycle contained sweeping current from 100 mA down to 20 µA (45 s per each point). The reproducible Tafel curves were obtained mostly after 10 cycles. At the steady-state, the last curve was recorded and corrected for an ohmic drop deduced from EIS measurements. The kinetic parameters, i.e. Tafel slope (b), exchange current density (j_0), and overpotential at the current density of 250 mA cm^{-2} (η_{250}) were evaluated for each

electrode. The EIS measurements were performed at the steady-state, a 5 mV amplitude AC potential (14 mV peak-to-peak) superimposed on a DC potential was applied, and a wide range of the frequency, 10 kHz to 0.1 Hz, was scanned with ten points per decade in logarithmic scale. Measurements were performed by using Potentiostat/Galvanostat PARSTAT 2273. The EIS data were approximated using ZView® software and the modified complex nonlinear least squares (CNLS) method. The structure of the investigated electrodes was determined by X-ray diffraction (XRD) analysis (Philips-X'Pert-MPD) using Cu Kα wavelength of 1.5418 Å.

3. Results and discussion

3.1. Electrode composition and surface morphology

Composition, physical stability, and activity of the Ni-P-C electrodes for the HER depend on various parameters of the preparation bath such as current density, concentration of the chemical reagents in the bath, temperature, and electrodeposition procedure. The SEM micrographs obtained on the surface of as-deposited Ni-P-C composite electrode (Fig. 1) displayed a rough surface and globular fungi-form structure. The surface roughness contributes substantially to the enlargement of the electrode real surface area and to the number of catalytically active sites. The surface of the investigated electrodes toward HER at the studied temperatures (298 to 358K) showed no change in morphology, and therefore predicted the activity of the Ni-P-C composite electrodes mainly from their intrinsic activities (i.e. synergetic effect) not from the surface roughness. The diffraction pattern of the studied Ni-P-C composite electrode is shown in Fig. 2 and revealed that the investigated electrode was amorphous and exhibited a single broad peak centered at 42.5°. The XRD patterns obtained here for Ni-P-C composite coatings prepared via the L-lysine method by electrodeposition are very similar to those prepared via the graphite method by electroless-deposition [18], confirming formation of Ni-P-C composite coatings in

this work. As an approximation, Scherrer's equation was used to calculate the mean size of the ordered (crystalline) domain [19]. This value was about 3.4 nm for the Ni-P-C electrode.
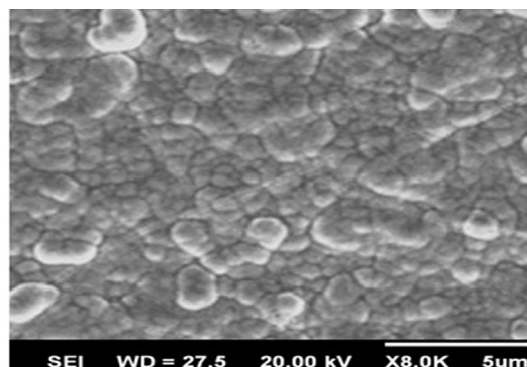

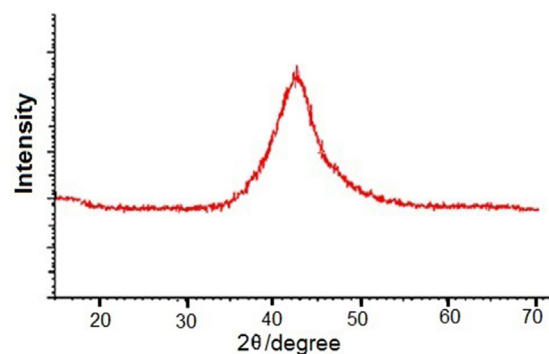**Fig. 1. The SEM images of as-deposited Ni-P-C composite electrode.**

Fig. 2. XRD spectra of as-deposited Ni-P-C electrode using CuKa wavelength of 1.5418 Å.

3.2. Kinetic studies

3.2.1. Steady-state polarization curves

Typical Tafel curves obtained for the HER in 1 M NaOH on the Ni-P-C composite electrodes at 298, 323, 348 and 358 K are displayed in Fig. 3. The steady-state polarization Tafel curves obtained on the studied electrodes showed only one slope in the whole potential range. This behavior is similar to previous findings for Ni-P-C composite electrodes at room temperature [17]. Kinetic parameters of the HER determined from the linear part of the Tafel curves, i.e. exchange current density, Tafel slopes, and η_{250} are presented in Table 2. The Tafel slopes have high values,

which increase with solution temperature. In addition, there is a significant increase in the exchange current density of the HER with increasing temperature. A comparison between j_0 and η_{250} at various temperatures revealed that temperature plays an important role in the increase of activity of the Ni-P-C composite electrode. The steady-state polarization studies alone are not enough to explain the kinetics of HER. Thus, more precise information was obtained by the EIS and analyzed in conjunction with the Tafel curve data.
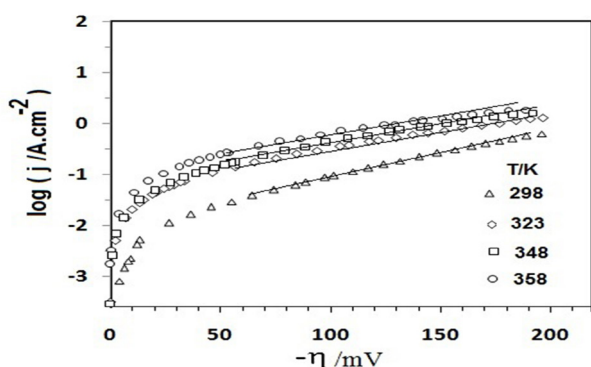

Fig. 3. Steady-state polarization Tafel curves obtained on Ni-P-C composite electrode in 1 M NaOH at various temperatures (298, 323, 348 and 358 K).

Table 2. Experimental parameters of kinetics of the HER on Ni-P-C electrode in 1 M NaOH solution at various temperatures, obtained by the Tafel curves.

T/ K	$j_0 \times 10^3$ (A cm^{-2})[1]	b (mV dec^{-1})[2]	$-\eta_{250}$ (mV)[3]
298	12.2	125	146
323	73.6	166	85
348	95.7	170	73
358	181.9	200	51

[1] Exchange current density
[2] Tafel slopes were obtained from linear part of the Tafel curves analysis
[3] Overpotential at j = 250 mA cm^{-2}

3.2.2. Electrochemical impedance spectroscopy

In the present work, the EIS has been used to examine the interfacial behavior and to find the activities of Ni-P-C composite electrodes toward the HER. The experimental electrochemical impedance spectra of

the Ni-P-C composite electrode in alkaline solution at a constant overpotential of η= -130 mV vs. Hg/HgO/1 M NaOH, taken from the Tafel region of the HER polarization curves (Fig. 3) and at various temperatures, are presented as Nyquist (A) and Bode (B) diagrams in Fig. 4.
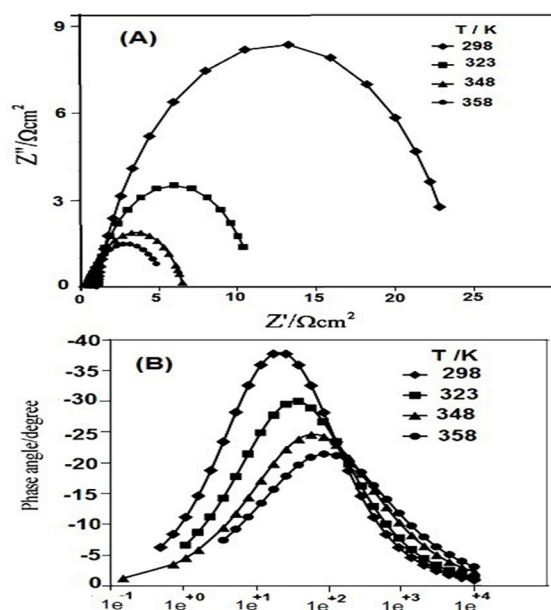

Fig. 4. Complex plane (A) and Bode (B) plots of the EIS measurements obtained for the HER on Ni-P-C composite electrode in 1 M NaOH, taken in overpotential η = -130 mV vs Hg/Hg/1 M NaOH at different temperatures (298, 323, 348 and 358 K) and a constant overpotential of η=-130 mV. Continues lines show the approximated data using linear regression analysis and symbols represent the experimental data.

The EIS measurements obtained on the studied electrodes at various temperatures displayed only one depressed semicircle on the complex plane plots (Fig. 4A) for the entire range of the studied temperatures. The Nyquist diagrams confirm the charge transfer controlled kinetics, and as expected show a decrease in the charge transfer resistance for the HER with solution temperature. After testing the models related to the HER, considering fit criteria such as "number of model parameters" and "Chi square values", the one CPE model was found to be enough for approximations of the EIS data of investigated electrode at various temperatures. This model consists

of a solution resistance (R_s) in series with the parallel connection of the CPE element and charge transfer resistance (R_{ct}). Accordingly, approximation of the experimental EIS data with one-CPE model permitted estimation of the R_s, T, R_{ct}, and parameters. Although the exact determination of the R_f (roughness factor) is not easy, comparison of double layer capacitances (C_{dl}) with 20 μF cm^{-2} for a smooth electrode is one of the suggested methods [20]. The values of 239, 373, 529 and 557 were obtained for R_f of the Ni-P-C cathodes toward the HER at 298, 323, 348 and 358 K, respectively (Table 3).

Table 3. Average double layer capacitance (Cdl,ave) and roughness factor (Rf) obtained on Ni-P-C cathode toward the HER in 1M NaOH at different temperatures by EIS and CV methods.

| T/K	EIS			CV	
	$C_{dl,ave}$ (μFcm^{-2})	R_f	R_{ct}/Ω cm^2	$C_{dl,ave}$ (μFcm^{-2})	R_f
298	4790	239	23.1	4928	246
323	7460	373	10.4	7462	382
348	10580	529	6.1	11050	552
358	11140	557	5.2	12028	601

3.2.3. Rate constants

A linear variation was observed for log ($1/R_{ct}$) as a function of η for the Ni-P-C composite electrode at various temperatures (Fig. 5). The slopes value obtained for the Ni-P-C electrode was 111.0, 142.0, 166.6 and 333.0 mVdec^{-1} at 298, 323, 348 and 358 K, respectively. These values are in agreement with those obtained from Tafel curves (Fig. 3 and Table 2). Different methods such as the galvanostatic step, open circuit potential decay, and Tafel-impedance have already been reported to be effective for evaluation of the rate constants of the HER in alkaline solutions, as previously described in [17]. The kinetic parameters were extracted by simultaneous fitting of the Tafel and EIS data (i.e. Tafel-impedance method) to the corresponding kinetic equations using the NLS method. The mechanism of HER in alkaline solution involves the formation of an adsorbed hydrogen atom intermediate, MH_{ads} (Volmer reaction):

$$H_2O + M + e^- \rightarrow MH_{ads} + OH^- \qquad (1)$$
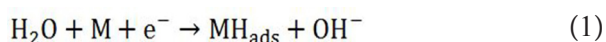
The electrochemical desorption of hydrogen into the solution (Heyrovský reaction):

$$H_2O + MH_{ads} + e^- \rightarrow H_2 + M + OH^- \qquad (2)$$
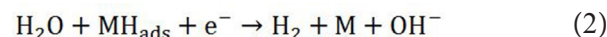
And/or a chemical desorption by the combination of two atoms (Tafel reaction):

$$MH_{ads} + MH_{ads} \rightarrow H_2 + 2M \qquad (3)$$
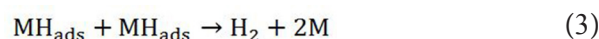
where M represents the electrode materials and MH_{ads} the hydrogen adsorbed on the electrode surface. Heyrovský or Tafel reactions are alternative desorption steps for H_2 formation but each follows the Volmer reaction. The distinction between Volmer, Heyrovský and Tafel reactions as rate-determining steps in the HER is usually accomplished from Tafel slopes or by calculating the rate constants of the forward and backward reactions through simultaneous fitting of polarization and impedance data. The reaction rates for Volmer, Heyrovský and Tafel reactions can be expressed as follows [19-22]:

$$\upsilon_1 = K_1(1-\Theta)\exp(-\beta_1 f\eta) - K_{-1}\Theta \exp(1-\beta_1)f\eta \qquad (4)$$

$$\upsilon_2 = K_2\Theta\exp(-\beta_2 f\eta) - K_{-2}(1-\Theta)\exp(1-\beta_2)f\eta \qquad (5)$$

$$\upsilon_3 = K_3\Theta^2 - K_{-3}(1-\Theta) \qquad (6)$$

where k are the rate constants, β_1 and β_2 are the charge transfer coefficients for Volmer and Heyrovský reactions, respectively, Θ is the surface coverage by adsorbed hydrogen, and f= F/RT.

The kinetic parameters were extracted by simultaneous fitting of the Tafel and EIS data (i.e. Tafel-impedance method) to the corresponding kinetic equations using the NLS method. The experimental curves (log j- η and log $1/R_{ct}$- η) were fitted to the equations below [19 21]:

$$i = F\{K_1(1-\Theta)e^{-\beta f\eta} + K_2\Theta e^{-\beta_2 f\eta}\} \qquad (7)$$

$$R_{ct}^{-1} = \left(\frac{F^2}{RT}\right)\{K_1\beta_1(1-\Theta)e^{-\beta_1 f\eta} + K_2\beta_2\Theta e^{-\beta_2 f\eta}\} \qquad (8)$$

It was sufficient to assume the Volmer–Heyrovský mechanism to explain the experimental data.

The apparent rate constants and symmetry factors obtained for studied electrode are presented in Table 4. The rate constants obtained for electrochemical hydrogen desorption (k_2) at a temperature of 298 ($(5.5\pm0.1)\times10^{-9}$ mol cm^{-2}s^{-1}) to 358 K ($(7.1\pm0.4)\times10^{-8}$ mol cm^{-2}s^{-1}) increased more than one order; and therefore, one could conclude that the increase of temperature from 298 to 358 K could increase the HER activity of Ni-P-C [17] more than one order. However, the k_2 values were smaller than those obtained for the hydrogen adsorption rate constants (k_1) at all temperatures. This behavior revealed that the Heyrovský reaction is the rate-determining step for the HER kinetics on the studied electrode at all studied temperatures.
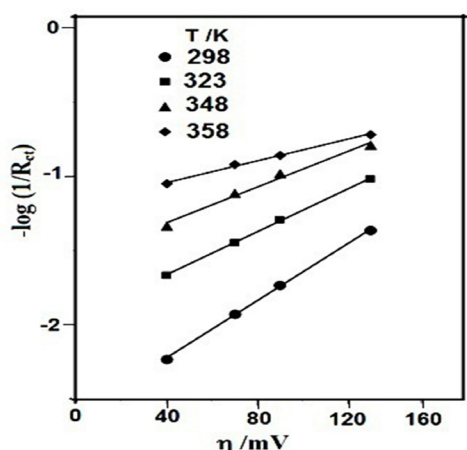

Fig. 5. Dependence of inverse of the charge transfer resistance ($1/R_{ct}$) on overpotential obtained for the HER in 1 M NaOH at different temperatures on the Ni-P-C composite electrode. Symbols indicate experimental results and solid lines approximated data.

Table 4. Kinetic parameters of the HER obtained on Ni-P-C electrode from the steady-state polarization curves and EIS measurements in 1M NaOH, at various temperatures using NLS program.

T(K)	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})[1]	β_1	β_2
298	$(9\pm0.3)\times10^{-8}$	$(2.6\pm0.2)\times10^{-8}$	$(5.5\pm0.1)\times10^{-9}$	$(3.4\pm0.2)\times10^{-8}$	0.55 ± 0.05	0.58 ± 0.09
323	$(2.7\pm0.3)\times10^{-7}$	$(2.9\pm0.3)\times10^{-8}$	$(2.1\pm0.2)\times10^{-8}$	$(5.7\pm0.1)\times10^{-8}$	0.58 ± 0.02	0.62 ± 0.04
348	$(5.5\pm0.2)\times10^{-7}$	$(3.1\pm0.3)\times10^{-8}$	$(6.2\pm0.1)\times10^{-8}$	$(7.7\pm0.1)\times10^{-8}$	0.57 ± 0.02	0.63 ± 0.04
358	$(7.4\pm0.1)\times10^{-7}$	$(3.4\pm0.2)\times10^{-8}$	$(7.1\pm0.4)\times10^{-8}$	$(8.3\pm0.1)\times10^{-8}$	0.54 ± 0.02	0.58 ± 0.04

[1]k $_{-2}$ = k$_1$k$_2$/k$_{-1}$ Taken from Ref. [19]

3.2.4. Cyclic voltammetry

The CV measurements were also employed to find the C_{dl} of the Ni-P-C composite electrode in 1 M NaOH at various temperatures for a scan rate of 400 mV/s in the no reaction region, i.e. -0.800 to -1.000V vs Hg/HgO/1 M NaOH, and are displayed in Fig. 6. In this region the average of capacitive current is proportional to the double layer capacitance, $j_{dl,ave}$=$C_{dl}U$ [23]. The variation of the average of double layer current densities ($j_{dl,ave}$= ($|j_c|$ + $|j_a|$)/2 at E = −0.920 V) as a function of scan rate (υ) for various temperatures are shown as the inset (Fig. 6). The increasing temperature increased the slope of the $j_{dl,ave}$-υ curve, i.e. C_{dl}. The R_f was found for Ni-P-C at various temperatures (Table 3). These results are in agreement with those obtained from EIS measurements (Table 3).
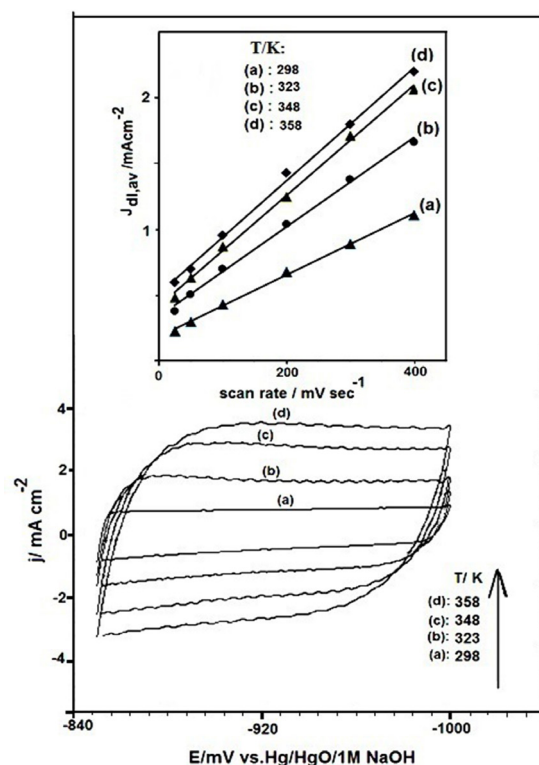

Fig. 6. Cyclic voltammograms obtained on the Ni-P-C composite electrode in the potential range of −0.800 to −1.000V vs. Hg/HgO/1 M NaOH electrode in 1 M NaOH at different temperatures and in scan rate of 400 mV/s. Inset shows variation of the average double layer current densities as a function of scan rate at different temperatures.

4. Conclusion

A Ni-P-C composite electrode, as an active material for the HER, was prepared at low current densities by incorporation of carbon nanoparticles into the Ni-P matrix via $_L$-lysine reduction during electrodeposition from an aqueous solution, and then studied toward the HER in 1 M NaOH slution at temperatures of 298, 323, 348 and 358 K for the first time. The effect of temperature on the electrocatalytic behavior of the investigated cathode for the HER was studied quantitatively by polarization Tafel curves, EIS and CV techniques for the first time. The rate constants for the investigated catalyst were evaluated by simultaneous fitting of the Tafel and EIS data (i.e. Tafel-impedance method) at all studied temperatures. The k_2 values were smaller than those obtained for hydrogen adsorption rate constants (k_1) at all temperatures. This behavior revealed that Heyrovský reaction is the rate-determining step for the HER kinetics on the studied electrode at all studied temperatures. The increased temperature of the HER, increased more effectively in the Heyrovský reaction i.e. electrochemical desorption of the hydrogen from surface of the Ni-P-C electrodes.

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