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ENHANCEMENT OF HYDROGEN EVOLUTION REACTION ON NICKEL BASED ELECTRODES MODIFIED WITH PLATINUM NANOPARTICLES

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Abstract

Nickel-platinum based electrodes with different Pt content have been prepared by spray pyrolysis technique. The electrochemical characterization for hydrogen evolution reaction (HER) was investigated by electrochemical impedance spectroscopy (EIS) technique. The present study concerns the preparation of several Ni based platinum electrode materials and the evaluation of their electrocatalytic properties toward the reaction of hydrogen evolution reaction (HER).

Keywords: Hydrogen evolution reaction, Nickel electrode, Platinum nanoparticles, Electrochemical impedance spectroscopy.

INTRODUCTION

The hydrogen evolution reaction (HER) is one of the most intensively investigated electrochemical processes and has served as a model for electrocatalysis studies over the past six decades. The reaction rate of the HER on platinum is very fast with the exchange current density on the order of mA/cm^2 (Bockris J. O'M. et al, 1969) when pure hydrogen gas is fed, and the reaction is usually controlled by the mass transport of hydrogen at the electrode/electrolyte interface. This reaction, nevertheless, still deserves further investigation, as new aspects of the mechanism are continually being discovered.

Choice of the electrode or electrolyte as well as variation of other conditions at the electrode and solution interface can cause the change of the Tafel slopes for hydrogen oxidation and evolution reactions due to the different mechanism dominating in the given system. As the overall HER involves transfer of two electrons, it can therefore be divided into two elementary steps involving the participation of adsorbed H atoms. So far, two reaction pathways are considered as the most probable for the hydrogen evolution reaction (Bockris J. O'M. et al, 1969): discharge-recombination path and discharge-electrochemical desorption path. In case of alkaline solution, the discharge-recombination path, which is also well known as the Volmer-Tafel mechanism, can be expressed as:

$M + H_2O + e^- \rightarrow MH + OH^-$ (Volmer Reaction) (Eq. 1)

$2MH \rightarrow 2M + H_2$ (Tafel Reaction) (Eq. 2)

where M indicates the metal electrode, and MH is the adsorbed state of the hydrogen atom on metal electrode surface.

The discharge- electrochemical desorption path, also known as the Volmer- Heyrovsky mechanism, can be expressed as:

$M + H_2O + e^- \rightarrow MH + OH^-$ (Volmer Reaction) (Eq. 3)

$MH + H_2O + e^- \rightarrow H_2 + M + OH^-$ (Heyrovsky Reaction) (Eq. 4)

The first discharge step that water discharges on the metal electrode surface and forms an adsorbed H atom is common to both paths, but the mode of the removal of the adsorbed H atom is different. Each step can be rate determining (assuming that the reaction is activation controlled and not by mass transport), and the theoretical forecast of the criteria for kinetic parameters of each mechanism was provided by Bockris (Bockris J. O'M. et al, 1969), which is also used as a reference for the present work. When noble metal electrodes like platinum are used, the exchange current density reaches as high as 10^{-3} A/cm^2, then the overall reaction can be governed by the diffusion of the molecular hydrogen away from the electrode surface:

$$H_{2,s} \rightarrow H_{2,b}$$

where $H_{2,s}$ and $H_{2,b}$ are the molecular hydrogen at the electrode surface and in the bulk of the solution, respectively.

The electrochemical impedance spectroscopy is a powerful, nondestructive, and informative technique (Barsoukov E. et al, 2005), which is usually used for characterization and study of the corrosion phenomena (Mansfeld F. et al, 1991, Priyantha N. et al, 2004), coatings and conductive polymers (Inzelt G. et al, 1994, Gimenez-Romero D. et al.,2006), adsorption behavior of inorganic thin films (Benavente J. et al, 1996), self-assembled monolayer (Nahir T.M.et al, 1994, Shervedani R.K. et al, 2006), fuel cells and batteries (Lasia A., 2002, Lasia A, 2003), sensors and biosensors (Shervedani R.K. et al, 2006, Ma Y. et al, 2005) and kinetics of the HER (Lasia A. et al, 1990, Los P. et al, 1993, Hitz C. et al, 2002).

Typical models for the HER on solid electrodes contain a constant phase element (CPE) instead of the double layer capacitance (Lasia A., 2002, Lasia A, 2003). Presence of the CPE was initially attributed to roughness or porosity (geometric factors) (Pajkossy T., 1994) and by the recent studies to the atomic scale in homogeneities of the surface (Kerner Z. et al, 2000).

MATERIAL AND METHOD

Materials

Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) and isopropanol (99.7%) obtained from Sigma-Aldrich were used for preparation of Pt salt precursor solution. All reagents were of analytical grade purity and used as received.

A smooth nickel plate with a diameter of 10 mm was used as electrode substrate. A fixed quantity of mixture was then sprayed, using an ultrasonic nebulizer SONO-TEK Corporation Exacta Coat onto the top surface of the nickel plate to prepare the electrode. After deposition, the electrode was heated at 350°C for 30 minutes to achieve the solvent evaporation and to obtain the Pt nanoparticles.

Methods

EIS measurements were carried out using the FRA module of Biologic SP150, in the frequency range from 0.01 Hz to 100 kHz and AC voltage amplitude of 10 mV. For each spectrum 60 points were collected, with a logarithmic distribution of 10 points per decade. The experimental electrochemical impedance data were fitted to the electrical equivalent circuit by CNLS Levenberg – Marquardt procedure using ZView – Scribner Associates Inc. software.

Electrochemical experiments were performed in a three-electrode electrochemical cell. The three-electrode system consisted of a working electrode (i.e. smooth Ni, smooth Ni-Pt1 and smooth Ni-Pt3), embedded in a Teflon holder, exposing a geometric surface area of 0.5 cm^2, two graphite roads as counter electrodes, and a Ag/AgCl as reference electrode (Ag/AgCl = +0.197 V vs. NHE; NHE represents the normal hydrogen electrode). All experiments were carried out in 1 M NaOH supporting electrolyte solution at different temperatures using a Thermo Scientific DC 10 thermostat, having an accuracy of ± 0.1 K.

RESULTS AND DISSCUSIONS

The electrochemical impedance spectroscopy (EIS) technique was used to further investigate the electrode/ electrolyte interface characteristics and the corresponding processes. EIS measurements were carried out at eight different selected overpotentials situated in the hydrogen region, in 1M NaOH supporting electrolyte at ambient temperature 298 K.

The experimental data were fitted to the equivalent circuit given in Figure 1, using a complex non-linear least squares procedure. It contains an ohmic resistance (R_s) in series with a parallel connection between the charge transfer resistance (R_{ct}) at the electrode/solution interface and the double layer capacity (*CPE*).

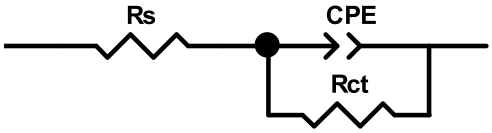


Fig. 1 Equivalent electric circuit for modelling HER on different Ni electrodes in 1 M NaOH solution.

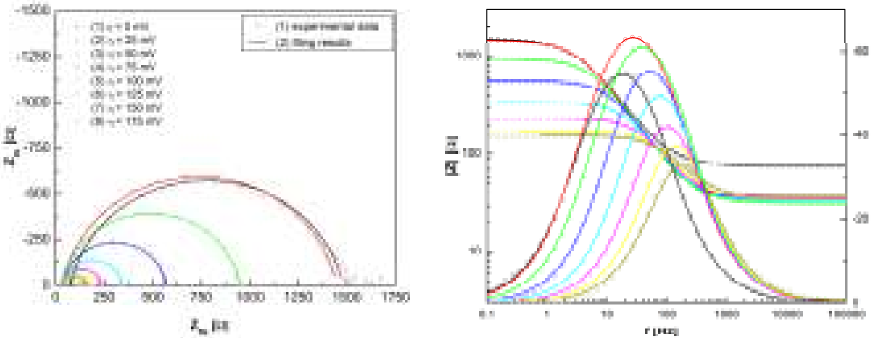
The resistance Rs includes the uncompensated solution resistance. The double layer capacity is usually replaced by a constant phase element (CPE) since it has been observed that it describes more accurately the behaviour of real electrochemical systems.

The impedance of a constant phase element is given by:

$$Z_{CPE} = 1/T(j\omega)^n$$

where T is a parameter related to the double layer capacity, n is an exponent between 0 and 1 and ω is the angular frequency. The case n=1 describes an ideal capacitor while the case n=0 describes a pure resistor. When the value of 0.5 implies that the circuit reflected the Warburg impedance (Chung S.C. et al, 2000).

Fig. 2a and b presents Nyquist and Bode plots on smooth Ni electrode.



a) b)

Fig. 2 Experimental Nyquist (a) and Bode (b) plots recorded for HER on smooth Ni electrode at different overpotential in 1 M NaOH solution. Open symbols are experimental points and continuous line are simulated by the CNLS fitting according to the equivalent circuit.

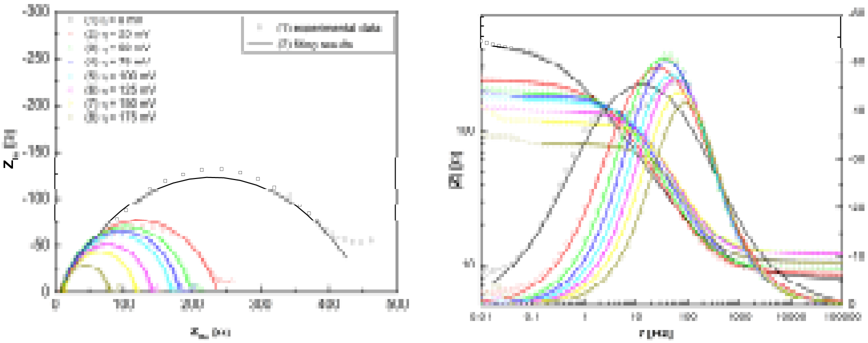
Table 1 shows the obtained values of the circuit elements for HER on smooth Ni electrode at different overpotential in 1 M NaOH solution.

Table 1

Calculated values of the circuit elements during HER on smooth Ni in 1 M NaOH solution; experimental error is specified in parentheses

η [mV]	**R_s [Ω cm^2]**	**T · 10^5 [F cm^{-2} s^{n-1}]**	**n**	**R_{ct} [Ωcm^2]**	**Chi^2 · 10^3**
0	76.1 (0.19%)	4.95 (0.81%)	0.87 (0.18%)	1405 (0.30%)	0.80
25	35.6 (0.11%)	4.40 (0.37%)	0.89 (0.07%)	1410 (0.14%)	0.17
50	32.1 (0.15%)	4.12 (0.57%)	0.90 (0.11%)	919 (0.18%)	0.33
75	34.8 (0.20%)	3.80 (0.99%)	0.91 (0.18%)	535 (0.25%)	0.08
100	33.6 (0.27%)	3.47 (1.62%)	0.92 (0.28%)	307 (0.33%)	1.46
125	36.1 (0.30%)	3.25 (2.31%)	0.92 (0.38%)	196 (0.42%)	1.89
150	35.1 (0.35%)	2.91 (3.14%)	0.93 (0.49%)	141 (0.48%)	2.77
175	37.1 (0.32%)	2.66 (3.35%)	0.94 (0.51%)	117 (0.48%)	2.09

In figure 3a and b are presented Nyquist and Bode plots on smooth Ni-Pt1 electrode.



a) b)

Fig. 3 Experimental Nyquist (a) and Bode (b) plots recorded for HER on smooth Ni - Pt1 electrode at different overpotential in 1 M NaOH solution. Open symbols are experimental points and continuous line are simulated by the CNLS fitting according to the equivalent circuit.

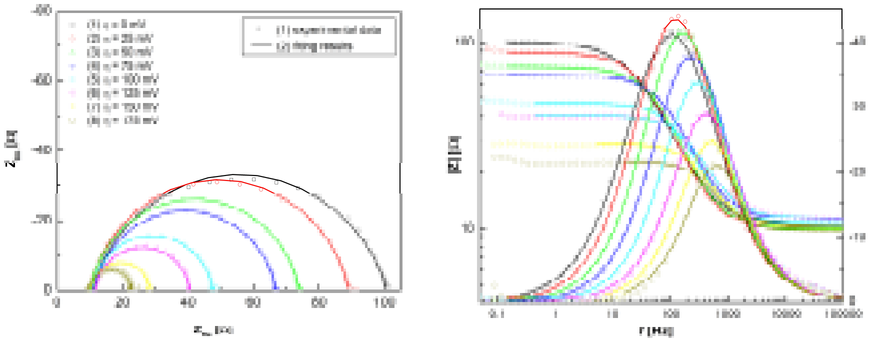
Table 2 shows the obtained values of the circuit elements for HER on smooth Ni-Pt1 electrode at different overpotential in 1 M NaOH solution.

Table 2

Calculated values of the circuit elements during HER on smooth Ni-Pt1 in 1 M NaOH solution; experimental error is specified in parentheses.

η [mV]	**R_s [Ω cm^2]**	**T · 10^5 [F cm^{-2} s^{n-1}]**	**n**	**R_{ct} [Ωcm^2]**	**Chi^2 · 10^3**
0	7.9 (1.37%)	18.83 (1.67%)	0.80 (0.31%)	445 (2.02%)	1.01
25	8.5 (0.85%)	12.45 (1.34%)	0.86 (0.23%)	228 (0.92%)	0.92
50	9.4 (0.33%)	9.79 (1.25%)	0.87 (0.20%)	188 (0.43%)	0.48
75	10.6 (0.15%)	7.60 (1.51%)	0.87 (0.24%)	172 (0.17%)	0.36
100	12.4 (0.10%)	6.66 (2.18%)	0.89 (0.32%)	158 (0.12%)	0.14
125	12.1 (0.54%)	5.49 (3.43%)	0.90 (0.50%)	130 (0.11%)	0.15
150	12.5 (0.10%)	5.49 (4.16%)	0.92 (0.58%)	106 (0.13%)	0.17
175	10.6 (0.11%)	5.11 (4.89%)	0.93 (0.64%)	69 (0.13%)	0.21

Fig. 4a and b presents Nyquist and Bode plots on smooth Ni- Pt3 electrode.



a) b)

Fig.4 Experimental Nyquist (a) and Bode (b) plots recorded for HER on smooth Ni - Pt3 electrode at different overpotential in 1 M NaOH solution. Open symbols are experimental points and continuous line are simulated by the CNLS fitting according to the equivalent circuit.

Table 3 shows the obtained values of the circuit elements for HER on smooth Ni-Pt3 electrode at different overpotential in 1 M NaOH solution.

Table 3

Calculated values of the circuit elements during HER on smooth Ni-Pt3 in 1 M NaOH solution; experimental error is specified in parentheses.

η [mV]	**R_s [Ω cm^2]**	**T · 10^4 [F cm^{-2} s^{n-1}]**	**n**	**R_{ct} [Ωcm^2]**	**Chi^2 · 10^3**
0	10.3 (0.29%)	11.59 (3.17%)	0.64 (0.98%)	91 (0.33%)	0.97
25	9.9 (0.21%)	4.98 (2.90%)	0.75 (0.71%)	79 (0.24%)	0.67
50	10.0 (0.18%)	3.07 (1.37%)	0.81 (0.30%)	64 (0.20%)	0.52
75	11.2 (0.19%)	2.39 (0.67%)	0.82 (0.83%)	56 (0.21%)	0.65
100	10.6 (0.23%)	1.97 (0.47%)	0.83 (0.10%)	37 (0.28%)	0.88
125	11.5 (0.30%)	1.73 (0.51%)	0.85 (0.10%)	29 (0.39%)	1.76
150	10.2 (0.28%)	1.54 (0.62%)	0.86 (0.12%)	18 (0.53%)	1.10
175	9.9 (0.26%)	1.53 (0.73%)	0.87 (0.13%)	13 (0.63%)	0.93

Based on the results gathered in Table 1, 2 and 3 it can be noticed that the charge transfer resistance R_{ct} is significantly lower for smooth Ni-Pt1 and smooth Ni-Pt3 electrodes compared with smooth Ni electrode. Also, decreased value of charge transfer resistance indicated an improving catalytic activity for hydrogen evolution reaction.

Double layer capacitance can be calculated for HER on different smooth Ni electrodes-modified with Pt nanoparticles from the results presented above. C_{dl} relationship can be expressed as:

$$T = C_{dl}{}^{n}\left(R_S^{-1} - R_{ct}^{-1}\right)^{1-n}$$

from which results:

$$C_{dl} = T^{1/n}\left(\frac{1}{R_S} - \frac{1}{R_{ct}}\right)^{\frac{n-1}{n}}$$

Table 4

Calculated values of the C_{dl} during HER on different Ni electrodes in 1 M NaOH solution

η [mV]	**$C_{dl} \cdot 10^5$ [F cm^{-2}]**		
	smooth Ni	**smooth Ni-Pt1**	**smooth Ni-Pt3**
0	3.38	10.14	26.09
25	3.17	6.83	16.96
50	2.88	5.50	12.51
75	2.60	4.06	9.90
100	2.36	3.89	7.32
125	2.15	3.10	6.71
150	1.87	3.42	5.71
175	1.57	3.34	6.28

CONCLUSIONS

Electrochemical impedance spectroscopy results confirm an overall enhancement of hydrogen evolution reaction on different types of smooth Ni-based electrodes modified with Pt nanoparticles, as indicated by the lower values of charge transfer resistance.

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