Chemical Bulletin of "Politehnica" University of Timisoara, ROMANIA
Series of Chemistry and Environmental Engineering
Chem. Bull. "POLITEHNICA" Univ. (Timisoara) ***Volume 59(73), 2, 2014***

Hydrogen Evolution Reaction on Nickel-Based Platinum Electrodes

A. Iacob, M. Dan, A. Kellenberger and N. Vaszilcsin

*Department of Applied Chemistry and Engineering of Inorganic Compounds and Environment, University Politehnica Timisoara, Vasile Parvan 6, 300223, Timisoara, Romania, Tel.: +40256404180; Fax: + 40256403060,
e-mail: nicolae.vaszilcsin@upt.ro

Abstract. Spray pyrolysis technique was used to prepare smooth nickel-based platinum nanoparticles electrode. The structure and the distribution of Pt nanoparticles on the electrode surface have been investigated by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The hydrogen evolution reaction (HER) was studied in 1 M NaOH solution by linear sweep voltammetry (LSW) technique. The kinetic parameters were determined from Tafel polarization curves. It was found that the increased activity for the HER is due to an increased real surface area in case of the smooth Ni-Pt electrode. The temperature influence on the HER was investigated and the electrochemical activation energy was determined for smooth Ni-based platinum nanoparticles electrode.

Keywords: platinum nanoparticles, hydrogen evolution reaction, water alkaline electrolysis, Tafel polarization

1. Introduction

In the last three decades a great interest has been devoted to the research of hydrogen evolution reaction (HER) due to its importance in many industrial processes. Choice of the electrode or electrolyte as well as a variation of other conditions at the electrode and solution interface can cause the change of the Tafel slopes for HER due to the different mechanism dominating in the given system.

Kinetics of the HER has been investigated on a wide variety of electrodes, i.e. Ni [1, 2, 3], Cu, Au, Mo, Pd, Rh, Fe [3, 4, 5], RuO_2 [6] and Ti [7] looking for more efficient conditions (lower overpotential, higher electrocatalytic activity, good chemical and electrochemical stability). Consequently, the approach used in the design of a good HER electrocatalysts should be based on the increase of the active surface area of the electrode material as well as the design of a catalyst with a high intrinsic catalytic activity. In this context, noble metals such as platinum (Pt) are unbeatable catalyst for HER which has the exchange current density of 4.5×10^{-4} A/cm^2, and the Tafel slope as small as 30 mV/decade [8]. However, homogenous deposition of Pt nanoparticles on the electrode surface is still a challenge in current technology.

The aim of the present work was to prepare new electrode material based on smooth Ni-based platinum nanoparticles electrode and to investigate the kinetic of HER using linear-sweep voltammetry technique. The factors (the catalysts deposition, temperature and potential scan rate) influencing the HER activity were also investigated. The electrodes prepared by spray pyrolysis technique present good electrocatalytic properties toward the reaction of hydrogen evolution reaction (HER), long-time stability and high energetic efficiencies.

2. Experimental

2.1. Chemicals and deposition of Pt nanoparticles

Chloroplatinic acid hexahydrate (H_2PtCl_6 $6H_2O$) and isopropanol (99.7%) obtained from Sigma-Aldrich were used for preparation of Pt salt precursor solution. All reagents were of analytical grade and used without and further purification.

Platinum nanoparticles were deposited on smooth nickel substrate by spray-pyrolysis technique using an ultrasonic nebulizer SONO-TEK Corporation Exacta Coat. After deposition, the electrodes were heated at 350°C for 30 minutes to achieve the solvent evaporation and to obtain the Pt nanoparticles.

2.2. Electrochemical measurements

Electrochemical experiments were performed with a computer controlled Autolab potentiostat/galvanostat PGSTAT 302 (EcoChemie, The Netherlands) in a three-electrode electrochemical cell. The three-electrode system consisted of a working electrode (i.e. smooth Ni and smooth Ni-Pt), 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 ($E_{Ag/AgCl}$ = 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 (293 K- 336 K) using a Thermo Scientific DC 10 thermostat, having an accuracy of ± 0.1 K. During linear sweep voltammetry (LSV) measurements, N_2 (Linde Gas, 99.99%) was continuously bubbled through the electrolyte in order to eliminate the dissolved oxygen.

Also, before each measurement, the working electrode was held at -1.6 V vs. Ag/AgCl for 120 seconds in order to reduce the oxide film on the electrode surface and obtain reproducible electrode surface.

The equilibrium potential for the HER in 1 M NaOH solution was calculated according to Eq. (1), taking into account the effect of temperature on the ionic product of water:

$$E_e = \left(\frac{RT}{F} \ln(a_{H^+}) \right) = \frac{RT}{F} \ln \left(\frac{K_{H_2O}}{f \pm \cdot m_{HO^-}} \right) \quad (1)$$

where $f \pm$ is the mean activity coefficient of NaOH equal to 0.679 [9]. The $f\pm$ value depends on temperature but for the concentration and temperatures considered in our study its variation is insignificant. The molal concentration of HO^-(m_{HO^-}) is considered to be equal with the molar concentration.

Based on Tafel plots $\eta = f(\log i)$, where η represents the overpotential (V) and i represents the current density (A m^{-2}), the kinetic parameter have been calculated. Also, considering the dependence lg $|i_o| = f(T^{-1})$ and using Arrhenius equation, the apparent activation energy has been determined [9].

2.3. Surface morphology

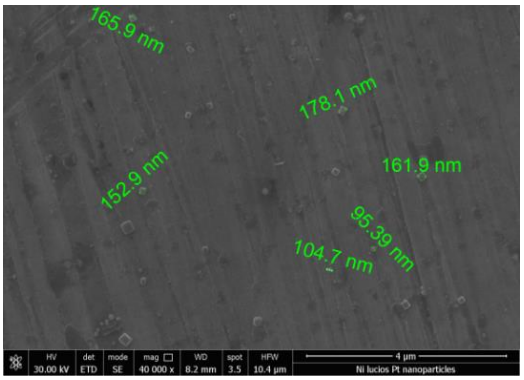
The surface morphology of the developed electrodes was analyzed by Scanning Electron Microscopy using SEM QUANTA FEG 250 - USA equipment coupled with Energy Dispersive X-ray (EDX) analysis with an APOLLO X detector in order to determine Ni and Pt contents. EDX analyses were carried out in different sites in order to obtain an average composition of the entire coating surface.

3. Results and Discussion

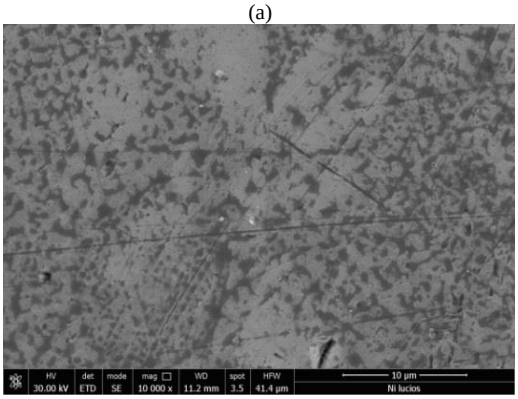
3.1. SEM and EDX characterization

The surface morphology of the electrodes, i.e., smooth Ni and smooth Ni-Pt was observed during the SEM images shown in Figure 1.a and b. It can be clearly seen from Figure 1b that Pt nanoparticles are nano-sized and uniformly distributed. The average particle size ranges from 100 nm to 200 nm for smooth Ni-Pt. The elemental composition of the coating was determined by energy dispersive X-ray (EDX) analysis. The obtained values are listed in Table 2. Moreover, the EDX analysis demonstrates the coexistence of Pt in proportion of 1.16% on the smooth Ni-Pt.

The average compositions of the electrodes were evaluated by EDX microanalysis, whose results are given in Table 2.



(a)



(b)

Figure 1. SEM images of (a) smooth Ni, (b) smooth Ni-Pt electrodes.

TABLE 2. Chemical composition of the as-prepared electrodes

Element (wt%)	Electrode type	
	Smooth Ni	Smooth Ni-Pt
Ni	100	98.84
Pt	-	1.16

3.2. Cathodic polarization curves

The cathodic polarization of the HER for smooth Ni-Pt electrode is displayed in Figure 3a. The polarization curves of smooth Ni electrode are also included for comparison (Fig. 4a). The measurements were obtained under potentiostatic conditions at low sweep rate of 5 mV s^{-1} and in the temperature range 293 K-336 K allowing the evaluation of both exchange current density i_o and transfer coefficient *1-α.* Also, the apparent activation energies for HER charge transfer process were calculated from the slope of the linear dependence log $i_o = f(T^{-1})$ according to Eq. (2).

$$Ea = -2.303R \frac{\partial(lgi_o)}{\partial(T^{-1})} \quad (2)$$

The values of the kinetics parameters extracted from these data are reported in Table 3.

TABLE 3. Experimental values of Tafel slope, transfer coefficient (1-α) and exchange current (i_o) at different temperatures

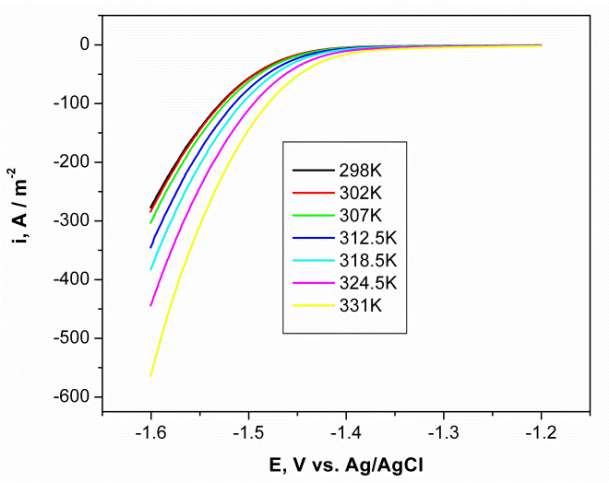
Electrode type	T [K^{-1}]	-*b* [mV dec^{-1}]	1-*α*	i_0 [A m^{-2}]
Smooth Ni	298	118	0.50	0.0050
	302	117	0.50	0.0053
	307	117	0.51	0.0054
	312.5	114	0.53	0.0058
	318.5	114	0.55	0.0075
	324.5	111	0.57	0.0104
	331	110	0.59	0.0151
Smooth Ni-Pt	293.5	105	0.56	0.072
	305	103	0.57	0.079
	310	96	0.60	0.087
	313.5	95	0.61	0.107
	318	93	0.62	0.173
	324	93	0.63	0.204
	330	92	0.64	0.251
	336	91	0.65	0.288

As it is seen from Table 3, Tafel slopes ranges between 91 and 118 mV dec^{-1} suggests that the hydrogen coverage is reasonably high on these electrodes, which suggests a fast discharge followed by a rate determining step [10, 11]. The HER on this electrodes follows the Volmer-Heyrovsky mechanism. The reaction rate is controlled by the recombination of adsorbed H atoms on the electrode surface.

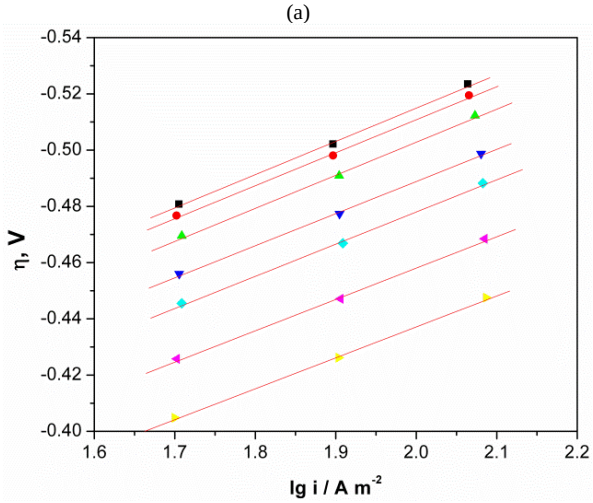
Smooth Ni-Pt electrode appears to be more active in comparison with smooth Ni electrode for the HER, because it has the highest exchange current density, transfer coefficient and the reduction of Tafel slopes.

From Figure 4a it can be seen that the cathodic current densities at different temperatures on smooth Ni-Pt electrode, which are directly proportional to the hydrogen evolution rate, were higher in comparison to that on the smooth Ni electrode (Figure 3a). This seemed to suggest that the deposition of Pt nanoparticles on the electrode surface enhances its intrinsic electrocatalytic activity for HER in addition to an increase in surface area. Accordingly, the main contribution to the improvement of electrocatalytic activity of smooth Ni-Pt electrode toward HER arises not only from the increase of real surface area, but also a significant synergistic interaction between Pt and Ni is present.

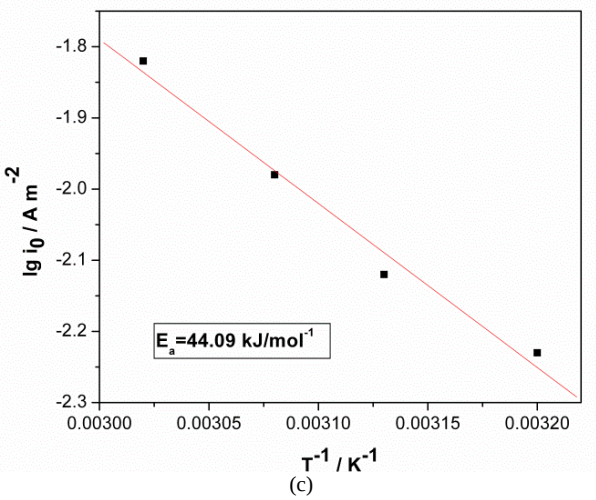
Figure 3c and Figure 4c shows the Arrhenius plots on smooth Ni electrode and smooth Ni-Pt electrode, respectively. The calculated E_a value for smooth Ni electrode is 44.09 kJ mol^{-1} while for smooth Ni-Pt is 38.83 kJ mol^{-1}. It is obviously that the charge transfer rate is favored by deposition of Pt nanoparticles.



(a)

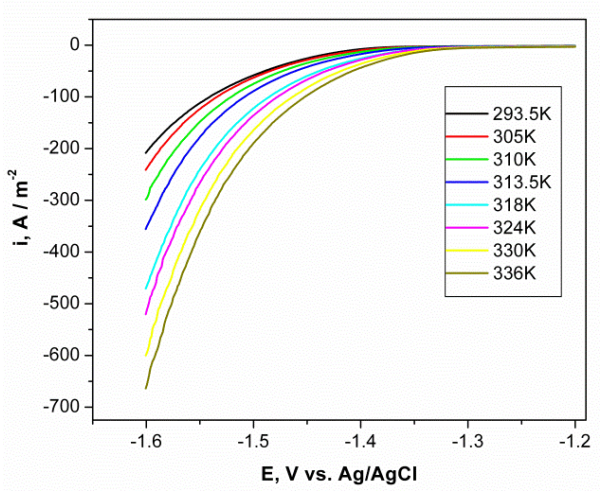


(b)

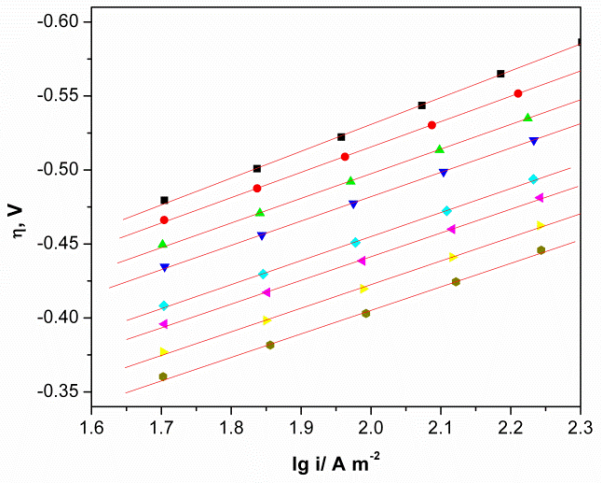


(c)

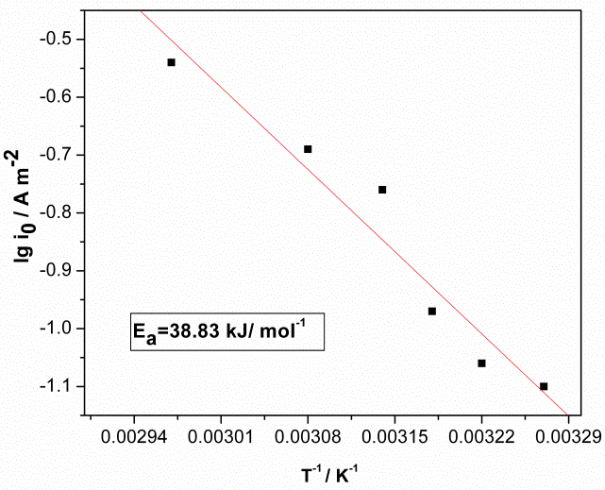
Figure 3. (a) LSWs on **smooth Ni electrode** in 1 M NaOH solution at 298K, 302K, 307K, 312.5K, 318.5K, 324.5K, 331K; scan rate: 0.005 V s^{-1}. (b) Tafel plots on smooth Ni electrode. (c) Arrhenius plot



(a)



(b)



(c)

Figure 4. (a) LSWs on **smooth Ni-Pt electrode** in 1 M NaOH solution at 293.5K, 305K, 310K, 313.5K, 318K, 324K, 330K, 336K; scan rate: 0.005 V s^{-1}. (b) Tafel plots on smooth Ni-Pt electrode. (c) Arrhenius plot

4. Conclusions

Smooth Ni-Pt electrode was successfully prepared by spray-pyrolysis technique and characterized by different techniques in the view of possible application as an electrocatalytic material for the HER in alkaline solution. The insertion of Pt nanoparticles has a significant effect on the HER activity. The prepared smooth Ni-Pt electrode exhibit higher current densities and lower activation energy in comparison with smooth Ni electrode.

ACKNOWLEDGEMENTS

This work was partially supported by the strategic grant POSDRU/159/1.5/S/137070 (2014) of the Ministry of National Education, Romania, co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013.

REFERENCES

1. Lasia A. and Rami A.,J., *Journal Electroanalytical Chemistry and Interfacial Electrochemistry*, 29 (1), **2007**, 123-141.
2. Conway B.E and Bai L., *Journal of Chemical Society - Faraday Transactions 1 Physical Chemistry and Condensed Phases*, 81(8), **1985**, 1841-62.
3. Jaksic J.M., Vojnovic M.V. and Krstajic N.V., *Electrochimica Acta*, 45(25), **2000**, 4151-4158.
4. Pentland N., Bockris J.M. and Sheldon E., *Journal of Electrochemical Society*, 104(3), **1957**, 182-194.
5. Badawy W.A., Feky H.E., Helal N.H. and Mohammed H.H., *International Journal of Hydrogen Energy*, 38(23), **2013**, 9625-3962.
6. Jaccaud M., Leroux F. and Millet J.C., *Materials Chemistry and Physics*, 22(1), **1989**, 105-119.
7. Miousse D. and Lasia A., *Journal of New Materials for Electrochemical Systems*, 2, **1999**, 71-78.
8. Conway B.E. and Tilak B.V., *Electrochimica Acta*, 47(22-23), **2002**, 3571-3594.
9. Cretu R., Kellenberger A. and Vaszilcsin N., *International Journal of Hydrogen Energy*, 38, **2013**, 11685-11689.
10. Ferreira A.C., Gonzalez E.R., Ticianelli E.A., Avaca L.A. and Matvienko B., *Journal of Applied Electrochemistry*, 18, **1988**, 894-898.
11. Orinakova R., Turonova A., Kladekove D., Galova M. and Smith R.M., *Journal of Applied Electrochemistry*, 36, **2006**, 957-972.

Received: 27 November 2014
Accepted: 15 December 2014