Enhancement of Hydrogen Evolution Reaction on Pt-Co Layer Deposited on Copper

D A Duca¹, M L Dan¹, A Z Vidinaru¹, R Muntean¹² and N Vaszilcsin¹*  
¹Faculty of Industrial Chemistry and Environmental Engineering, Politehnica University Timisoara, Romania  
²Department of Materials Science and Testing, Westphalian University of Applied Science, Gelsenkirchen, Germany  
*Corresponding author: nicolae.vaszilcsin@upt.ro

Abstract. Hydrogen is still considered an excellent energy carrier and fuel of the future, since in the combustion process only water is produced, without carbon dioxide. Whereas, water splitting by electrolysis is indeed a green procedure for hydrogen production, the research on hydrogen evolution reaction (HER) is focused especially on the catalytic activity of cathodic materials. In this paper, Pt-Co alloy deposition on copper substrate as catalyst for HER is presented. Pt-Co alloy has been obtained using pulsed plating current technique in order to achieve a uniform dispersion of Pt-Co particles onto the metal surface. Morphological and structural characterization of the obtained layers has been carried out by scanning electron microscopy and XR diffractometry. Electrochemical behaviour and stability of the electrocatalytic Pt-Co layers has been emphasised by cyclic voltammetry. Further, kinetic parameters for cathodic HER have been determined by Tafel plots method in alkaline solutions. Exchange current density $i_0$, as well as cathodic transfer coefficient $1-\alpha$, revealed an increased catalytic activity in the temperature range of 25 – 65°C.

1. Introduction
Despite the fact that apparently Li ion batteries have just won against H₂ fuel cells in the race for automotive applications, the cathodic HER is still a challenge for researchers in order to minimize the specific power consumption [1-5]. Hydrogen still remains an excellent energy carrier and a fuel of the future, especially in the space technology and stationary power engines. On the other hand, hydrogen applications are not limited to automotive applications. It is also used as reagent in the synthesis of some large production chemicals, like ammonia and methanol, and as well as in a specific petrochemical processes: hydro-dealkylation, -desulfurization and -cracking [6,7]. Last but not least, electrochemical hydrogen production by water splitting is indeed a green procedure, taking into account that, in other applied industrial processes, for each ton of hydrogen an amount of 5.5 tons of CO₂ is released in the atmosphere in the steam reforming of methane, respectively 11 tons of CO₂ in the coal gasification [8].

Early researches have been focused on the electrocatalytic activity on the cathodic HER of non-noble metals having a large specific area [9,10]. Furthermore, the enhancement of HER using proton carriers in the electrolyte solution have been investigated [11,12]. Current trends in the electrochemical hydrogen production are directed towards high pressure water electrolyzers, able to operate a high current densities and elevated temperature [13,14]. In this respect, there are two
commercial technologies that use alkaline electrolysis and proton exchange membrane electrolysis. As well, under consideration is the development of solid oxide electrolyzers, operating at high temperature (800 – 900°C) [15].

In order to reduce electrolyzers costs, three kind of non-noble electrocatalysts are used: metal alloys, inorganic compounds of transition metals and doped nanostructures [9]. According to the literature data, the most active electrocatalysts for HER are platinum alloys. J. Zheng has been obtained Pt-M alloys (M = Fe, Co, Ni, Pd) supported on Ti foils, having good catalytic activity as electrodes in water electrolyzers both for hydrogen and oxygen evolution reaction [16,17]. Similar results have been reported by Y. Zang et al [18]. Small overpotential for HER (90 mV at 8 mA cm⁻²) was registered on platinum-rhodium alloy [19]. PdNi alloy nanoparticles are highly efficient bifunctional catalysts for hydrogen and oxygen evolution reaction. Low overpotentials for HER were observed: 55 mV at a current density of 10 mA cm⁻² in an acid solution and 187 mV in 1 mol L⁻¹ KOH solution at the same current density [20]. Interesting achievement has been noted by D.M.F. Santos et al, using platinum – lanthanides (cerium, samarium and holmium) alloys in 8 mol L⁻¹ KOH aqueous solution, at temperature range of 25 – 85°C. The calculated kinetic parameters showed that Pt – lanthanides alloys increase the HER rate in comparison to pure platinum [21,22]. Recently, high-performance as bifunctional electrocatalysts for HER has been reached by platinum – palladium alloy introduced in N-doped graphene [23].

In a previous paper [24], a new way to realize Pt-Co alloy as electrocatalyst has been presented, considering that it is difficult to obtain this material by cathodic deposition from a salts electrolyte solution. The Pt-Co alloy composition may be controlled just applying a pulsed plating electrochemical technique [25].

In the present paper, Pt-Co alloys deposition on copper support is described, using pulsed plating current technique in order to achieve a uniform dispersion of Pt-Co particles onto the metal surface, as well as its electrocatalytic behavior for HER.

2. Materials and methods
Experimental studies have been focused on manufacturing the Pt-Co electrodes and testing them as catalysts for HER in alkaline media.

2.1. Electrodes manufacturing
The electrodes have been manufactured in two steps. The first step consisted in the preparation of the non-catalytic support (Cu disks – 1 cm² surface), and the second one in the electrodeposition of Pt-Co alloy on this support, using pulse deposition technique.

Copper disks surface have been grinded with various grit emery papers (1,200 – 4,000 µm), polished with 3 µm polycrystalline diamond, cleaned in an ethanol ultrasonic bath for 30 minutes at 30°C and finally dried in hot air.

Pt-Co alloy deposition has been performed using a potentiostat/galvanostat Ivium Technologies Vertex, in a classic electrochemical cell, where the copper disks (0.8 cm² exposed area) previously prepared were used as working electrodes and a graphite bar as counter-electrode. The electrodeposition has been carried out from a weak acidic solution of K₂PtCl₄ (0.005 mol L⁻¹) and CoCl₂·6H₂O (1 mol L⁻¹) as a source of Pt²⁺, respectively and Co²⁺ ions. The molar ratio of Pt²⁺:Co²⁺ ions was 1:20. In the electrolyte solution, 1 mol L⁻¹ KCl has been added to increase the conductivity of the solution, and 0.5 mol L⁻¹ H₃BO₃ to maintain the pH at a constant value. During the electrodeposition, N₂ (gas) was bubbled in the solution and after, the working electrode was washed with distilled water and dried in hot air.

The composition and morphology of deposited Pt-Co layers have been characterized by scanning electron microscopy and XR diffractometry.
2.2. Tests for HER
Electrochemical behaviour and stability of the electrocatalytic Pt-Co layers in alkaline media has been studied by cyclic voltammetry (CV). Cyclic voltammograms (CVs) have been recorded at different concentrations of NaOH, between 1 and 6 mol L\(^{-1}\), with multiple scan rates.

Kinetic parameters (exchange current density \(i_0\) and cathodic coefficient transfer 1-\(\alpha\)) for HER have been calculated from linear voltammograms (LVs) by Tafel plots method. LVs have been drawn with low scan rate, 2 mV s\(^{-1}\), in 25 – 65\(^\circ\)C temperature range.

Electrochemical measurements have been performed using a PARSTAT 2273 potentiostat/galvanostat in a 150 mL thermostatted glass cell. Pt-Co electrodes, having 0.8 cm\(^2\) exposed area, have been used as working electrodes, two graphite rods as counter electrodes and Ag/AgCl as reference. All further potentials from the experimental work are referred to this electrode (\(E_{Ag/AgCl} = +0.197\) V vs normal hydrogen electrode).

3. Results and discussion

3.1. Pt-Co electrodeposition
Pt-Co electrodeposition was made using pulse deposition method due to its advantages, as rigorous control of particle size, uniform distribution and increased adhesion.

The variables of the pulse deposition process are applied pulse time \(t_{on}\), pause time \(t_{off}\), current density \(i\) and number of deposition cycle. This study focuses on the variation of these parameters in order to achieve the optimal characteristics. Nucleation process and the size of the deposited alloy particles are influenced by \(t_{on}\) and \(i\), whilst during \(t_{off}\), the metal ions concentration from the vicinity of interface is completed and desorption of the previously adsorbed ions occurs. In order to determine the optimal parameters, electrodeposition tests have been done varying the current density, deposition and pause time of a pulse and number of cycles. Thus, current densities ranging between 250 and 1,000 A m\(^{-2}\) were applied for pulses whose \(t_{on}\) varied from 10 to 20 ms, and \(t_{off}\) from 5 to 100 ms. The number of cycles varied between 10,000 and 20,000. During \(t_{off}\), the density of applied current was equal to 0.

3.1.1. Current density influence on Pt-Co layer morphology.
To study the current density influence on the morphology of the deposited layers, tests have been done applying three current densities: 250, 750 and 1,000 A m\(^{-2}\), while the other parameters were maintained constant (\(t_{on} = 10\) ms, \(t_{off} = 100\) ms and 10,000 deposition cycles).

Figure 1 presents SEM images obtained for the Pt-Co layers deposited on the Cu support at the specified current densities.
From the analysis of the SEM micrographs and knowing that the current density at which the electrodeposition process is carried out influences significantly the quality and structure of the deposited layer, it can be observed that for 250 A m\(^{-2}\) current density (the lowest used in experimental studies) Pt-Co microcrystalline structure is obtained, with evenly distributed particles over the surface of the copper substrate. Increasing the current density has as effect the increase of the deposited particles size, as at 1,000 A m\(^{-2}\) current density dendrites appear. Consequently, layers obtained at this current density are inappropriate to be used as catalyst for HER.

In order to determine the thickness of the Pt-Co alloy layers deposited on the copper support by pulse deposition, SEM analysis were performed in a section of the layer. Current density influences also the thickness of the deposited layers; at a value of 250 A m\(^{-2}\) a Pt-Co layer of 1.5 μm thickness is obtained, and this value increases up to 5 μm at 1,000 A m\(^{-2}\).

SEM micrographs presented above revealed the significant influence of current density on the quality and crystalline structure of Pt-Co layers deposited on copper support. It was found that depositions obtained at 250 A m\(^{-2}\) are optimal for use in the enhancement of HER because of its finest microcrystalline structure, evenly distributed on the support. Despite that thicker layers are obtained at higher current densities, they do not qualitatively correspond because the particle size is large or even in the form of dendrite.

3.1.2. *Influence of pulse deposition time on Pt-Co layer morphology*

Specific pulsation parameters, \(t_{on}\) and \(t_{off}\) influence both the chemical composition of the alloy and quality of the galvanic deposit obtained (microcrystalline structure, nucleation and growth of crystallites). In the case of a binary alloy, such as Pt-Co, during \(t_{off}\) (i = 0 A m\(^{-2}\)), the less noble metal cobalt can be dissolved on the surface of the cathode by the noble metal, platinum, according with a cementation reaction:

\[
\text{Pt}^{2+} + 2\text{Co} \rightarrow \text{Co}^{2+} + \text{Pt}
\]  

Also, a longer \(t_{off}\) between pulses is recommended for the metal ions concentration at interface to return to its initial value, homogenizing the solution due to the migration/diffusion of the Pt\(^{2+}\) and Co\(^{2+}\) ions from the solution bulk to the emergent zone of the cathode [24].

In preliminary experimental studies, \(t_{off}\) value ranged from 5 to 100 ms. Based on the theoretical aspects and on the obtained Pt-Co layers, \(t_{off} = 100\) ms was chosen to be the optimal value. A more obvious influence is the deposition time \(t_{on}\) specific of a pulsation.

Figure 2 presents SEM images of Pt-Co layers obtained after 10,000 deposition cycles, at 250 A m\(^{-2}\) current density and \(t_{off} = 100\) ms , varying the pulse deposition time \(t_{on}\) from 10 to 20 ms.
From the analysis of SEM micrographs, it can be observed that increasing the deposition time for a pulse from 10 to 20 ms leads to a finer microcrystalline structure with a higher density of crystals. The optimal value chosen was $t_{on} = 20$ ms.

### 3.1.3. Number of deposition cycles influence on Pt-Co layer morphology

The number of cycles or the number of applied pulses has also a considerable influence on the deposition of the Pt-Co layers obtained on copper substrate from weak acid electrolyte solution. Figure 3 presents SEM images of the Pt-Co layers obtained by pulse deposition technique at 250 A m$^{-2}$ current density, $t_{on} - 20$ ms, $t_{off} - 100$ ms, varying the number of deposition cycles from 10,000 (Figure 3a) to 20,000 (Figure 3b).

**Figure 3.** SEM images for Pt-Co layers obtained after a) 10,000 and b) 20,000 deposition cycles.

Analysing the SEM micrographs, it can be seen that increasing the number of deposition cycles, as the particle size remains almost constant, increases the nucleation rate and so, the number of crystals deposited on the surface of the metal support. This leads to obtaining an electrode with microcrystalline structure and a large specific surface. Also, the thickness of the deposited alloy layer increases, implicit increasing the corrosion resistance, respectively the duration of use of these electrodes for HER in alkaline media.
3.1.4. **Structural characterization of deposited Pt-Co layer**

XRD measurements have been performed in order to determine the structural characteristics, and so the alloy phase composition of the Pt-Co layer. Beneath, XRD patterns of Pt-Co alloy deposited on Cu are shown at two values of current density: 250 (Figure 4a) and 750 (Figure 4b) A m\(^{-2}\).

![Figure 4. XRD patterns for Pt-Co layers deposited on Cu substrate at a) 250 and b) 750 A m\(^{-2}\).]

For both Pt-Co samples, a single alloy phase CoPt\(_3\) was detected. Unalloyed metallic Pt is not found in the electrodes structure. The peaks observed at 2\(\theta\) values of 43\(^o\), 51\(^o\), 74\(^o\) and 90\(^o\), characteristic for copper correspond to the Cu material support used in the electrodeposition process.

Figure 5 shows comparatively the XRD patterns for the working electrode, pure Pt and also pure Co. It can be observed the diffraction patterns of CoPt\(_3\) alloy phase and pure Pt are similar, no additional peaks being observed. Also, no additional peaks for pure Co can be observed.

![Figure 5. XRD patterns for working electrode, pure Pt and pure Co.]

The Pt-Co characteristic peaks are slightly shifted at higher angles compared with pure Pt peaks, aspect indicating a contraction of the lattice constant and also a high alloying degree due to incorporation of Co atoms into the Pt-Co alloy structure [24].

Previous studies revealed that decreasing Pt-Pt bond length, the binding energy is also reduced and so the catalytic activity increase considerable [24].

Pure Co could not be identified in Pt-Co structure, meaning all cobalt atoms have been incorporated in the Pt structure, forming Co-Pt alloy.

3.2. Tests for HER
Based on previously presented results, the electrodes manufactured by pulse electrodeposition technique at 250 A m\(^{-2}\) current density, applied pulse time \(t_{on} = 20\) ms, paused time \(t_{off} = 100\) ms and 10,000 (Pt-Co-10k electrode), respectively 20,000 number of deposition cycles (Pt-Co-20k electrode) have been tested for HER.

3.2.1. Cyclic voltammetry
In order to evaluate the processes occurring in alkaline media on Pt-Co electrode and the influence of electrolyte solution concentration, CVs have been recorded at different concentrations of NaOH (1 – 6 mol L\(^{-1}\)). Figure 6 presents comparatively the CVs recorded on Pt-Co-10k (Figure 6a) and Pt-Co-20k (Figure 6b) with 10 mV s\(^{-1}\) scan rate.

![Figure 6. CVs recorded on a) Pt-Co-10k and b) Pt-Co-20k electrode in different concentrations of NaOH, at 10 mV s\(^{-1}\) scan rate.](image)

Analysing the CVs, starting from open circuit potential towards anodic polarization, on both electrodes, two oxidation peaks, around \(-0.45\) V and \(-0.15\) V are observed. They correspond to the oxidation of Co in two steps (Co \(\rightarrow \) Co\(^{2+}\) and Co\(^{2+}\) \(\rightarrow\) Co\(^{3+}\)). Further, around + 0.6 V, a less pronounced wave, better visible on Pt-Co-20k electrode, attributed to platinum oxides formation is noticeable. At more positive potential values, oxygen evolution reaction begins. Sweeping the potential in opposite direction, in the cathodic domain it can be seen the reduction wave of Co\(^{3+}\) and Co\(^{2+}\) from the proximity of the interface to metallic Co (at \(-0.75\) V), followed by HER.

One may observe that HER depends on the NaOH concentration. A concentration up to 3 mol L\(^{-1}\) NaOH enhances HER, its potential value being shifted towards positive values with the concentration increase. At higher concentrations, between 4 and 6 mol L\(^{-1}\), the characteristic potential for HER becomes more negative, so the overpotential increases.
3.2.2. Linear voltammetry
To study the effect of the electrolyte solution concentration on HER and to determine the kinetic parameters of this process, LVs on both Pt-Co-10k and Pt-Co-20k electrodes have been recorded at concentrations between 1 and 6 mol L\(^{-1}\) NaOH in 25 – 65°C temperature range. Figure 7 presents comparatively the LVs drawn on the two electrodes with 2 mV s\(^{-1}\) scan rate at 25°C.

**Figure 7.** CVs recorded on a) Pt-Co-10k and b) Pt-Co-20k electrode in different concentrations of NaOH, at 25°C; 2 mV s\(^{-1}\) scan rate.

In both cases, a decrease of HER overpotential is noticed with the increase of NaOH concentration, most obvious for 3 mol L\(^{-1}\), when a shift of approximately 100 mV towards more positive values is observed as against 1 mol L\(^{-1}\), the lowest concentration of NaOH used in the experimental study. At higher concentrations this catalytic effect is diminished. One can conclude this is the optimum concentration to be used for HER on Pt-Co electrodes.

Knowing from the literature data the favourable effect of temperature rise on HER, LVs have been recorded at different temperatures, between 25 and 65°C. Figure 8 shows the LVs drawn in 3 mol L\(^{-1}\) NaOH.

**Figure 8.** CVs recorded on a) Pt-Co-10k and b) Pt-Co-20k electrode in 3 mol L\(^{-1}\) NaOH, at different temperatures; 2 mV s\(^{-1}\) scan rate.
Analysing the LVs, it is observed HER depends on the thickness of the Pt-Co layer. As expected, Pt-Co-20k is a better fit for the enhancement of HER, the deposited layer being thicker, as previously presented. For this electrode, an overpotential decrease of about 150 mV is seen for the temperature increase from 25 to 65°C.

For a better understanding of HER, from the linear dependence $\eta = f (\lg|i|)$, kinetic parameters (exchange current density $i_o$ and cathodic coefficient transfer 1-$\alpha$) have been calculated. Figure 9 presents Tafel plots for HER on Pt-Co-20k electrode in different concentrations of NaOH.

![Figure 9. Tafel plots for HER on Pt-Co-20k in different concentrations of NaOH at 25°C.](image)

The calculated values of exchange current density $i_o$ and cathodic coefficient transfer 1-$\alpha$ are presented in table 1.

**Table 1.** Kinetic for HER on Pt-Co-20k electrode in 3 mol L$^{-1}$ NaOH at 25°C.

| Pt-Co-20k electrode | NaOH conc. [mol L$^{-1}$] |
|---------------------|---------------------------|
|                     | 1 | 2 | 3 | 4 | 5 | 6 |
| $1-\alpha$          | 0.44 | 0.54 | 0.59 | 0.55 | 0.53 | 0.5 |
| $i_o$ [A m$^{-2}$]  | 0.008 | 0.021 | 0.025 | 0.011 | 0.010 | 0.009 |

Similar results have been reported by other authors [10,26,27].

**4. Conclusions**

In this study, new type of Pt-Co electrodes have been manufactured and tested for HER.

First, the characteristic parameters for pulse electrodeposition technique have been varied in order to find the optimal values to achieve the desired characteristics for Pt-Co deposited layer. The influence of current density $i$, pulse time $t_{on}$, and $t_{off}$, and also the number of deposition cycles was studied.

It was found that a high current density leads to large particles or even dendrite formation. It is preferably to carry out the electrodeposition at 250 A m$^{-2}$ when compact, even distributed and small particles are formed.

As regards the applied and paused time of a cycle, it was concluded the longer $t_{on}$ and $t_{off}$ are, the finer microcrystalline structure with a higher density of crystals and optimal platinum amount is obtained. The optimal values chosen were $t_{off} = 100$ ms and $t_{on} = 20$ ms.
The number of electrodeposition cycles does not influence significantly the microcrystalline structure but have a strong influence on the layer thickness, the higher the number of cycles is, the thicker the layer is.

XRD patterns demonstrate that using the above parameters by pulse electrodeposition CoPt₃ homogenous alloy is obtained.

Electrochemical behaviour of CoPt₃ alloy in alkaline solutions has been studied by CV. Furthermore, kinetic parameters for HER on CoPt₃ electrode were determined. The results revealed the best catalytic effect is obtained in 3 mol L⁻¹ NaOH.

5. References

[1] Opitz A, Badami B, Shen L, Vignaroonan K and Kannan AM 2017 Renew. Sust. Energ. Rev. 68 685-92
[2] Budde-Meiwes H, Drillkens J, Lunz B, Muennix J, Rothgang S, Kowal J and Sauer DU 2013 J. Automob. Eng. 227 761-76
[3] Schipper F and Aurbach D 2016 Russ. J. Electrochem. 52 1229-58
[4] Wang H and Gao L 2018 Current Opinion in Electrochemistry 7 7-14
[5] Safizadeh F, Ghali E and Houlachi G 2015 Int. J. Hydrogen Energy 40 256-74
[6] Zuttel A, Borgschulte A and Schlabach L 2008 Hydrogen as a Future Energy Carrier (Weinheim: Wiley-VCH Verlag)
[7] Press RJ, Santhanam KSV, Miri MJ, Bailey AV and Takacs GA 2008 Introduction to Hydrogen Technology (New York: Wiley and Sons Publication)
[8] Vaszilcsin N, Kellenberger A and Medeleanu M 2016 Kimya Problemleri 4 366-71
[9] Eftekhari A 2017 Int. J. Hydrogen Energy 42 11053-77
[10] Kellenberger A, Vaszilcsin N, Brandl W and Duteanu N 2007 Int. J. Hydrogen Energy 32 (15) 3258-65
[11] Cretu R, Kellenberger A, Medeleanu M and Vaszilcsin N 2014 Int. J. Electrochem. Sci. 9(8) 4465-77
[12] Jakab A, Vaszilcsin N, Manea F and Dan M 2015 Studia UBB Chemia 60 (3) 63-76
[13] Bensmann B, Hanke-Rauschenbach R, Pena Arias IK and Sundmacher K 2013 Electrochem. Acta 110 570-80
[14] Marangio F, Santarelli M and Cali M 2009 Int. J. Hydrogen Energy 34 1143-58
[15] Marangio F, Pagani M, Santarelli M and Cali M 2011 Int. J. Hydrogen Energy 36 7807-15
[16] Zheng J 2017 Appl. Surf. Sci. 413 72-82
[17] Zheng J 2017 Appl. Surf. Sci. 413 360-5
[18] Zhang Y, Li P, Yang X, Fa W and Ge S 2018 J. Comp. Alloys 732 248-56
[19] Lu J, Zhang L, JingS, Luo L and Yin S 2017 Int. J. Hydrogen Energy 42 5993-9
[20] Chen Jw, Chen Jd, Yu D, Zhang M, Zhu H and Du M 2017 Electrochem. Acta 246 17-26
[21] Santos DMF, Sequeira CAC, Maccio D, Saccone A and Figueiredo JL 2013 Int. J. Hydrogen Energy 38 3137-45
[22] Santos DMF, Sljukic B, Sequeira CAC, Maccio D, Saccone A and Figueiredo JL 2013 Energy 50 486-92
[23] Zhong X, Qin Y, Chen X, Xu W, Zhuang G, Li X and Wang J 2017 Carbon 114 740-8
[24] Muntean R, Pascal DT, Marginean G and Vaszilcsin N 2017 Int. J. Electrochem. Sci. 12 4597-609
[25] Woo S, Kim I, Lee JK, Bong S, Lee J and Kim H 2011 Electrochem. Acta 56 3036-41
[26] Lasia A and Rami A 1990 J. Electroanal. Chem. 294(1-2) 123-41
[27] Krstajic N, Popovic M, Grgur B, Vojnovic M and Sepa D 2001 J. Electroanal. Chem. 512 16-26

Acknowledgement

This work was partially supported by Politehnica University Timisoara in the frame of PhD studies.