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Enhancement of electrochemical activity of Raney-type NiZn coatings by modifying with PtRu binary deposits: Application for alkaline water electrolysis

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ABSTRACT

This study presents electrochemical preparation and characterization of PtRu-modified Cu/Ni/NiZn electrodes (Cu/Ni/NiZn–PtRu) as cathode materials for alkaline water electrolysis. The electrodes were characterized using energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. Their electrochemical activities as cathode materials for alkaline water electrolysis were evaluated with the help of current–potential curves. The results showed that the PtRu-modified layers have porous structures with relatively low Pt and Ru chemical compositions. The modification of the alkaline leached Cu/Ni/NiZn surface by Pt and/or Ru enhances the electrochemical activity of the electrode. Their catalytic activity depends on the molar ratios of Pt and Ru; the PtRu binary deposit with the percentage weight ratio of approximately 56:44 exhibits the highest hydrogen evolution activity among the studied electrodes. The enhanced hydrogen evolution activity of the PtRu-modified electrodes was related to the porous surface and/or a possible synergistic effect between the metals.

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Introduction

Fossil fuels are the major part of energy sources consumed on the world today [1]. However, their combustion products are causing the global problems, such as the greenhouse effect, ozone layer depletion, acid rains, and pollution, which are posing a great danger for our environment and eventually for the life in our planet [2]. Since the fossil fuel sources are being

depleted it is vital for human to find alternative energy sources to maintain the current life standards. Many scientists agree that the solution to these global problems would be to replace the existing fossil fuel system by the hydrogen energy system [2–8]. Hydrogen is an intermediary or secondary form of energy or an energy carrier. Although there are some production methods, hydrogen gas can be produced in large quantities by water electrolysis. The electricity needed for the electrolysis can be supplied by renewable energy sources such

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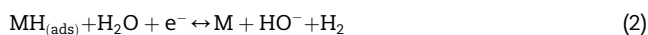
as solar energy. However, cost and energy consumption, which are directly proportional to cell voltage, are currently high. Efforts are being devoted to develop new electrode materials and reduce the cost of electrolytic hydrogen. Lowering the cost of electrolytic hydrogen production can be accomplished by the reduction of overpotentials of anodic and cathodic reactions by suitable material choice.

It is generally accepted that the hydrogen evolution reaction (HER) in alkaline solutions takes place through the following three steps [9–13]:

- i) The first step is the primary electron transfer from the reduction of one water molecule resulting in the formation of the adsorbed hydrogen on electrode surface (Volmer reaction).



- ii) Either the formation of one hydrogen molecule by desorption of the surface hydrogen and simultaneous reduction of one water molecule (Heyrovsky reaction).



- iii) or the formation of one hydrogen molecule by the combination of two neighboring adsorbed hydrogen atoms (Tafel reaction).



Herein, the strength of M–H₂O and M–H_{ads} interactions plays a key role in the reaction mechanism and in the rate of the HER. Both Volmer-Heyrovsky and Volmer-Tafel reaction mechanisms require the formation and then dissociation of M–H_{ads} bond. The M–H₂O interaction should be strong enough to favor the splitting of water molecule. However, this effect may render the next steps slower. So, the M–H interaction should not be so strong as to hinder hydrogen desorption. Hence, a cathode material should balance between the reactions (i) and (ii)/(iii) [13–16]. However, except noble metals (*e.g.* Pt, Ru, Pd, Ir etc.), other metals have low HER activity. The nickel-based alloys prepared by leaching out the active component have been reported to be very effective catalysts for the HER [17–25]. The activities of nickel-based electrodes have been further increased by co-deposition of Ni with noble metals [15,26–28].

The noble metals, *i.e.* Pt, Ir, Pd, Ru, are regarded as ideal catalysts for the electrochemical production of hydrogen due to their high electrocatalytic activity, low overpotential, and good electrochemical stability [27–36]. However, the commercial applications of the noble metals are limited due to their high cost and low abundance [36,37]. Considering the above facts, the main aim of material science employed in

hydrogen systems is reducing the amount of noble metals in electrode materials and increasing their electrocatalytic activity or at least keeping the same level of efficiency [38–42]. The search for new methods to reduce the amount of platinum group metals for the HER catalysis has been a topic of current interest [30,31,37,43–49]. The supporting materials with high surface area are essential for reducing the amount of precious metals. Recently, we have reported some porous substrates for the deposition of noble metals [28,29,50–52].

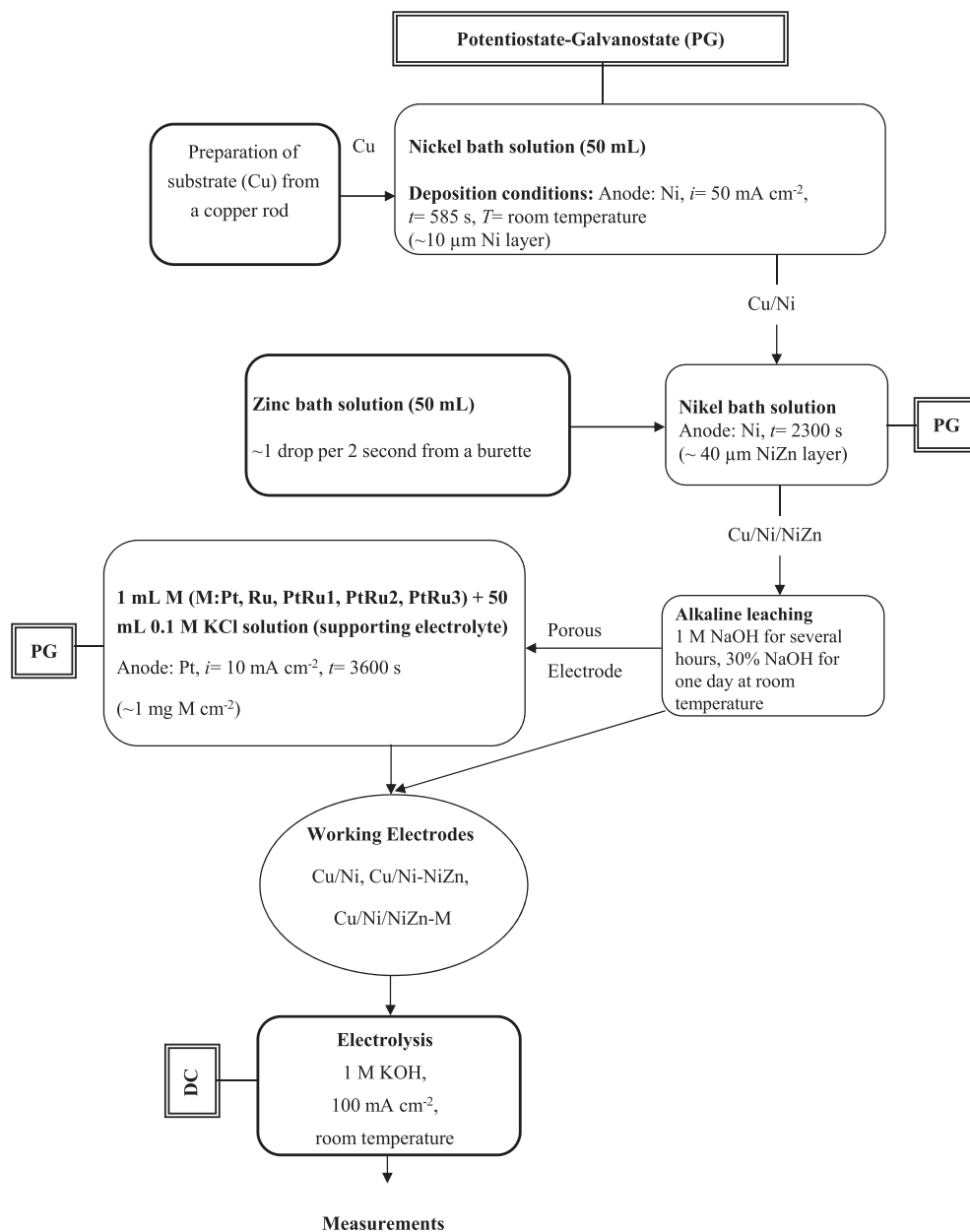
In this study, Raney-type NiZn coatings were modified by binary PtRu deposits with the various metal ratios and characterized with various techniques. The electrodes were tested as cathode materials for the alkaline water electrolysis.

Experimental

The composite coatings were prepared on copper specimens, which were cut from a cylindrical rod to a length of 5 cm and coated with polyester block except a surface area of 0.283 cm² which was exposed to the electrolyte. Before electrodeposition, the surface of copper was abraded with emery papers (320–1000 grain sizes), then washed with distilled water, thoroughly degreased with acetone, washed once more with distilled water and immediately immersed into the deposition baths.

The preparation of electrodes consists of two steps; (i) the preparation of porous Cu/Ni/NiZn electrode, and (ii) the modification of the porous layer by the noble metals. The procedures applied for the preparation of electrodes are summarized in Scheme 1. Table 1 shows the chemical compositions of the deposition baths. All the deposition baths were prepared and stored as stock solutions. The electrochemical deposition was performed by applying a constant current density using a potentiostat-galvanostat instrument with a three-electrode configuration. During the electrodeposition, a nickel (for Ni and NiZn depositions) or a Pt (for noble metal depositions) electrodes were used as the auxiliary electrodes. The reference electrode was an Ag/AgCl electrode. As it is summarized in Scheme 1, the preparation of the Ni/NiZn composite coating contains two steps: (i) Firstly, the copper electrode was immersed into the nickel plating bath as cathode and a constant 50 mA cm⁻² current density was applied to the electrolysis system for 585 s in order to obtain a thin nickel underlayer (Cu/Ni, ~10 μm thickness). It was reported that [25], a thin Ni under layer enhances the corrosion resistance of electrodes. (ii) Then, zinc solution was started to put drop into the same nickel bath from a burette at approximately 1 drop per 2 s. After starting zinc solution dropping, 50 mA cm⁻² current density was continued to apply for 2300 s (~40 μm thickness). In this way, more adherent NiZn deposits were obtained on the previously nickel-modified copper (Cu/Ni/NiZn). The similar procedure was applied in literature to obtain NiMoZn deposits [22]. The thicknesses of the coatings were theoretically calculated through the deposition charge taking into account the current efficiency is 100%, and neglecting the pore volume [53].

The Cu/Ni/NiZn electrodes were rinsed with distilled water in order to remove residues of bath chemicals and unattached particles. Then, the electrodes were alkaline leached in



Scheme 1 – Schematic representation of electrode preparation.

Table 1 – The chemical composition the deposition baths.

| Deposits | Bath composition |
|----------|---|
| Ni | 0.1068 M NiSO ₄ ·7H ₂ O + 4.2 mM NiCl ₂ ·6H ₂ O + 20.22 mM H ₃ BO ₃ |
| Zn | 5.34 mM ZnSO ₄ ·7H ₂ O + 0.21 mM ZnCl ₂ + 20.22 mM H ₃ BO ₃ |
| Pt | 1.45 mM K ₂ PtCl ₆ + 0.1 M KCl |
| Ru | 2.79 mM RuCl ₃ ·H ₂ O + 0.1 M KCl |
| PtRu1 | 1.0875 mM K ₂ PtCl ₆ + 0.6975 mM RuCl ₃ ·H ₂ O + 0.1 M KCl |
| PtRu2 | 0.725 mM K ₂ PtCl ₆ + 1.395 mM RuCl ₃ ·H ₂ O + 0.1 M KCl |
| PtRu3 | 0.3625 mM K ₂ PtCl ₆ + 2.0925 mM RuCl ₃ ·H ₂ O + 0.1 M KCl |

1 M NaOH and 30% NaOH solutions according to the published procedure [23,25]. The electrodes were carefully rinsed with distilled water once again and transferred into the noble metal deposition baths. Finally, the porous Cu/Ni/NiZn electrodes were modified by electrodeposition of the noble metals in

order to enhance their HER activity. The deposition conditions are shown in Scheme 1 and Table 1. The electrodes which were modified by binary noble metals with different metal ratios were named as Cu/Ni/NiZn–PtRu1, Cu/Ni/NiZn–PtRu2, and Cu/Ni/NiZn–PtRu3 (Table 1).

The surface morphologies were examined with a SEM instrument (Jeol 6510). The mean values of the chemical composition of the layers and the distribution of some elements over the surface (EDX dot mapping) were analyzed with EDX, which was connected to the SEM instrument. X-ray diffraction analysis (XRD) was performed with a Rigaku Ultima 4 machine using a Cu K α radiation. XRD patterns were recorded between a 2θ range of 20–100° with a step size of 0.01.

The electrochemical measurements were performed using a computer-controlled CHI Electrochemical Analyzer. A double-walled-one-compartment cell with a three-electrode configuration was used in the electrochemical tests. The auxiliary and reference electrodes were a platinum sheet (with 2 cm² total surface area) and an Ag/AgCl, respectively. In this study all potential values were given versus this reference electrode. Before electrochemical measurements, the potential of working electrode was held at –1.80 V (vs. Ag/AgCl) for 30 min in order to reduce the possible spontaneously formed oxides on the electrode surface and obtain a reproducible electrode surface. Then, the current–potential curves were potentiodynamically obtained as described previously [54]. All electrochemical measurements were repeated at least three times.

The hydrogen evolution activities of the electrodes were tested in 1 M KOH solution at 298 K. For each experiment, newly prepared electrodes and solutions were used. All the chemicals were analytical purity and used without further purification.

Results and discussion

Characterization

Fig. 1 shows the SEM images of the Cu/Ni/NiZn surfaces before and after the alkaline leaching as well as those of noble metal-modified porous electrodes. The magnified images were also given on the corresponding micrographs as insets. From the SEM images, it can be seen that an adherent and compact NiZn layer forms on the substrate (Fig. 1a inset, before leaching). However, as it is clearly shown in Fig. 1a, the alkaline leaching of Zn from the surface leads to formation of numerous crack and pore structures, which are suitable for the HER [29].

Both Pt (Fig. 1b) and Ru (Fig. 1c) individual deposits almost uniformly dispersed on the layer. The appearances of surface structures of PtRu binary deposits are between the structures of Pt and Ru, individually and the metal particles are evenly homogeneously distributed over the surface of the Raney-type NiZn layer (Fig. 1d–f). It can be seen that binary PtRu-modified surfaces have porous and high-quality surface; that of Cu/Ni/NiZn–PtRu1 has the best among them.

The representative EDX spectrum of the Cu/Ni/NiZn–PtRu1 surface is shown in Fig. 2. The average of percent metal ratios (wt.%) are given in Table 2. The data given in Table 2 correspond to the entire surface of the electrodes, and the results are average of two-to-four repetitions. As it can be seen from Table 1, the Zn content of the surface reduces considerable after exposing to 30% NaOH solution. Fig. 2 and Table 2

show that all the precious metal catalysts are successfully deposited over the porous NiZn surface. The Pt and Ru contents of the PtRu binary composites range from 4.1% to 6.2% and are lower than those of Ni and Zn.

To further examine chemical composition of the surfaces, the distribution of Pt and Ru elements over the Cu/Ni/NiZn–PtRu1 surface (EDX dot mapping) was determined and the data obtained are given on Fig. 2. The changes of Pt and Ru elements through a line were also obtained and given on the same figure. The EDX dot mapping of the deposit clearly shows that Pt (blue zones) and Ru (purple zones) as well as Ni and Zn evenly distributed over the layer. No local Ni, Zn, Pt or Ru enrichment could be detected on specific zones.

The structural analysis of the PtRu1-modified layer was investigated with XRD using the Rietveld refinement method. Fig. 3 shows the related XRD pattern of the deposit. XRD data showed that the layer has highly crystalline structure and composed of NiZnPtRu alloy. Ni, Zn, Pt and Ru elements have (111), (101), (200) and (101) orientations, respectively (details were not given here). Taking into account the alloy structure, it can be said that (111) orientation is dominant in the crystalline structure. In general, XRD data are in good agreement with the data of EDX.

Hydrogen evolution activity

The cathodic current–potential curves ($E-i$) of the electrodes were performed in 1 M KOH solution, and the data recorded are presented in Fig. 4a. As a reference point, the same experiments were also performed for the nickel-coated copper electrode (Cu/Ni). In order to determine the kinetic parameters, the corresponding Tafel curves ($E-\log i$) were presented in Fig. 4b. Current densities at –1.250 V(Ag/AgCl) ($i_{-1.250}$), cathodic Tafel slopes (b_c), charge transfer coefficients (α), exchange current densities (i_0) and overpotentials at 100 mA cm^{–2} cathodic current density (η_{100}) were determined from the corresponding curves and are given in Table 3.

As it is seen from Fig. 4 and Table 3, the Cu/Ni electrode has the lowest hydrogen evolution activity. The hydrogen evolution starts at a lower overpotential at the alkaline leached Cu/Ni/NiZn electrode. Moreover, as it is seen from Fig. 4a, the modification of porous NiZn surface by the Pt or Ru leads to enhancement in the electrode activity. The Pt-modified Cu/Ni/NiZn–Pt electrode exhibits better hydrogen evolution activity most probably due to the well-known good intrinsic catalytic activity of Pt. The hydrogen evolution activity of the binary PtRu composites depends on their chemical compositions. The Cu/Ni/NiZn–PtRu1 exhibits the lowest onset potential for the HER with the highest current density at a fixed potential, –1.250 V(Ag/AgCl), which is directly proportional to the rate of the hydrogen evolution (Table 3). The i_0 values, which can be directly taken as a measure of the catalytic activities [13], are considerably higher at the noble metal-modified electrodes. The i_0 of PtRu1-modified electrode was 5.3 and 9.4 times higher than those of the Pt and Ru-modified electrodes, respectively. However, the PtRu3-modified electrode has lower hydrogen evolution activity than those of Pt and Ru-modified electrodes (Table 3), which could be related to its surface structure or intrinsic activity (Fig. 1e). Surely, the contribution of the real surface area of the electrodes cannot

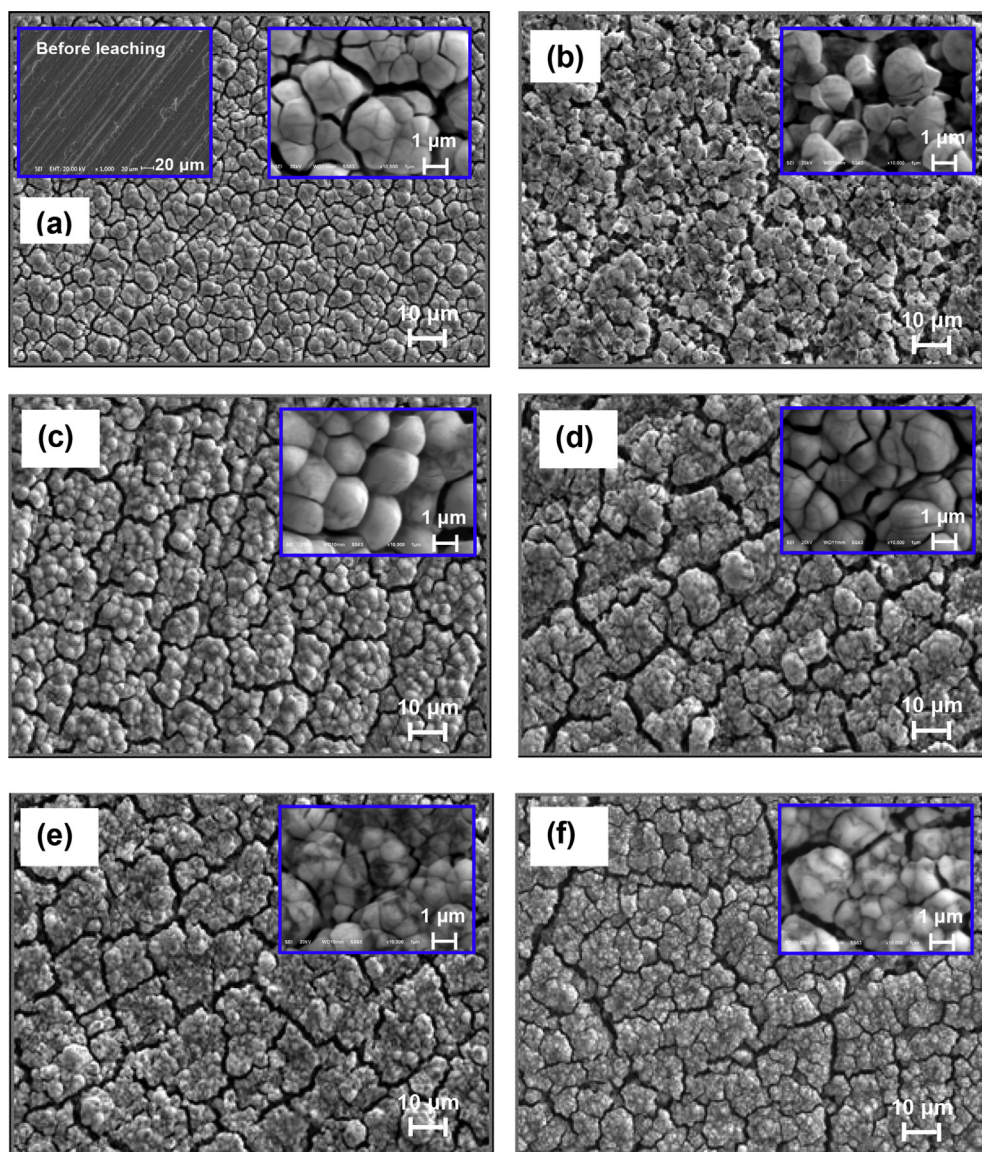


Fig. 1 – The SEM images of Cu/Ni/NiZn surface before etching (inset in Fig. 1a), after alkaline leaching (a). Cu/Ni/NiZn–Pt (b), Cu/Ni/NiZn–Ru (c), Cu/Ni/NiZn–PtRu1 (d), Cu/Ni/NiZn–PtRu2 (e) and Cu/Ni/NiZn–PtRu3 (f) surfaces (Mag: $\times 1.000$): Insets shows the related magnified mages (Mag: $\times 10.000$).

be ignored. Although the transfer coefficients are nearly the same (around 0.5), the intrinsic activities of Pt and Ru are different. So, the roughness factor cannot be calculated from data of current potential curves [19,55].

As it is seen from Table 3, the overpotentials at 100 mA cm^{-2} current density are reduced at the noble metal-modified electrodes depending on the chemical composition. The reduction of overpotential at PtRu1 modified electrode is 130 mV with respect to the Cu/Ni/NiZn electrode.

The rate determining step of multi-step reactions depends on the charge transfer coefficient (α), and symmetry factor, β . If $\alpha = \beta$ is very close to the 0.5, the Volmer reaction (Eq. (1)) is rate determining step [56,57]. The Tafel slopes of the electrodes were between 93 and 132 mV dec^{-1} which are close to the theoretical value of -118 mV dec^{-1} , and the α values were very close to 0.5 suggest that the Volmer step must control the HER at these electrodes [58–62]. The electrochemical

modification of the porous NiZn surface by the binary PtRu deposits does not change the hydrogen evolution mechanism. The current–potential curves show a typical Tafel behavior indicates that the HER is kinetically controlled [56,58,63].

As it is shown in Eq. (1), the Volmer step in the mechanism of the HER involves the adsorption of water molecules to produce the intermediate M-H_{ads} . So, it can be concluded that the surface modification of the porous Cu/Ni/NiZn electrode by Pt and/or Ru should enhance the adsorption of water molecules on the surface, which increases the surface coverage by the hydrogen. As a consequence, the hydrogen evolution is accelerated [12,15]. According to published literature, Pt exhibits good catalytic activity for the HER because of its intermediate M-H bonding strength [13,37]. The improvement of catalytic activity of the composite systems is generally attributed to synergism or the surface structures [59,64–66]. So, the high HER activity of the PtRu-modified

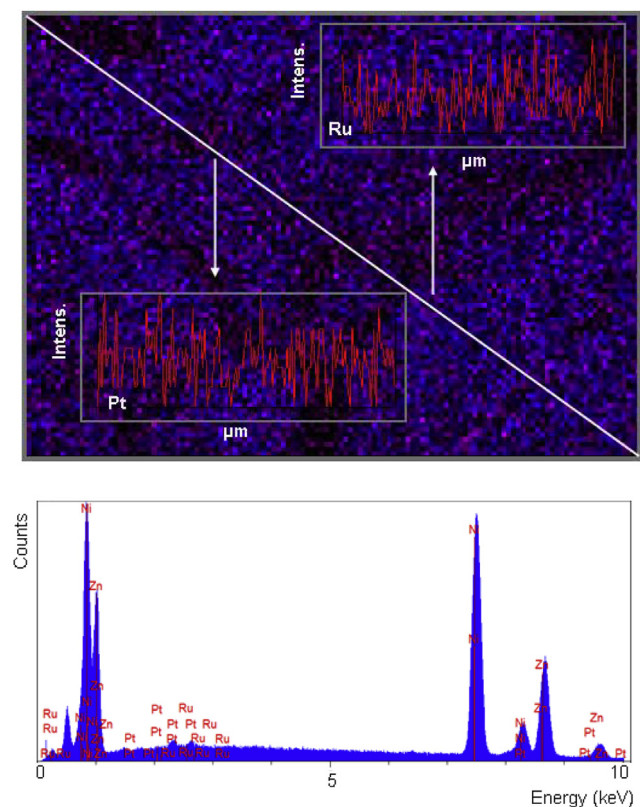


Fig. 2 – The distribution of metals (EDX dot mapping) over the surface (that was given on Fig. 1d), the change of Pt and Ru elements through a line over the surface (that was given on Fig. 1d as inset) and EDX spectrum of Cu/Ni/NiZn–PtRu1 electrode.

Table 2 – The elemental analysis of the layers determined by EDX.

| Working electrodes | Ni (wt.%) | Zn (wt.%) | Pt (wt.%) | Ru (wt.%) |
|-------------------------|-----------|-----------|-----------|-----------|
| ^a Cu/Ni/NiZn | 25.1 | 74.9 | – | – |
| Cu/Ni/NiZn | 64.5 | 35.5 | – | – |
| Cu/Ni/NiZn–Pt | 66.8 | 24.7 | 8.5 | – |
| Cu/Ni/NiZn–Ru | 52.2 | 37.4 | – | 10.4 |
| Cu/Ni/NiZn–PtRu1 | 51.8 | 38.8 | 5.3 | 4.1 |
| Cu/Ni/NiZn–PtRu2 | 52.0 | 38.7 | 4.7 | 4.8 |
| Cu/Ni/NiZn–PtRu3 | 50.2 | 39.2 | 4.4 | 6.2 |

^a Before alkaline leaching.

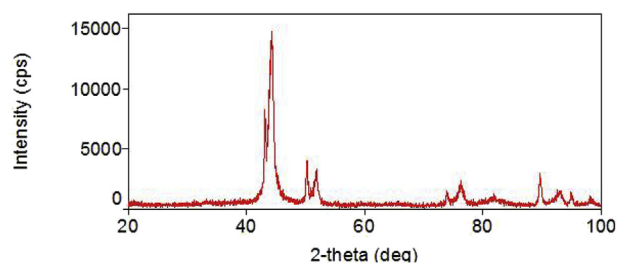


Fig. 3 – XRD diffractogram of Cu/Ni/NiZn–PtRu1 electrode.

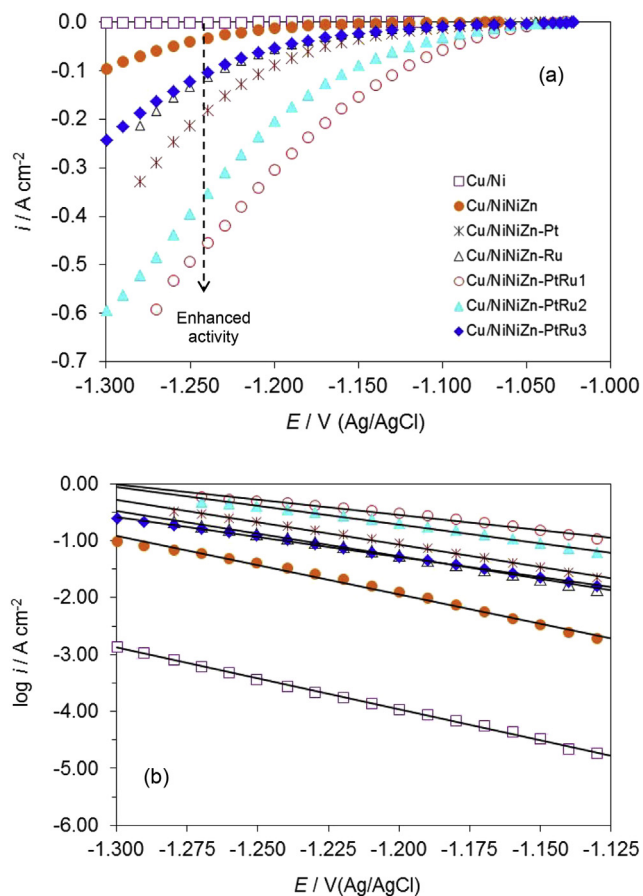


Fig. 4 – The current–potential curves (a) and Tafel plots (b) of the electrodes.

Table 3 – Electrochemical parameters determined from the current–potential curves.

| Working electrodes | $i_{-1.250}$ mA cm ⁻² | $-b_0$ mV dec ⁻¹ | α | i_0 mA cm ⁻² | $-\eta_{100}$ mV |
|--------------------|-------------------------------------|--------------------------------|----------|------------------------------|---------------------|
| Cu/Ni | 0.37 | 93 | 0.64 | 0.012 | 350 |
| Cu/Ni/NiZn | 40.0 | 97 | 0.61 | 0.31 | 236 |
| Cu/Ni/NiZn–Pt | 212.3 | 120 | 0.49 | 4.05 | 164 |
| Cu/Ni/NiZn–Ru | 133.0 | 119 | 0.50 | 2.30 | 189 |
| Cu/Ni/NiZn–PtRu1 | 493.3 | 132 | 0.45 | 21.59 | 106 |
| Cu/Ni/NiZn–PtRu2 | 395.8 | 120 | 0.49 | 10.48 | 131 |
| Cu/Ni/NiZn–PtRu3 | 121.2 | 124 | 0.48 | 2.05 | 216 |

NiZn–PtRu coatings can be related to the porous surface and well-known good intrinsic catalytic activity of Pt and Ru. The synergistic interactions between the metals are also possible.

Although the HER activity of the Cu/Ni/NiZn is lower than those reported in the literature for the similar coatings, NiZn [18,67], the results obtained showed that the modification of the Raney NiZn coatings by the noble metals can improve their catalytic activity. The hydrogen evolution activity of the NiZn deposits is strictly depends on the deposition conditions [17,18,68,69]. Because it is not the main aim of the present study, herein, the optimization studies of the NiZn coatings were not performed for the HER. The activity of the Cu/Ni/

NiZn–PtRu1 is higher than Fe–P–Pt [26], Pd-modified porous CoZn [52] and Pt-modified porous CoZn [50] coatings but lower than those reported for porous Ni modified by spontaneous deposition of Ru and Ir [44].

Conclusions

The Raney-type porous NiZn layers were prepared and modified by the PtRu binary composites. The modified electrodes were tested as cathode materials for the HER using electrochemical techniques. It was found that the coatings have porous structures. The alkaline leached Cu/NiZn electrode has good electrocatalytic activity towards the HER. Moreover, the deposition of small amounts of Pt, Ru and PtRu binary composites over the NiZn layer enhances markedly the hydrogen evolution performance of the electrode. The Cu/Ni/NiZn–PtRu1 electrode has the best activity toward the HER among the tested electrodes. The high HER activity of the PtRu-modified electrodes was related to their porous surface, good intrinsic catalytic activity of Pt and Ru as well as the synergistic interaction between the metals.

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