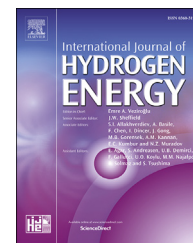


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Investigation of noble metal loading CoWZn electrode for HER

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ABSTRACT

It is important to metal deposition on the electrode surface to increase the electrocatalytic activity of the electrodes. CoWZn coated the graphite rod was used to prepare the cathode electrode. Moreover, then Pt and Ru metals were deposited on the electrode surface. These electrodes were named as CoWZnPt and CoWZnRu. Cyclic voltammetry, electrochemical impedance spectroscopy, and potentiodynamic polarization techniques were used for characterization of electrodes in alkaline media. Hydrogen evolution efficiency was determined by accumulated of hydrogen gas. The catalytic activity for hydrogen evolution reaction of CoWZn, CoWZnPt, and CoWZnRu electrodes was compared. It was reported that modification of the CoWZn electrode with low amounts of Ru enhances the HER activity of the electrodes. The enhancement in the hydrogen evolution activity of the electrodes was attributed to the increase in their real surface area and/or a possible synergistic effect between Co, W, Zn and Ru as well as the well-known intrinsic catalytic activity of Ru.

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Introduction

Hydrogen is considered as the fuel of the future due to unit capacity and high combustion heat when compared to oil and petroleum products. Hydrogen combustion products are not harmful to the environment. Hydrogen is the best fuel has been reported in previous studies [1].

Electrolysis of water is the best way to produce hydrogen. Electrolysis of water to produce hydrogen and oxygen gasses is a long multistep process. Water electrolyzer produces hydrogen and oxygen with electricity by the direct current source of pure water [2]. Increasing performance in hydrogen production with electrolyzer technology at low temperature and reducing the operation cost are needed. Electric power

consumption forms the largest fraction of the cost of the hydrogen production by electrolysis of water [3]. There are several ways to reduce the cost of hydrogen production. For example; the original design of the electrolysis stack array, improving electrode performance, reducing the energy consumption of auxiliary devices.

The disadvantage of the electrolysis is low electrode efficiency and production cost [4–6]. The efficiency of the electrode material is improved by the synergistic combination of electrocatalytic components or by increasing the ratio between the real and the geometric surface area of the electrode [7]. The choice of electrode materials is evaluated in many ways. Good electrode materials are needed to maximum electrical conductivity, high corrosion resistance, and minimum overvoltage. To develop new and cheaper electrode

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Table 1 – All of the bath compositions for electrodeposition.

	Bath composition	Time (s)
CoWZn	0.314 g $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 0.025 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 5.44 g Sodium Citrate, 0.015 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.56 g H_3BO_3	2700
Pt	2.49 mg Pt + 0.1 M KCl (50 mL volume)	70
Ru	2.05 mg Ru + 0.1 M KCl (50 mL volume)	203

materials with high electrocatalytic activity for HER attracts great interest for research [8–10].

Carbon-based materials have attracted much attention because of the unique mechanical and electrical conductivity and thermal properties [11–13] and expensive applications such as flow channels in the fuel cell, the probe of the electron microscope and field emission sensors [14,15]. Catalytic activity increases as a combination of low overvoltage and the high surface area with deposition of a transition metal on the carbon substrate.

Deactivation of the cathode is determined by either current loss in electrode potential or the increase in hydrogen overvoltage at constant current. Many researchers have focused on this issue to avoid deactivation problem and improve the energy efficiency of water electrolysis cells [16]. To the electrodeposition of ionic species on cobalt, electrode increases the efficiency and drops the overvoltage. The electrodeposition reduces the gap between the electrode and bulk solution. This approach reduces ohmic drops and provides more efficiency. The transition metals such as Ni, Fe, Co, Cu, and Zn can deposit on the electrode surface to achieve higher efficiency in hydrogen evolution reactions from water [17–20].

The development of materials with low overvoltage may be based on two fundamental characteristics for HER; increasing activity using more layered catalysts and increase the actual surface area.

For several years some noble metals have been used as ideal catalysts for many electrochemical processes. Their high catalytic activity, low overvoltage, and electrochemical stability are their advantages. The most suitable materials for the hydrogen evolution reaction according to the literature are Pt, Ir, Rh and Ru [21,22]. So many studies were carried out to develop high-performance of the electrodes with low Pt installation [23]. However, the use of Pt as solid metal for industrial processes is not appropriate because of its high cost and low abundance [24,25]. Therefore, it is important to increase the activity with less use of noble metals [26]. The studies such as C/Ni–NiIr, Mild Steel/Ni/NiZn–Pt, Cu/Ni/NiZn–PtRu, NiCoZn–Pt, Cu/Ni/NiZn–Pd and 3D-AgND showed that these metals are catalytically active [27–32]. The activity of C/Ni–NiIr electrode was also higher than that of the C/Ni and C/Ni–Ir [27]. The deposition of a small amount of Pt over the MS/Ni/NiZn could further improve its catalytic activity compared to MS/Ni/NiZn [28]. The alkaline leached Cu/NiZn electrode had good electrocatalytic activity towards the HER. Moreover, the deposition of small amounts of Pt, Ru and PtRu binary composites over the NiZn layer enhanced the hydrogen evolution performance of the electrode markedly. The Cu/Ni/NiZn–PtRu electrode had the best activity toward the HER [29]. NiCoZn–Pt electrode was found to be more effective for HER when compared to NiCoZn–Pd and NiCoZn–Ag [30]. The enhanced hydrogen evolution activity of the Pd-modified electrodes (Cu/Ni/NiZn–Pd) was assigned to the well-known better intrinsic catalytic activity of Pd, large active sites which afford abundant, accessible catalytic sites for the HER as well as to the possible synergistic effect between

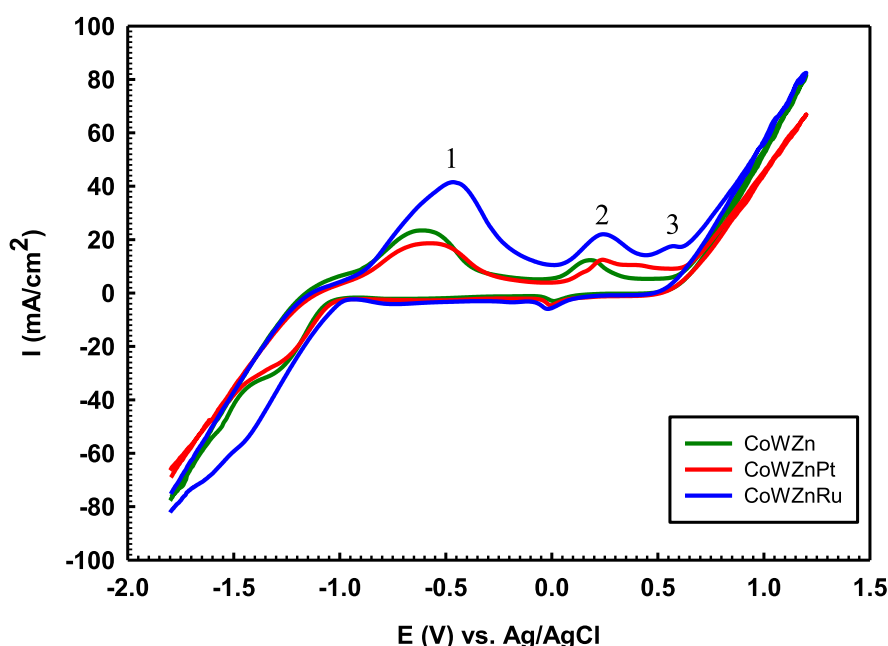


Fig. 1 – Cyclic voltammograms of CoWZn, CoWZnPt and CoWZnRu electrodes in 1.0 M KOH solution at room temperature.

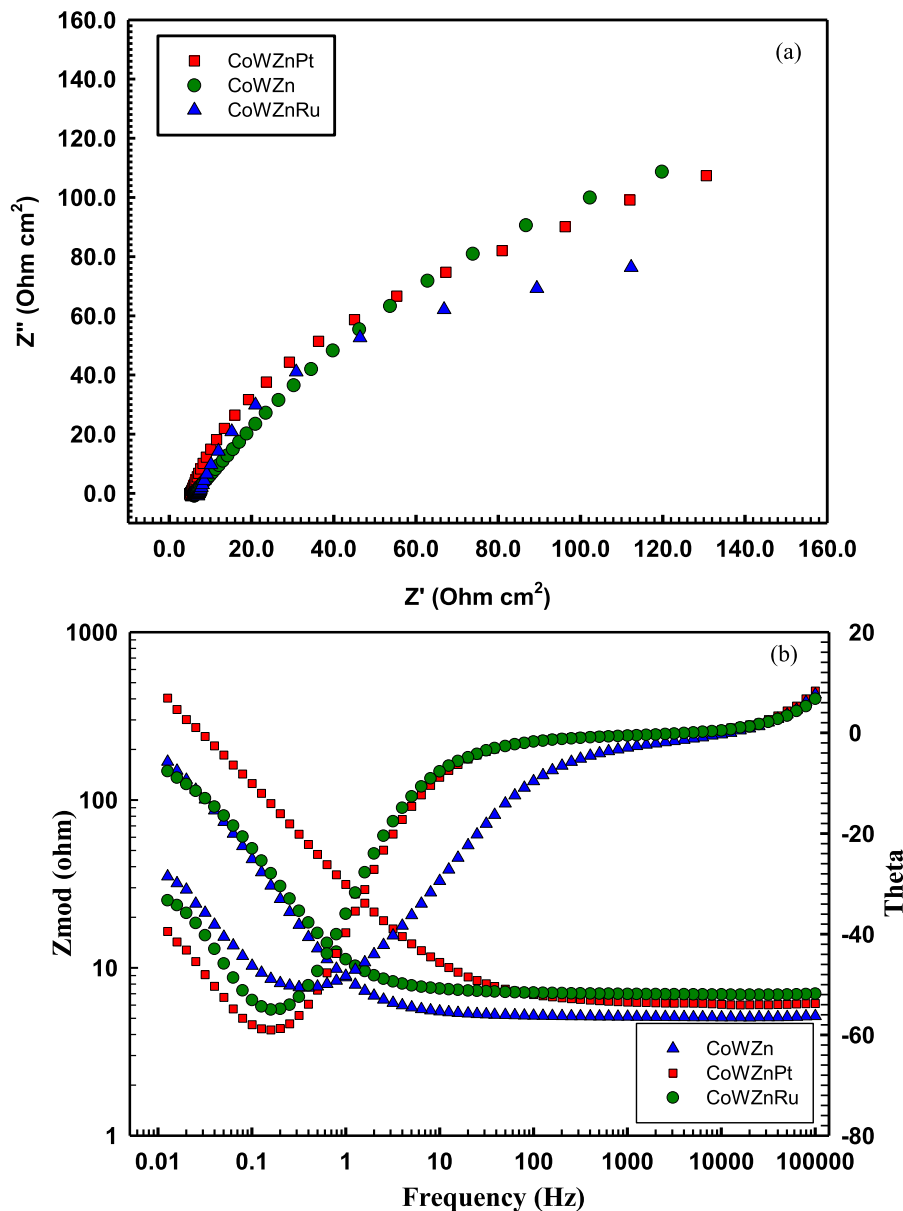


Fig. 2 – The Nyquist (a) and Bode-Phase angle (b) plots of CoWZn, CoWZnPt and CoWZnRu electrodes in 1.0 M KOH.

Ni, Zn and Pd atoms [31]. 3D-AgND electrode was also characterized by higher current density at a fixed over-potential when compared to bulk Ag. The superior hydrogen evolution performance of AgNDs was assigned to their high roughness and large real surface area [32].

Catalytic activity increases with increasing of d-electrons and reaches a maximum at which nearly filled d orbitals. After completion with 1 or 2 electrons in s-orbital then sharply decreases. Then with the successive addition of electrons to p- and d-orbitals increases again [33,34]. It is known that combination of two d metals limits the synergistic effect (Brewer theory) with increasing electroactivity towards hydrogen evolution [35,36].

C, which has low-cost and has high surface area, was used as a potential supporting material for preparation of catalytic electrodes. In this study, W and Zn co-deposited on graphite electrode. A small amount of platinum and ruthenium were

deposited onto the CoWZn to further enhance its catalytic activity for the HER. The aim of the study is to fabricate stable and cheap cathode materials with high hydrogen evolution activity. For this purpose, CoWZn, CoWZnPt, and CoWZnRu electrodes as catalysts were tested by different electrochemical analyses for HER in the alkaline electrolyte.

Experimental

The graphite rod was cut the length of 5 cm pieces from a cylindrical disc to prepare the working electrode. All pieces drilled from just one side to provide electrical conductivity by using copper wire. The electrodes were immersed into a polyester bath. Then, they dried under ambient air for 24 h. One side of the electrode which has 0.283 cm^2 surface area was abraded by emery papers (320–1200 grain size) before

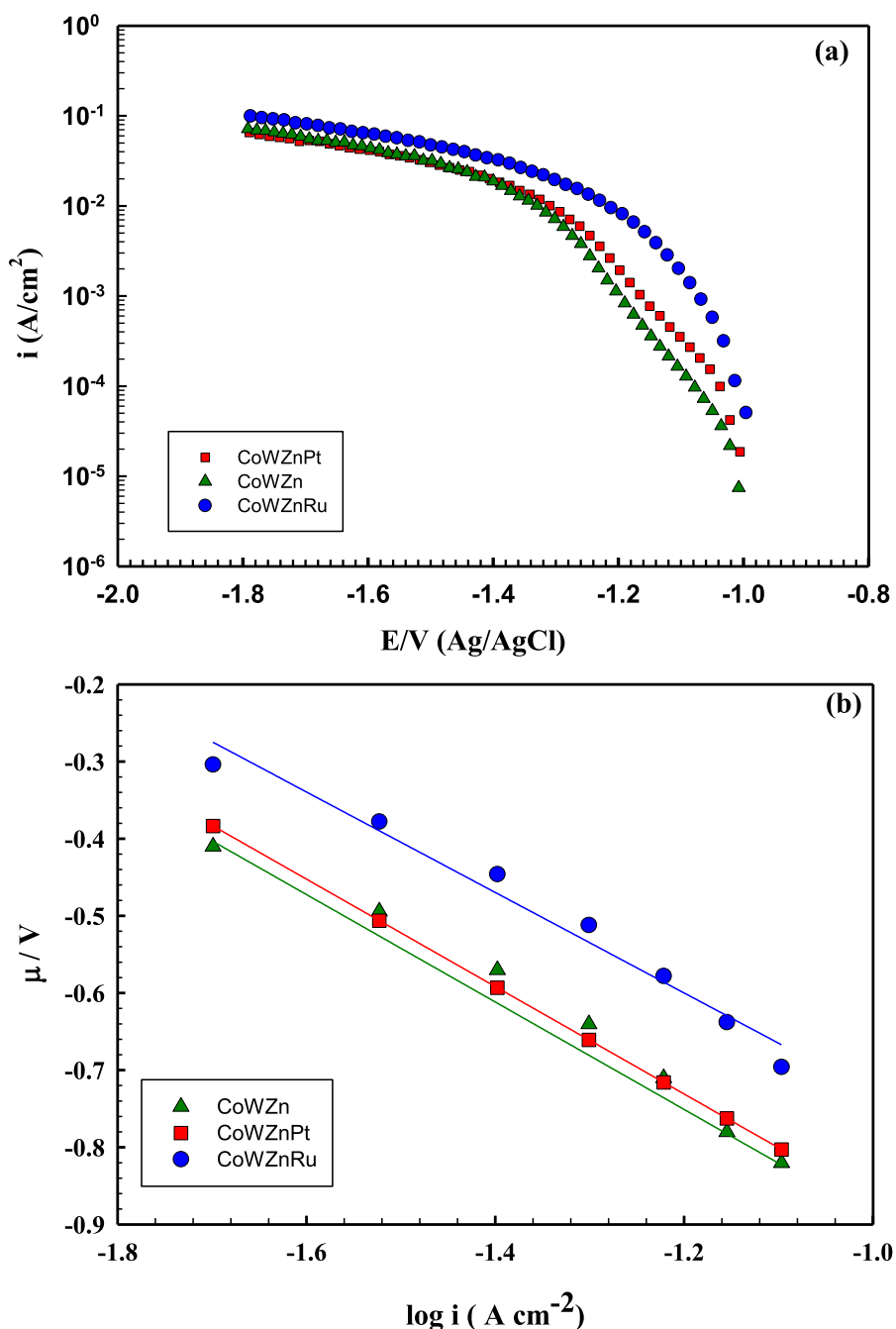


Fig. 3 – Cathodic potentiodynamic curves of CoWZn, CoWZnPt and CoWZnRu electrodes; (a) Tafel, (b) overpotential diagrams.

each experiment. The electrode surfaces were washed with distilled water, ethanol and distilled water again, respectively. Electrodeposition techniques were applied by two-electrode technique, and other characterization techniques were performed using potentiostat-galvanostat (Gamry Interface 1000 by three-electrode technique). Ag/AgCl and Pt were used as a reference and counter electrodes, respectively.

The electrodeposition of Co, W, Zn, Pt and Ru on graphite support electrode was performed galvanostatically using direct current power supply instrument (TT Technic-YH-303D). The working the counter electrodes were graphite disk and platinum sheet, which has a 2 cm² surface area,

respectively. CoWZn was coated on the graphite surface by a constant current density of 15 mA cm⁻² to the electrolysis system during 2700 s.

1 mg cm⁻² Ru or Pt was deposited on the CoWZn electrode by 15 mA cm⁻². The electrode was washed with distilled water and used for further electrochemical measurements. All of the bath compositions were given in Table 1.

The electrochemical characterizations of electrodes were analyzed by EIS, CV, and potentiodynamic polarization techniques. EIS experiments were obtained by a range of frequencies from 10^6 to 0.01 at 5 mV amplitude. CV analysis was determined at 100 mV s⁻¹ scan rate. Moreover,

Table 2 – The electrochemical data determined from cathodic potentiodynamic polarization curves at different overpotentials.

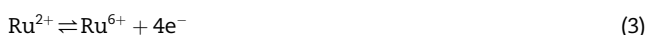
	$-\eta_{10}$ (mV)	$-\eta_{50}$ (mV)	$-\eta_{100}$ (mV)	i_0 (mA cm ⁻²)	β_c (mV dec ⁻¹)
CoWZn	1.308	1.672	2.260	0.076	135.0
CoWZnPt	1.326	1.658	2.170	0.262	120.0
CoWZnRu	1.220	1.512	1.786	0.835	114.0

potentiodynamic polarization plots were analyzed at 1 mV s⁻¹ scan rate at cathodic direction. All experiments were done in 1.00 M KOH solution at room temperature.

The electrolysis cell was set up by a burette, KOH solution, an anode and a cathode, preparing by electrodeposition for the hydrogen evolution measurement. The 1.0 M KOH solution filled burette was dipped into a beaker, including 1.0 M KOH solution. Preparing electrodes, which was used as the cathode, placed under the open end of burette's in the electrolyte. The platinum sheet, having 2 cm² surface area, was used as the anode electrode. The initial volume was recorded, and 30 mA cm⁻² constant current density was applied to electrodes during 1 h, and the volume of hydrogen was calculated by the volume change from the level of the solution at room temperature. The hydrogen gas and water vapor were measured in the burette as the total volume under these conditions. The hydrogen volume was calculated with considerations water vapor correction.

Results & discussions

Fig. 1 shows the cyclic voltammograms of CoWZn, CoWZnPt and CoWZnRu electrodes in 1.0 M KOH solution at 100 mV s⁻¹ scan rate. As it is seen from Fig. 1, at the anodic directions, 1, 2 and 3 peaks are Co/Co(II), Zn/Zn(II) and Ru(II)/Ru(VI) oxidation peaks [37,38].



The noble metal loadings on the surface affect the catalytic efficiency of electrodes for HER. The peak potentials of CoWZnPt and CoWZnRu electrodes are slightly more positive than CoWZn electrode. The electrode activity changed slightly with Pt loadings. The highest peak potentials were observed for CoWZnRu electrodes.

The Nyquist (a), Bode and phase angle-frequency (b) curves of CoWZn, CoWZnPt and CoWZnRu electrodes in 1.0 M KOH in the open-circuit potential in the ambient air are seen in Fig. 2. The electrodes have a single loop as semi-circles in the high-

frequency regions which controlled with charged transfer resistance and the Nyquist curves while an angular part was formed in low-frequency regions, including diffuse layer resistance, the angular part shows that the event was diffusion controlled [39]. The angular part of Ru loading electrode is more depressed comparing with CoWZn and CoWZnPt electrodes. The Bode and phase angle-frequency plots support the Nyquist curves, which are seen in Fig. 2. The single loop observed in the high-frequency regions became smaller when Ru loading. Pt loading on CoWZn reduced the angular part at low-frequency region comparison with CoWZn electrode. However, it cannot improve the Nyquist plot as well as Ru loading. Studies on ruthenium in the literature have shown that ruthenium is catalytically active for the HER reaction [40–45]. The addition of trace amount metallic Ru on the CoWZn electrode increased the efficiency of the catalysts and decreased the polarization resistance.

The potentiodynamic polarization curves of CoWZn, CoWZnPt, and CoWZnRu electrodes at the cathodic direction in 1.0 M KOH solution at 1 mV s⁻¹ scan rate are seen in Fig. 3. The potential ranges are preferred from –1.80 V to open circuit potential. As it can be seen in Figure, Ru loading electrode has the highest current density for HER by comparison with CoWZn and CoWZnPt electrodes. Moreover, the current densities on the CoWZnRu electrode show an important increase among the catalysts. The high current density shows that the prepared electrode is effective on the cathodic reaction in the water electrolysis. The open-circuit potentials of the CoWZn, CoWZnPt, and CoWZnRu electrodes were measured as –1.002 V, –0.998 V and –0.990 V respectively. Thus, the open-circuit potential at the CoWZnRu electrode tends to be more positive. These results may suggest that the high catalytic activity of Ru [38].

Tafel slope is an important property of electrocatalysts, and a slope of 120 mV dec⁻¹ could be observed when the Volmer reaction was the rate-limiting step (RLS) of the HER, whereas when the Heyrovsky or Tafel reactions were the rate-limiting steps of the HER, the Tafel slopes were 40 or 30 mV dec⁻¹, respectively [46]. For a complete hydrogen evolution (H₂), either the Volmer–Tafel or Volmer–Heyrovsky combinations of steps should be involved [47,48]. It could also be realized that the Tafel slope value of CoWZnRu measured as 114 mV dec⁻¹. It is about 120 mV dec⁻¹. These values implied to the proton discharge electrosorption (Volmer reaction) as the RLS for the HER.

The reaction kinetics of the hydrogen evolution was evaluated in three principle reactions. The total hydrogen reduction reaction is;



The reaction proceeds through the partial reactions of

Table 3 – Hydrogen gas volumes produced on preparing electrodes by electrolysis technique applying 30 mA cm⁻² constant current density over 1 h.

Cathode	V_{H_2} (mL cm ⁻²)
CoWZn	55.5
CoWZnPt	59.5
CoWZnRu	68.5

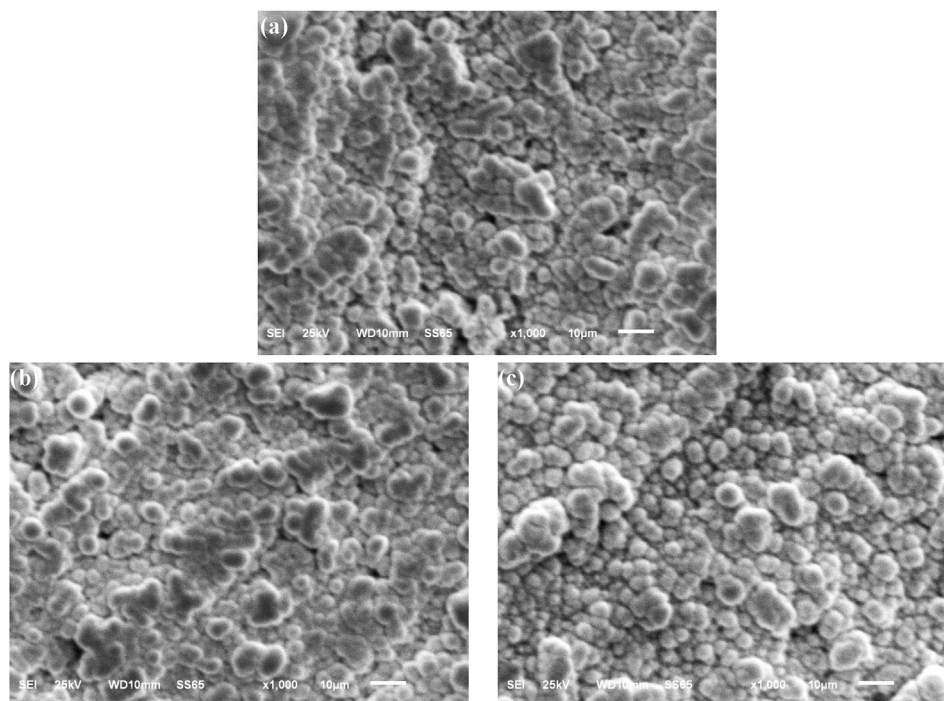
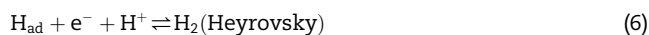


Fig. 4 – SEM images of CoWZn (a), CoWZnPt (b) and CoWZnRu (c) electrodes.



β_c values were calculated from Tafel slopes for each electrode. The highest β_c value was determined for the CoWZn electrode. The highest value specifies the worst electrocatalytic properties for HER [49].

Overpotential is one of the most practical methods for catalytic effect of the electrode in HER at a given current density (Table 2), in our studies at 10, 50 and 100 mA cm⁻² ($-\eta_{10}$, $-\eta_{50}$, $-\eta_{100}$). The overpotential is directly related to the catalytic efficiency of electrodes. Increasing overpotentials cause the decreasing of current density [20]. Analyses of potentiodynamic polarization curves were detected at 1 mV s⁻¹ scan rate in 1.0 M KOH solution in Fig. 3. Fig. 3a and b shows Tafel plots and overpotential diagrams, respectively. $-\eta_{100}$ for CoWZn and CoWZnPt electrodes were calculated by extrapolation method. Therefore, it is important to follow the changes while comparing of electrode activity. Having lower overpotential as the same current density within the various

electrode materials shows higher catalytic activity for the HER.

The electrolysis was applied to obtained electrodes at 30 mA cm⁻² current density during 1 h. The measured volumes of hydrogen are given in Table 3. As it can be seen in Table 3, the CoWZnRu catalysts produced more hydrogen gas than other electrodes. Hydrogen ions adsorbed onto the noble metal coated electrodes, and hydrogen evolution may continue to electrochemical reactions using more active area. The hydrogen gas volume increases at the CoWZnRu coating.

As it is seen in Fig. 4, the surface of the CoWZn had a granular structure. It is observed that the particles of the CoWZn have a diameter of about 3–5 μm (Fig. 4a), whereas the forming particles on the surface were measured about 7–10 μm after the Pt (Fig. 4b) and Ru (Fig. 4c) joints. It is understood that these newly formed particles belong to Ru and Pt metals. All SEM images were obtained under the same conditions (magnitude: 1.000× and 10 μm). The chemical compositions of prepared electrodes were determined by EDX. The compositions were given in Table 4.

Conclusion

The CoWZn, CoWZnPt and CoWZnRu electrodes were prepared and tested for potential use of the cathode catalyst for hydrogen evolution reaction. The prepared electrodes were characterized by using cyclic voltammetry, electrochemical impedance spectroscopy, and potentiodynamic polarization techniques. CoWZnRu electrode is the more effective electrode for hydrogen evolution when compared with CoWZn, CoWZnPt electrodes. The reduction of hydrogen was raised by using the CoWZnRu with a synergistic combination, and high

Table 4 – The chemical compositions of prepared electrodes.

	%Co	%W	%Zn	%Pt	%Ru
CoWZn	88.4	4.6	7.0	–	–
CoWZnPt	88.0	2.3	8.9	0.8	–
CoWZnRu	88.0	5.1	6.1	–	0.8

surface porosity. As a result of the experiments, the CoWZnRu electrode could be preferred for use in HER.

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