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## Copper – Zinc and Copper-Iron Binary Electrode for Hydrogen Evolution Reaction

Esra Telli\*<sup>1</sup>

### ABSTRACT

The different coatings with high hydrogen evolution reaction (HER) durability activity were prepared by electrodeposition. Iron, copper and zinc alloys were deposited on graphite electrode. The binary coating prepared on the graphite electrode. Zinc alloys were etched in alkaline solution to produce a porous and electrocatalytic surface suitable for use in the HER. The scanning electron microscopy (SEM) was used for surface characterization. Electrolysis was carried out in 1.0 M KOH solution by DC power supply. Cathodic current–potential curves, electrochemical impedance spectroscopy and cyclic voltammetry measurements were performed for chemical characterization. The experimental results show that the etching zinc alloys have compact and porous structures with good physical stability in comparison with other deposit for HER.

**Keywords:** Hydrogen evolution, Metal deposition, Cathode catalyst

## Hidrojen Çıkış Reaksiyonu İçin Bakır-Çinko ve Bakır-Demir İkili Kaplama

### ÖZ

Yüksek hidrojen gelişim reaksiyonu (HER) için dayanıklılık aktivitesine sahip farklı kaplamalar elektrokimyasal kaplama yöntemi ile hazırlanmıştır. Demir, bakır ve çinko alaşımları grafit elektrot üzerine çöktürüldü. Grafit elektrotu üzerine ikili kaplamalar hazırlanmıştır. Çinko alaşımları, HER' de kullanım için uygun gözenekli ve elektrokatalitik bir yüzey oluşturmak için alkali çözeltide aşındırılmıştır. Yüzey karakterizasyonu için taramalı elektron mikroskobu (SEM) kullanılmıştır. Elektroliz, DC güç kaynağı ile 1,0 M KOH çözeltisi içinde gerçekleştirilmiştir. Kimyasal karakterizasyon için katodik akım-potansiyel eğrileri, elektrokimyasal impedans spektroskopisi ve dönüşümlü voltametri ölçümleri yapılmıştır. Deneysel sonuçlar, aşındırılmış çinko alaşımlarının, HER için diğer elektrotlara kıyasla, fiziksel istikrarı iyi olan kompakt ve gözenekli yapılara sahip olduklarını göstermektedir.

**Anahtar Kelimeler:** Hidrojen gelişimi, Metal biriktirme, Katot katalizörü

\* Corresponding Author

<sup>1</sup> Affiliation, [esratelli@osmaniye.edu.tr](mailto:esratelli@osmaniye.edu.tr)

## 1. INTRODUCTION

Fossil fuel sources are rapidly approaching the end. Hydrogen energy is very attractive due to the depletion of fossil fuels and environmental problems. In addition, hydrogen plays an important role in many applications [1]. Hydrogen with high energy capacity and zero carbon emissions, recyclable is a clean energy source that can replace fossil fuels [2]. Some techniques such as electrolysis, photocatalysis, and thermolysis are used to obtain hydrogen [3]. Hydrogen production from water electrolysis in acidic or alkaline solutions using various metal catalysts is one of the most studied reactions because of the production of high purity hydrogen [4]. Where non-noble metals are used as catalysts, an alkali solution is generally preferred. Because excessive amounts of hydroxide ions make possible the hydrogen evolution reaction (HER), when alkaline solutions are used [5]. The efficiency of HER depends on the metal used as the catalyst. So, alkaline water electrolysis is often preferred for HER.

Alkaline water electrolysis is widely used to obtain high purity hydrogen. However, the cost is still quite expensive [6]. Because noble metals such as Pt group are commonly preferred as a catalyst because of their high catalytic efficiency [7]. However, they have high cost and low availability. Therefore, it is important to develop low cost and high abundance electrocatalyst for HER [8, 9].

It is not easy to find new materials among pure metals with high catalytic activity for HER as well as precious metals. The use of alloys of two or more metals is an important approach to increase electrocatalytic activity for HER [10]. According to the electrocatalytic theory, it is explained that the electrocatalytic activity is due to the adsorption heat of the intermediates on the electrode surface by the well-known volcano curves [11].

In volcano curve, some metals with strong hydrogen bonds such as Cu, Fe, and Ni are chosen for catalysts preparation. Copper metal with the porous surface is used in applications such as electrocatalysis, fuel cell, batteries, capacitors, sensors, and super-hydrophobicity [12, 13]. The benefit of the porous electrocatalytic surface is that true surface area per unit geometric area is muchfolds. This reduces the actual current density and requires less overvoltage, which significantly reduces energy consumption [14]. Electrodeposition is very convenient for controlling cost, deposit morphology and various

parameters such as electrolyte composition, temperature and time for obtaining a porous copper surface [15, 16]. The binary and ternary alloys prepared by leaching of zinc are used as highly effective electrocatalysts for HER [17-23]. The leaching of zinc causes a loss of mass as well as a highly porous surface to use in alkaline water electrolysis.

The aim of this study was electrochemical preparation and characterization of the CuFe and CuZn composite coatings, which are not found in literature, in view of their possible applications as electrocatalytic materials for the HER in alkaline medium. The HER activity of prepared electrodes has been investigated using electrolysis, cyclic voltammetry (CV), cathodic polarization and electrochemical impedance spectroscopy (EIS) techniques in 1 M KOH solution.

## 2. EXPERIMENTAL

The graphite electrodes were cut from a cylindrical rod to a length of 5 cm and coated with polyester to a surface area of 0.283 cm<sup>2</sup>. The electrical conductivity was provided by a copper wire. The electrode surface was polished with emery paper (320–1000 grain size), then washed with distilled water, ethanol and distilled water again, respectively. The electrodes were immersed in the bath solution.

The electrodeposition was performed galvanostatically using a direct current power supply instrument (TT Technic-YH-303D). The positive electrode was the platinum sheet (with 2 cm<sup>2</sup> surface area). The coatings were applied on the graphite surface by a constant current density of 15 mA cm<sup>-2</sup> to the electrolysis system during 2700 s. During the deposition, bath solutions whose chemical compositions are given below were continuously stirred using a magnetic stirrer at room temperature. The deposition current density and deposition time for all electrodes were 15 mA cm<sup>-2</sup> and 2700 s, respectively.

- Copper bath (C/Cu): 27.72 % CuSO<sub>4</sub>·5H<sub>2</sub>O, 1.25% H<sub>3</sub>BO<sub>3</sub> (w/w) [23]
- Iron bath: 30.86 % FeSO<sub>4</sub>·7H<sub>2</sub>O and 1.25% H<sub>3</sub>BO<sub>3</sub> (w/w) [9]
- Zinc bath: 31.92 % ZnSO<sub>4</sub>·7H<sub>2</sub>O and 1.25% H<sub>3</sub>BO<sub>3</sub> (w/w) [9]
- Copper–iron co-deposition (CuFe): 10 mL copper bath and 20 mL iron bath were mixed.

- Copper–Zinc co-deposition (CuZn): 10 mL copper bath and 20 mL zinc bath were mixed.
- Copper–Zinc etching process (Cu@Zn): After the deposition of CuZn on graphite, more active Zn was leached out from the surface of the CuZn deposit by etching in 1.0 M NaOH for one hour, then 30% NaOH solution for 3 hours at room temperature.

The scanning electron microscopy (SEM) analyze was performed to investigate electrode surfaces morphologies. The electrochemical measurements were carried out galvanostatically using Potentiostat–galvanostat (Gamry Interface 1000) with a three-electrode configuration. A platinum sheet (with 2 cm<sup>2</sup> surface area) and Ag/AgCl electrode were used as the auxiliary and the reference electrodes, respectively. The electrochemical characterizations of electrodes were analyzed by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and potentiodynamic polarization techniques. EIS experiments were obtained by a range of frequencies from 10<sup>6</sup> to 0.01 at 5 mV amplitude. CV analysis were determined at 100 mV s<sup>-1</sup> scan rate. The potentiodynamic polarization plots were analyzed at 1 mV s<sup>-1</sup> scan rate at cathodic direction. All experiments were performed in 1.00 M KOH solution at room temperature.

The electrolysis cell was set up by a burette including 1.0 M KOH solution, an anode and a cathode which were prepared by electrodeposition for the hydrogen evolution measurement. The initial volume was recorded and 30 mA cm<sup>-2</sup> constant current density was applied to electrodes during 1 hour, 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 total volume under these conditions. The hydrogen volume was calculated with considerations water vapor correction.

### 3. RESULTS & DISCUSSIONS

The cyclic voltammograms of Cu, CuFe, CuZn and Cu@Zn electrodes obtained in 1.0 M KOH at 100 mV s<sup>-1</sup> scan rate and room temperature were given in Fig 1. As seen in the voltammograms, all binary coatings exhibit higher activity than the single coating of copper. In binary coatings, whereas zinc doping was more effective than iron doping, it is seen that the electrode obtained by

applying etch process to zinc doping has a higher catalytic activity than all other electrodes.

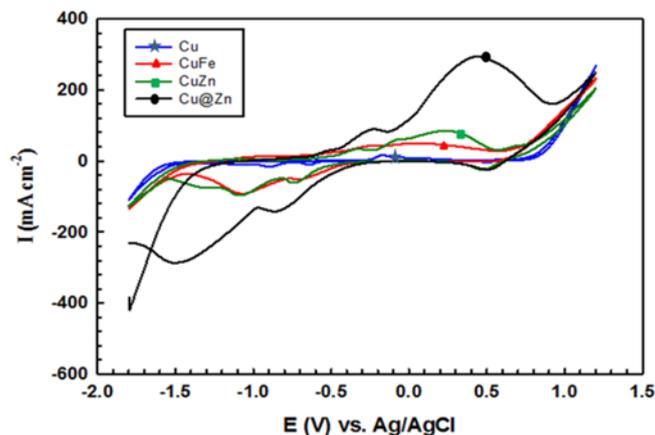


Figure 1. The cyclic voltammograms of Cu, CuFe, CuZn and Cu@Zn electrodes obtained in 1.0 M KOH at 100 mV s<sup>-1</sup> scan rate and room temperature.

With iron doping, Fe/Fe<sup>+2</sup> oxidation is observed at more negative potentials than the anodic copper peaks, but this transformation is not reversible, so the reduction peak of this transformation is not visible in the cathodic direction. After zinc adding, the peak formation is observed around 0.5 V. This peak belongs to Zn/Zn<sup>2+</sup> oxidation and the reduction of this peak reversibly is seen in cathodic scan. After the application of the etch process, there is a strong increase in the peak of the zinc oxidation as in all the peaks. It is understood from this that the etch-treated electrode exhibits the most catalytically active behavior. The obtained current densities for Cu@Zn is higher than the literature [24, 25].

Figure 2 shows the Nyquist and phase angle diagrams obtained by applying 5 mV amplitude in the frequency range of 10<sup>6</sup> Hz to 0.1 Hz in 1.0 M KOH solution of CuFe, CuZn and Cu@Zn electrodes. As seen in Fig. 2, CuFe and CuZn electrodes have a loop in the high frequency region and an angular portion in the low frequency region. The loop in the low frequency region corresponds to the charge transfer resistance. The angular portion indicates that the phenomenon is diffusion controlled. On the electrode subjected to the etch process, only a single loop corresponding to the load transfer resistance is observed. This shows us that the phenomenon in the etch-treated electrode is achieved by charge transfer rather than diffusion control. These results demonstrate that increasing surface area with etch process linearly affects the catalytic activity.

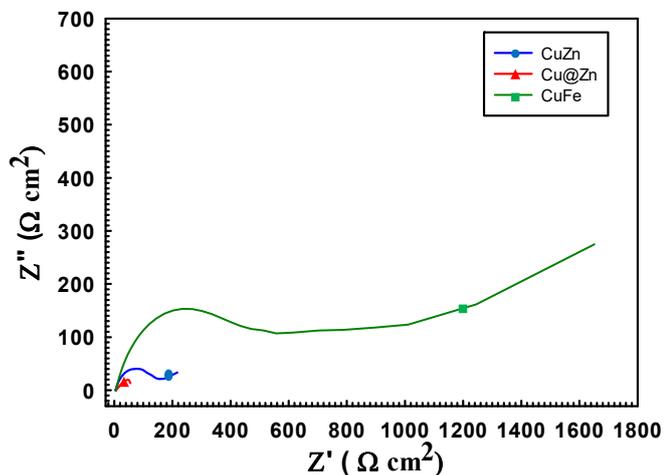


Figure 2. Nyquist plots for CuFe, CuZn and Cu@Zn electrodes at room temperature.

Polarization and overpotential curves of CuFe, CuZn and Cu@Zn in 1.0 M KOH solution at  $1 \text{ mV s}^{-1}$  scan rate at room temperature are seen in Fig 3. Cu@Zn has the lowest over-voltage at each current value. This explains that Cu@Zn electrode has the highest catalytic efficiency. The adsorption of water molecules plays an important role in the oxidation mechanism of hydrogen in the alkaline solution and in the discharge kinetics of hydrogen, and the generally accepted mechanism of hydrogen evolution in alkaline solution is achieved by the Volmer reaction. After this step, either the Heyrovsky reaction (electrochemical desorption) or the Tafel reaction (chemical recombination) is followed. As seen in Fig. 3b, the overpotential plots for all binary cathode are linear at negative potentials. This is indicating that the predominant mechanism of HER on these electrodes appears to be a discharge of water (Volmer reaction) followed by electrochemical desorption step (Heyrovsky)[23]. Table 1 shows that the electrochemical data was obtained from Fig. 2 and Fig. 3.

According to results, the lowest overpotential was seen for the Cu@Zn electrode at all current densities (10, 50 and  $100 \text{ mA cm}^{-2}$ ). The lowest ohmic resistance was obtained from the same electrode. This result when compared to the literature, Cu@Zn electrode lower than [26, 27]

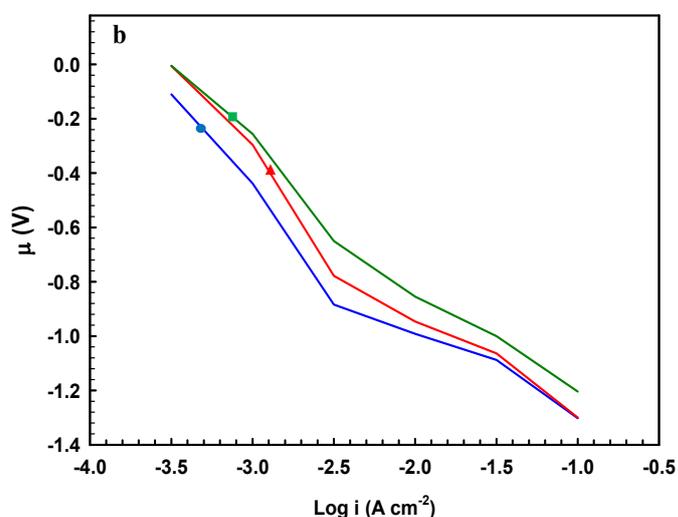
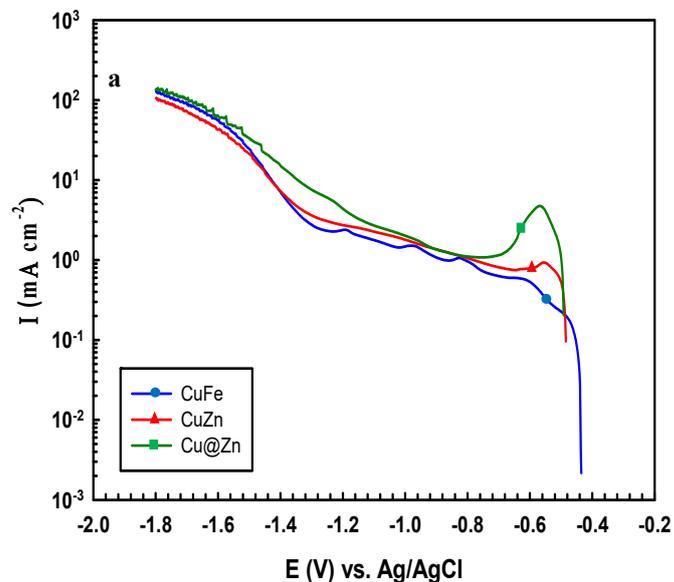


Figure 3. Polarization curves of CuFe, CuZn and Cu@Zn in 1.0 M KOH solution at  $1 \text{ mV s}^{-1}$  scan rate at room temperature (a) and overpotential diagram (b).

Table 1. The electrochemical data was obtained from Fig. 2 and Fig. 3.

	$\eta_{10}$	$\eta_{50}$	$\eta_{100}$	$\Omega \text{ cm}^2$
<b>CuFe (V)</b>	1.30	1.15	0.99	1651
<b>CuZn (V)</b>	1.30	1.10	0.95	217
<b>Cu@Zn (V)</b>	1.20	0.98	0.85	55

SEM micrographs of CuFe, CuZn and Cu@Zn are given in Fig 4. When the micrograph taken from the surface of the CuFe electrode is examined, it is observed that there is a nonporous pile stacked adjacent to each other on the surface (Fig 4a). In Fig. 4b, it can be seen that by the addition of some zinc with copper, pores are formed on the surface, and zinc deposits similar to crystal structure are formed on copper. It has been observed that spheres are formed in the range of 25 to  $100 \mu\text{m}$  on the electrode surface. As far as we can see from the comparison of Fig. 4a and b, it is seen that the

spherical formation on the surface is welded with zinc. A similar surface image can also be seen in the SEM image taken on the electrode exposed to the etch process (Fig 4c). Here, the abrasion on the surface can be clearly observed due to the etch process, and the sizes of the spheres on the surface are different from those of the non-etch process. The smallest sphere size on this electrode is 10  $\mu\text{m}$ , while the largest can exceed 100  $\mu\text{m}$ . The white residues on the surface are thought to originate from the NaOH used in the etching process.

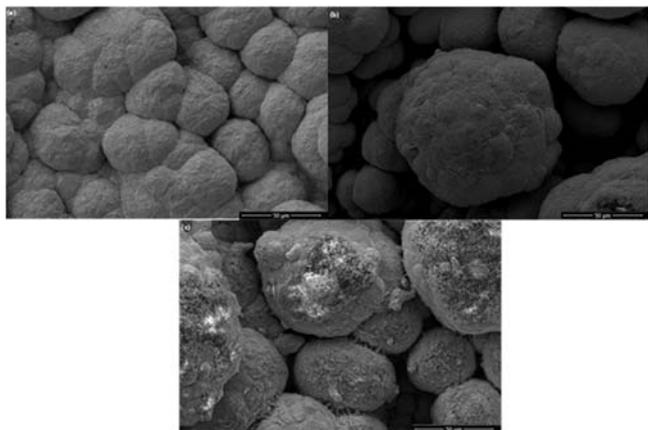


Figure 4. SEM micrographs of CuFe(a), CuZn (b), and Cu@Zn (c).

The electrodes were used to determine the volume of hydrogen as a cathode, immersed in a 1.0 M KOH solution with a current of 30  $\text{mA cm}^{-2}$  for 1 hour. At the end of 1 hour, the volume of the accumulated gas from the burette was determined by adjusting the volume originating from water vapor using the room temperature and pressure values. The measured hydrogen volumes for each electrode are given in Table 2. As can be understood from the table, the Cu@Zn electrode produces the most hydrogen after 1 hour.

Table 2. Hydrogen gas volumes produced on preparing electrodes by electrolysis technique.

Cathode	$V_{\text{H}_2}$ ( $\text{mL cm}^{-2}$ )
CuFe	72.8
CuZn	85.5
Cu@Zn	93.7

#### 4. CONCLUSION

The CuFe, CuZn, and Cu@Zn electrodes, which are not investigated at previous studies, were prepared and analyzed for potential use for hydrogen evolution reaction.

- From the data obtained as a result of electrochemical analysis, Cu@Zn electrode

was found to be catalytically active for hydrogen production.

- According to SEM images taken from electrode surfaces, zinc doping instead of iron results in a more porous structure on the surface of the binary electrode. The application of the etch process not only increases the voids on the electrode surface but also increases the catalytic activity.
- Compared with hydrogen volumes taken from the electrolysis cell, the most effective electrode seems to be Cu@Zn.

In the light of the above results, the Cu@Zn electrode can be used as a catalyst for the hydrogen reduction reaction in electrolysis cells.

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#### REFERENCES

- [1] J. K. Lee, Y. Yi, H. J. Lee, S. Uhm, and J. Lee, "Electrocatalytic activity of Ni nanowires prepared by galvanic electrodeposition for hydrogen evolution reaction," *Catalysis Today*, vol. 146, pp. 188-191, 2009.
- [2] E. Baran and B. Yazici, "Effect of different nano-structured Ag doped TiO<sub>2</sub>-NTs fabricated by electrodeposition on the electrocatalytic hydrogen production," *International Journal of Hydrogen Energy*, vol. 41, pp. 2498-2511, 2016.
- [3] T. Sun, E. Liu, X. Liang, X. Hu, and J. Fan, "Enhanced hydrogen evolution from water splitting using Fe-Ni codoped and Ag deposited anatase TiO<sub>2</sub> synthesized by solvothermal method," *Applied Surface Science*, vol. 347, pp. 696-705, 2015.
- [4] M. Wang, Z. Wang, X. Gong, and Z. Guo, "The intensification technologies to water electrolysis for hydrogen production—A review," *Renewable and Sustainable Energy Reviews*, vol. 29, pp. 573-588, 2014.
- [5] S. H. Hong, S. H. Ahn, J. Choi, J. Y. Kim, H. Y. Kim, H.-J. Kim, *et al.*, "High-activity electrodeposited NiW catalysts for hydrogen evolution in alkaline water

- electrolysis," *Applied Surface Science*, vol. 349, pp. 629-635, 2015.
- [6] Y. Zhu, X. Zhang, J. Song, W. Wang, F. Yue, and Q. Ma, "Microstructure and hydrogen evolution catalytic properties of Ni-Sn alloys prepared by electrodeposition method," *Applied Catalysis A: General*, vol. 500, pp. 51-57, 2015.
- [7] Z. Pu, Q. Liu, A. M. Asiri, A. Y. Obaid, and X. Sun, "One-step electrodeposition fabrication of graphene film-confined WS<sub>2</sub> nanoparticles with enhanced electrochemical catalytic activity for hydrogen evolution," *Electrochimica Acta*, vol. 134, pp. 8-12, 2014.
- [8] D. Brown, M. Mahmood, A. Turner, S. Hall, and P. Fogarty, "Low overvoltage electrocatalysts for hydrogen evolving electrodes," *International Journal of Hydrogen Energy*, vol. 7, pp. 405-410, 1982.
- [9] M. Farsak, E. Telli, A. O. Yüce, and G. Kardaş, "The noble metal loading binary iron–zinc electrode for hydrogen production," *International Journal of Hydrogen Energy*, vol. 42, pp. 6455-6461, 2017.
- [10] N. Krstajić, V. Jović, L. Gajić-Krstajić, B. Jović, A. Antozzi, and G. Martelli, "Electrodeposition of Ni–Mo alloy coatings and their characterization as cathodes for hydrogen evolution in sodium hydroxide solution," *International Journal of Hydrogen Energy*, vol. 33, pp. 3676-3687, 2008.
- [11] R. Parsons, "The rate of electrolytic hydrogen evolution and the heat of adsorption of hydrogen," *Transactions of the Faraday Society*, vol. 54, pp. 1053-1063, 1958.
- [12] S. Eugénio, T. Silva, M. Carmezim, R. Duarte, and M. Montemor, "Electrodeposition and characterization of nickel–copper metallic foams for application as electrodes for supercapacitors," *Journal of Applied Electrochemistry*, vol. 44, pp. 455-465, 2014.
- [13] F. Dogan, L. D. Sanjeeva, S.-J. Hwu, and J. Vaughey, "Electrodeposited copper foams as substrates for thin film silicon electrodes," *Solid State Ionics*, vol. 288, pp. 204-206, 2016.
- [14] K. Mazloomi, N. B. Sulaiman, and H. Moayedi, "Electrical efficiency of electrolytic hydrogen production," *International Journal of Electrochemical Science*, vol. 7, pp. 3314-3326, 2012.
- [15] H. C. Shin, J. Dong, and M. Liu, "Nanoporous structures prepared by an electrochemical deposition process," *Advanced Materials*, vol. 15, pp. 1610-1614, 2003.
- [16] H. Singh, P. Dheeraj, Y. P. Singh, G. Rathore, and M. Bhardwaj, "Electrodeposition of porous copper as a substrate for electrocatalytic material," *Journal of Electroanalytical Chemistry*, vol. 785, pp. 1-7, 2017.
- [17] R. Solmaz and G. Kardaş, "Fabrication and characterization of NiCoZn–M (M: Ag, Pd and Pt) electrocatalysts as cathode materials for electrochemical hydrogen production," *international journal of hydrogen energy*, vol. 36, pp. 12079-12087, 2011.
- [18] A. Döner, R. Solmaz, and G. Kardaş, "Enhancement of hydrogen evolution at cobalt–zinc deposited graphite electrode in alkaline solution," *international journal of hydrogen energy*, vol. 36, pp. 7391-7397, 2011.
- [19] R. Solmaz and G. Kardaş, "Hydrogen evolution and corrosion performance of NiZn coatings," *Energy Conversion and Management*, vol. 48, pp. 583-591, 2007.
- [20] R. Solmaz, A. Salcı, H. Yüksel, M. Doğrubaş, and G. Kardaş, "Preparation and characterization of Pd-modified Raney-type NiZn coatings and their application for alkaline water electrolysis," *International Journal of Hydrogen Energy*, vol. 42, pp. 2464-2475, 2017.
- [21] R. Solmaz, A. Döner, M. Doğrubaş, İ. Y. Erdoğan, and G. Kardaş, "Enhancement of electrochemical activity of Raney-type NiZn coatings by modifying with PtRu binary deposits: Application for alkaline water electrolysis," *International Journal of Hydrogen Energy*, vol. 41, pp. 1432-1440, 2016.
- [22] R. Solmaz, A. Döner, and G. Kardaş, "Preparation, characterization and application of alkaline leached CuNiZn ternary coatings for long-term electrolysis in alkaline solution," *International Journal*

- of Hydrogen Energy*, vol. 35, pp. 10045-10049, 2010.
- [23] A. Döner, R. Solmaz, and G. Kardaş, "Fabrication and characterization of alkaline leached CuZn/Cu electrode as anode material for direct methanol fuel cell," *Energy*, vol. 90, pp. 1144-1151, 2015.
- [24] S. Padmapriya, S. Harinipriya, V. Sudha, D. Kumar, S. Pal, and B. Chaubey, "Polyaniline coated copper for hydrogen storage and evolution in alkaline medium," *International Journal of Hydrogen Energy*, vol. 42, pp. 20453-20462, 2017/08/10/ 2017.
- [25] G. R. Monama, S. B. Mdluli, G. Mashao, M. D. Makhafola, K. E. Ramohlola, K. M. Molapo, *et al.*, "Palladium deposition on copper(II) phthalocyanine/metal organic framework composite and electrocatalytic activity of the modified electrode towards the hydrogen evolution reaction," *Renewable Energy*, vol. 119, pp. 62-72, 2018/04/01/ 2018.
- [26] S. R. Hosseini, S. Ghasemi, and S. A. Ghasemi, "Effect of surfactants on electrocatalytic performance of copper nanoparticles for hydrogen evolution reaction," *Journal of Molecular Liquids*, vol. 222, pp. 1068-1075, 2016/10/01/ 2016.
- [27] C. Canales, A. F. Olea, L. Gidi, R. Arce, and G. Ramírez, "Enhanced light-induced hydrogen evolution reaction by supramolecular systems of cobalt(II) and copper(II) octaethylporphyrins on glassy carbon electrodes," *Electrochimica Acta*, vol. 258, pp. 850-857, 2017/12/20/ 2017.