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Chapter

Investigation of Zn/Ni-Based Electrocatalysts for Electrochemical Conversion of CO₂ to SYNGAS

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Abstract

In the last decade, there is some research on the conversion of CO₂ to energy form. CO₂ can be converted to value-added chemicals including HCOOH, CO, CH₄, C₂H₄, and liquid hydrocarbons that can be used in various industries. Among the methods, electrochemical methods are of concern regarding their capability to operate with an acceptable reaction rate and great efficiency at room temperature and can be easily coupled with renewable energy sources. Besides, electrochemical cell devices have been manufactured in a variety of sizes, from portable to large-scale applications. Catalysts that optionally reduce CO₂ at low potential are required. Therefore, choosing a suitable electrocatalyst is very important. This chapter focused on the electrochemical reduction of CO₂ by Zn-Ni bimetallic electrocatalyst. The Zn-Ni coatings were deposited on the low-carbon steel substrate. Electrochemical deposition parameters such as temperature in terms of LPR corrosion rate, microstructure, microcracks, and its composition have been investigated. Then, the electrocatalyst stability and activity, as well as gas intensity and selectivity, were inspected by SEM/EDX analysis, GC, and electrochemical tests. Among the electrocatalysts for CO₂ reduction reaction, the Zn₆₅%–Ni₃₅% electrode with cluster-like microstructure had the best performance for CO₂ reduction reaction according to minimum coke formation (<10%) and optimum CO and H₂ faradaic efficiencies (CO FE% = 55% and H₂ FE% = 45%).

Keywords: electrocatalyst, electrochemical method, CO₂ reduction reaction, Zn-Ni, energy conversion, pollution, catalyst activity and stability

1. Introduction

Carbon dioxide is a chemical compound made up of one carbon atom and two oxygen atoms. It is existing in minimal concentrations in the atmosphere and behaves as a greenhouse gas that promotes environmental warming and pollution. However, carbon dioxide can be used as a source of high-value chemicals, as a source of sustainable energy. So far, many activities have been done to convert CO₂ into chemical materials, which can be applied as fuel for the industries.
With the increasing demand for energy and population growth, CO₂ emissions have grown as a by-product of power and industrial plants. In the last decade, CO₂ conversion has increased to other beneficial products. This process is useful for reducing pollution and warming of the earth. Developing a variety of electrocatalysts with high efficiency and good stability is a crucial issue [1].

The electrochemical CO₂ reaction reduction in recent decades has become crucial because it is a good reaction to artificial fuels and energy storage. When this process is linked to renewable energy sources such as solar cells, it can be a good alternative to fossil fuels. It also reduces CO₂ emissions in the atmosphere. But there are major problems for the reaction of CO₂ reduction, which includes low efficiency and low catalytic activity with cost-effective catalysts. Therefore, there is an important challenge in the present research, so that catalyst with better selectivity and higher activity and stability can be developed [2].

In recent years, several studies were done on various electrocatalysts, but yet, there are problems in Faradaic Efficiency (FE), Current Density (CD), Energy Efficiency, electrocatalyst deactivate, the internal resistance of electrocatalysts, and the potential for scalability to the large sizes without the loss of efficiency, because CO₂ is a thermodynamically stable molecule, it is fully oxidized [3–12]. A suitable electrocatalyst to reduce CO₂ is necessary to reach a low-cost process with acceptable selectivity and efficiency. In recent decades, the electrochemical reduction of CO₂ has interested a lot of consideration as low-cost electricity can come from renewable sources of energy such as solar and wind [13–18].

1.1 Zn-Ni coating

Zinc as another choice of cadmium has been studied for its ability to resist corrosion regarding its sacrificial properties and has demonstrated its ability to provide adequate corrosion behavior results through the study conducted on mechanical properties and corrosion protection of Zn electrodeposition [19]. Though Zn is considered a possible option, its corrosion behavior does not look acceptable in an aggressive condition with greater temperatures. Electrodeposited Zn coatings study tests indicated that pure Zn has weak corrosion resistance properties compared to cadmium [20]. Therefore, the need for metal coatings with corrosion properties outstanding to those of pure Zn and comparable or improved to cadmium has driven the industrial production of electrodeposits involving Zn alloys with VIIIB-group metals (e.g. Zn-Fe, Zn-Ni, Zn-Co) [21]. The electrodeposition of Zn and its eight-group metals including Co, Fe, and Ni have been extensively investigated and analyzed for their ability to be an excellent corrosion resistant alloy.

1.1.1 Zinc-nickel alloy corrosion behavior

In recent years, a lot of research has been performed to investigate the possibility that the Zn-Ni alloy could be a substitute with a corrosion property corresponding to the toxic coatings of cadmium. Much research has also been done to distinguish and determine the corrosion resistance of the Zn-Ni coatings [22–25]. The corrosion resistance of deposited Zn-Ni coatings on steel substrate indicated as having the acceptable corrosion property (corrosion rate: ~ 11 mm/year) was reached for Zn-Ni alloys in the range from 12 to 15 wt.% of Ni content in the coating so that the coating with Ni content from 12 to 15 wt.% maintains the anodic behavior of the steel, retaining the sacrificial behavior with a decrease corrosion rate after the addition of Ni, which increases the potential nearer to the substrate providing protection for a too time [21]. This has been endorsed by reports conducted by other authors [22–25] who have stated that Zn-Ni coating with a Ni amount of 12 to 15 wt.% supplies...
adequate corrosion protection. While the coating retains its sacrificial behavior regarding the steel substrate, whenever the alloy with more than 30 wt.% of Ni turns nobler than the substrate, missing its sacrificial behavior. Hence, it led to preferential corrosion of the steel, and Ni amount of less than 10 wt.% in the coating produced smaller barrier performance. Byk et al. [25] performed tests showing the greatest corrosion resistance properties utilizing a poor acid chloride solution with the Zn-(15 wt.%) Ni coating having the least corrosion CD, demonstrating the best corrosion protection, and this is qualified to the existence of the \( \gamma \) phase \((\text{Ni}_{5}\text{Zn}_{21})\) which is gained with Zn-Ni coatings with Ni amount from 12 to 15 wt.% [25]. The coatings of Zn-Ni coating with 10–15 wt.% of Ni have more suitable corrosion resistance, better weldability, and superior formability. The presence of Ni in the Zn-Ni alloy in the optimal range from 12 to 15 wt.% reduces the rate of Zn dissolution, supplying greater and longer corrosion resistance than pure Zn [24].

1.2 \( \text{CO}_2 \) reduction reaction

Environments change due to greenhouse gases (\( \text{CO}_2 \)) is a significant hazard to the protection of human society. The capture and conversion of carbon to the value-added chemical are attended to be the most agreeable method to prevent the rise of \( \text{CO}_2 \) in the environment as seen in Figure 1. But the cost of high technology accessible to capture, store, and convert \( \text{CO}_2 \) stops its functional operation [26]. Recycling \( \text{CO}_2 \) and transforming it into value-added chemicals create challenges for researchers in the area of catalysts. Among the various methods, the electrochemical method has unique advantages [27–29]. Most of the electrochemical reactions can be seen in small to industrial conditions. Besides, if the electricity is required from renewable sources, these sources of energy generate the required electricity, \( \text{CO}_2 \) will not be produced and, therefore, will have a good effect on the worldwide \( \text{CO}_2 \) level [30].

Studies showed that CO was an intermediator and also methane (\( \text{CH}_4 \)) or ethylene (\( \text{C}_2\text{H}_4 \)) was generated from HCO* or COH* intermediates. Norskov et al. presented details of reaction pathways to produce \( \text{C}_2\text{H}_4 \) and \( \text{CH}_4 \) from the \( \text{CO}_2 \) reduction reaction at copper catalysts using the Density Functional Theory (DFT) [31–34].

Figure 1.
Graphical schematic of the influence of \( \text{CO}_2 \) on the globe and conversion of \( \text{CO}_2 \) to the useable energy.
The outcomes demonstrated that the formation of HCO$^-$ was a key step for the reaction. They also compared the carbon dioxide reduction reaction in several transition-metal electrodes and determined that copper is the most efficient electrode for this case [35]. In the electrolysis of CO$_2$, the anode and cathode were located on separate sides, which were interconnected with a membrane in the middle of them. In the anode, the water oxidized to ion hydrogen (H$^+$) and molecular oxygen (O$_2$), while in the cathode, CO$_2$ was reduced to carbon compounds, and hydrogen was reduced [36]. The electrocatalysts for the reduction reaction of CO$_2$ totally divided into a few different classes as seen in Figure 2. Metals such as Ni, Pt, Al, Fe, Ti, and Ga were used as the catalysts for H$_2$ production, and CO was not created as the main product [37–40]. The H$_2$ evolution reaction rates by these group metals are commonly greater than that of the CO$_2$RR rate.

Another class of metals of Ag, Au, and Zn convert CO$_2$ to CO with an acceptable efficiency [41]. Catalysts consist of In, Pb, Hg, and Sn convert CO$_2$ to formate as the main product. On these metals, the mechanism of CO$_2$RR to formate is different in which there is no breaking of the C-O bond. Electrodes including W, Cr, and Mo have been reported as inadequate catalysts because of weak selectivity and reduction rate. Copper as a metal catalyst can react to a reduction in CO$_2$ to alcohol and hydrocarbons (C$_2$H$_6$, CH$_4$, CH$_3$OH). However, recent research had shown that the CO$_2$RR to these fuels was made at lower efficiency, which was influenced by the binding-energy of the intermediate species of CO. For example, Ag and Au catalysts can produce CO more rather due to less energy for intermediate carbon monoxide molecules. Since it can be evolved from the surface without more reaction. Therefore, producing higher carbon species at these levels is extremely minimal. However, Cu is a unique catalyst that allows it to produce various carbonaceous products (such as, alcohol and hydrocarbons) with higher activity [41].

Electrodes play a key role in all reactions according to heterogeneous electrochemical reactions, such as CO$_2$RR [42]. The durability and performance of the electrochemical cells are essentially defined by the processes happening at the electrolyte-electrode interface. Overall, electrodes include an electrocatalyst layer as well as a backing layer or substrate that attend multiple acts: firstly, to transport reactant gases, CO$_2$, from the electrolyte to the catalyst layer; secondly, to derive products from the catalyst layer into the membrane/electrolyte; and lastly, electrons connectivity with little resistance [42–45]. Most electrode efficiency, and accordingly electrochemical cell efficiency, requires enhancing all these three processes that greatly relate to the complicated microstructure of the electrodes. Till now, the...
nanoparticles of Ag [46, 47], Sn [48], Au [49], MoO$_2$ [50, 51], Bi [52], MoS$_2$ [49], etc., coated on low carbon steel substrate and Cu$_2$O/TiO$_2$/FTO [53] have been utilized to convert CO$_2$ to CO applying room-temperature ionic liquids (RTILs) as electrocatalysts. Nevertheless, none of these materials enabled the development of CO with a CD of >100 mA/cm$^2$ in CO$_2$RR during controlled potential electrolysis (CPE) tests in combination with any of the utilized RTIL assistant catalysts, which is required to commercially use any of these procedures. In the last decade, the electrochemical CO$_2$RR had been widely considered [54–56]. The reduction reaction products of electrochemical CO$_2$RR on the Cu-based electrodes are hydrocarbons for example C$_2$H$_4$ and CH$_4$ [57–59]. Practical investigations on the electrochemical CO$_2$RR in the base electrodes of copper showed that the exhaust gas contains CO, CH$_4$, C$_2$H$_4$, and primary alcohol that depended on their electrolyte [60, 61]. There were numerous studies of electrochemically CO$_2$ reduction reaction on Cu-based electrodes [62–64].

Table 1 shows the summarized characterization of electrocatalysts for the CO$_2$RR to various. As shown in Table 1 and Figure 3 for SYNGAS (CO + H$_2$) production,
there is not enough research in this field. Also, for the production of SYNGAS, the Au_{0.76}–Pd_{0.24} electrocatalyst has the highest Faraday efficiency (~90%) and CD (~10 mA/cm^2), which is a high-cost and unsuitable alloy electrode for large-scale use [67]. Other electrocatalysts for SYNGAS production have low FE and/or low CD, as can be seen in Table 1. The Ag/Au nanostructure catalysts for electrochemical CO_2RR to CO with a FE of further than 90% and a CD greater than 30 mAcm^2 have been stated by researchers [65–68]. Zinc performs as an electrocatalyst for CO_2RR to CO, while it is a cost-effective, non-noble, and abundant choice to gold and silver [69].
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There are also statements of nano-structured Zn catalysts including hexagonal, dendritic, and nanoscale [70–72]. Quan et al. have reported Zn nanoscale and Zn foil as a catalyst for the CO₂RR at the NaCl and NaHCO₃ electrolytes. They demonstrated that the nano-scale catalyst at NaCl cathodic solution has the greatest proficiency in terms of CD and FE about 6 mA.cm⁻² and > 90%, respectively, at a potential of −1.6 V by linear sweep voltammetry (LSV) method [70]. Rosen et al. have studied Zn balks and Zn dendrite catalysts for the electrochemical CO₂RR in 0.5 M NaHCO₃ cathodic solution. They stated Zn dendrite electrocatalyst has a CD of 4 mA.cm⁻² at the potential value of −1.14 V (vs. RHE) and FE of 80% [71]. By modifying the surface microstructure, morphology, or orientation of the Zn catalyst, the more FE and product selectivity can be attained for converting CO₂ to CO.

Nguyen et al. showed that microstructural or morphological changes in catalysts play a significant role in developing CO₂RR [73]. The surface of the Zn catalyst is simply oxidized although immersed in aqueous solutions or exposed to air. Thus, situations should be restricted to avoid zinc oxidation [73]. Nguyen et al. have also reported a porous nanostructure of the Zn catalysts which were prepared of zinc-oxide for the CO₂RR. By applying this porous metal, they obtained a faradaic efficiency of 78.5% for CO₂RR at a potential value of −0.95 V (vs RHE) in the KHCO₃ electrolyte [73]. Keerthiga and Chetty have reported a modified zinc-copper catalyst for the CO₂RR to hydrogen, C₂H₆, and CH₄ products. They coated zinc on the copper with different concentrations of electrolytes, and the outcomes were evaluated with pure Cu and Zn catalysts. They showed that zinc-copper with a high-level concentration of electrolyte had superior performance, also, the FE of CH₄ was the order Zn (7%) < Cu (23%) < Cu-Zn (52%). Moreover, the H₂ FE for Cu and Cu-Zn were 68% and 8%, respectively [74].

In this way, it has been selected inexpensive materials as electrocatalysts for commercial and industrial applications. Electro catalysts must be appropriate that could have acceptable efficiency and cheap price for the reforming process. By referring to Figure 2, zinc and nickel are affordable materials for carbon monoxide and hydrogen production, respectively. Hence, to produce SYNGAS (CO + H₂) in this study, the Zn-Ni bimetallic material is chosen from these two groups of catalysts for CO and H₂ products. Other electro catalysts are either inefficient or expensive. This work aims to investigate the Znₓ-Ni₁₋ₓ coatings for the electrochemical CO₂ reduction reaction.

2. Experimental methods

2.1 Preparation and investigation of Zn-Ni Electrocatalyst for CO₂ reduction reaction

Zinc-nickel Alloys were coated on the low-carbon steel substrate by chronopotentiometry method at different electrochemical parameters. Then, Zn-Ni coatings were investigated in terms of microstructure, microcrack formation, and coating composition using SEM / EDX analysis and corrosion resistance by Autolab potentiostat (Model: PGSTAT128N) to obtain the coating with the best performance and quality. Besides, the coatings were analyzed using SEM/EDX analysis after CO₂ reduction reaction for microstructure and coke formation, as well as gas efficiency by gas chromatography analyzer. Nickel chloride hexahydrate (NiCl₂·6H₂O), ammonium chloride (NH₄Cl), and zinc chloride (ZnCl₂) of raw materials were utilized for bath electrolyte preparation and ammonia solution (25%) for pH modification. All electrolytes were made using distilled water. The zinc and nickel alloy solutions were prepared in the laboratory to allow the study of the deposition at different bath solution temperatures. The pH of the solution was measured using a pH meter.
Ammonia solution (25%) was used to raise the pH of the electrolyte to the needed level of pH 5. The solution was stirred using a glass rod and the pH measuring was taken applying a pH meter, continuously. Chronopotentiometry electrodeposition was applied at different bath solution temperatures of 25°C, 40°C, 60°C, and 70°C. There were three types of electrodes, low carbon steel (working electrode), Ag/AgCl (reference electrode), and Pt mesh (counter electrode). The electrodeposition process was performed galvanostatically for each deposition temperature. The experimental setup for electrodeposition was performed as seen in Figure 4.

The deposited Zn-Ni coatings were analyzed on their compositional and micro-structural properties applying SEM. The morphologies were observed and investigated for the electrodeposited zinc-nickel alloy samples at different temperatures of the bath solution. The material composition is determined by the SEM equipped with EDX which shows the composition information of the alloy coating. Linear polarization resistance (LPR) analysis was performed regarding the ASTM standard of G 96–90 (Reapproved 2001)e1.

2.2 Electrochemical CO₂ reduction reaction

For CO₂RR an H-shaped electrochemical cell was used which has 2-chambers (cathodic and anodic sections) that were connected with membrane Nafion 117 as seen in Figure 5. CO₂ gas was inserted into the cathodic section for the reduction process. In this method, electrocatalyst, reference electrodes (Ag/AgCl), and CO₂ saturated cathodic electrolyte were in the cathodic part, while CO₂RR happened, in the other part, the counter electrode (graphite) and anodic electrolyte (0.1 M H₂SO₄) were placed where the oxidation occurred. It was, therefore, predicted that SYNGAS (H₂ + CO) and coke would form in the cathodic portion, and O₂ would be produced in the anodic portion. Working, reference, and counter electrodes (WE, RE, and CE), were linked to the Autolab potentiostat device (Model: PGSTAT128N) to inspect potential and current records. A gas bag was attached to the exhaust to collect products for gas chromatography to characterize gases. Images of the catalyst morphologies were examined utilizing SEM. The catalysts were analyzed by EDX for coke formation and electrocatalyst surface compositions.

Figure 4.
Electrodeposition setup for Zn-Ni coatings, (1) counter electrode, (2) reference electrode (3) working electrode, (4) thermometer.
3. Results and discussions

3.1 Zn-Ni electrodeposition

The cathodic protection (CP) graph at various temperatures for the Zn-Ni deposition is displayed in Figure 6. The graph of the potential in terms of time for Zn-Ni coating depositions at 25°C, 40°C, 60°C, and 70°C were seen throughout
the electrodeposition process. A decrease (more positive) in CP was detected over time with increasing temperature. The CP in chronopotentiometry was related to the ion’s concentration becoming reduced at the substrate surface in response to the utilized current.

The standard potential $E_0(V)$ for Ni and Zn is $-0.25V$ and $0.76\ V$ (vs. SHE), respectively [90]. The CPs seen in the deposition were nearest to $E_0(V)$ of the reactants that were converted to its metal. Therefore, the outcomes on the decrease in CP towards a further positive amount over time for electrodepositions at high temperature ($60^\circ$C and $70^\circ$C) demonstrated the CP’s deposition was shifting nearer to $E_0(V)$ of Ni reduction, favoring the reaction of Ni-ion reduction to Ni-solid on the substrate. This opinion was more confirmed by EDX outcomes (Figure 7).

The rise in Ni amount was assigned to a decrease in CP (more positive) over time through the electrodeposition reaction. This supposition is reported by Velichenko et al. [91], who stated the decrease in CP with rising Ni-ion concentration in the bath solution resulting in an improvement in Ni deposition. Qiao et al. [92] detected similar findings of reducing CP with increasing deposited Ni amount in the surface deposition with rising temperature.

3.2 Linear polarization resistance testing for Zn-Ni deposits

Zn and Ni amounts in the coatings have a considerable effect on the corrosion properties of Zn-Ni deposits. As revealed by Baldwin et al. [93] and Conde et al. [21], the lowest corrosion rate is obtained when the Ni amount is between 12 wt.% to 15 wt.% in the coating. Zn being a lower noble metal plays as an anode that sacrifices in relative to the substrate under a standard situation. Zn is extra favored compared with a nobler metal for instance Ni to be developed into coatings regarding its further sacrificial behavior. But adding more noble elements to Zn improves the corrosion resistance of Zn. By adding Ni to Zn, the rate of sacrificing of coating for the substrate is lower compared to bare Zn. Ni act to hinder or reduce the dissolution rate of Zn. But, when the Ni amount in the coating enhancements to more than 30%, the sacrificial performance decreases, and the coating turn nobler compared to the substrate (Steel). At this stage, the corrosion rate is entirely according to the coating characteristics. As seen in Figure 8, with rising temperatures, the corrosion rate increases. This shows that adding Ni to Zn no more enhances corrosion resistance. The coating turns nobler than the substrate and the existence of cracks that are detected causing a rise in the corrosion rate. As the bath solution temperature increases, hydrogen reduction occurs around the working electrode,
which creates bubbles form on the surface that prevents the deposition. On the other hand, hydrogen penetrates the coating and makes internal stress. The cracks and disruptions (as shown in Figure 9) in the coatings increase speed the corrosion rate of the substrate. These clarify the important variation in the corrosion rate for coatings deposited at 25°C and 40°C, 60°C, and 70°C.

The ratio of Zn and Ni for deposits formed at 25°C is in the optimal range of Ni amount from 12 to 15 wt.%. Therefore, the sacrificial performance of Zn is retained relative to the adding of the Ni, and this makes the steel substrate with decreasing corrosion rate as Zn acts as an anode. By adding 12–15 wt.% of Ni, the dissolution rate of Zn slows down, and the corrosion rate reduces. The cracks and defects in the

Figure 8.
LPR corrosion rate measurements taken for Zn-Ni alloy coatings vs. uncoated carbon steel for hourly for 24 h.

Figure 9.
SEM images for electrodeposition of Zn-Ni alloy coatings at temperature of (a) 25°C, (b) 40°C, (c) 60°C, and (d) 70°C of bath solution.
deposits do not substantially influence the corrosion properties of the metal layers, as further anodic Zn causes preferential corrosion.

### 3.3 SEM and EDX analysis for Zn-Ni deposits

As the bath electrolyte temperature raises, the ion mobility in the electrolyte rises. Hence, the coatings can be smoother. However, the SEM results displayed in Figure 9 indicate that microcracks are detected in all deposited coatings at various temperatures. The micro-cracks intensity with rising the bath solution temperature is considered to be $25^\circ C < 40^\circ C < 60^\circ C < 70^\circ C$. The microcracks formation can depend on the internal stress created and the evolution of hydrogen during the deposition. As the temperature increased, the evolution of hydrogen happened.

Enhancement of inner stress through deposition can be attributed to a lot of reasons. Alfantazi et al. [94] revealed the existence of microcracks in Zn-Ni coatings when the Ni amount in the coating increased. Qiao et al. [92] and Rehim et al. [95] reported the micro-cracks in the Zn-Ni coatings deposited in the acidic bath solution were attributed to $H_2$ embrittlement via the $H_2$ evolution. A rise in the hydrogen release was observed with the outputs of a rise in the hydrogen CD with the temperature rises. This $H_2$ reduction reaction causes $H_2$ atoms to penetrate the coated layer, straining the crystal lattice, and causing high-stress internal cracks.

### 3.4 Investigation of Zn-Ni bimetallic electrocatalysts for CO$_2$RR

To realize the impacts of the catalysts for the CO$_2$RR, the composition, morphology, and structure of the catalysts were investigated. Figure 10 and Figure 11 display EDX results and SEM images of the Zn-Ni with various compositions after the 48 h for the CO$_2$RR by cyclic voltammetry with scan rate 0.05 V. s$^{-1}$, graphite counter electrode, 0.1 M KCl cathodic, and 0.1 M H$_2$SO$_4$ anodic solutions. According to EDX analysis, as shown in Figure 10, carbon with $\sim$28–30 wt.% was deposited on the Zn$_{85\%}$-Ni$_{15\%}$ electrocatalyst after 48 h of testing. The microstructure of Zn$_{0.85}$- Ni$_{0.15}$ is a block-like morphology in which carbon is almost uniformly distributed in the substrate due to CO$_2$ reduction. As can be seen in Figure 11(a), some electrocatalytic regions are carbon-covered, preventing CO$_2$ reduction over time. Therefore, for further consideration of this electrocatalyst, gas chromatography of produced gases (the produced gases were collected with the gas bag) has been investigated.
According to EDX analysis, as shown in Figure 10, carbon with ~10 wt.% was deposited on the Zn$_{65\%}$-Ni$_{35\%}$ electrocatalysts after 48 h of testing. As shown in Figure 11(b), the microstructure of the Zn$_{65\%}$-Ni$_{35\%}$ electrocatalyst is a cluster-like morphology where coke formation is minimized by the reaction of CO$_2$ with this microstructure after 48 h. With comparing Zn$_x$-Ni$_{1-x}$ electrocatalysts, with decreasing Zn amount in Zn$_x$-Ni$_{1-x}$ coatings from 85 wt.% to 65 wt.% of Zn, coke formation upon Zn-Ni electrocatalysts decreases. Furthermore, the electrocatalyst microstructures have changed from block-like to cluster-like with decreasing Zn content from 85 wt.% to 65 wt.% Therefore, the activity and efficiency of electrocatalysts increase with decreasing Zn content from 85 wt.% to 65 wt.% in Zn-Ni electrocatalysts. By further reducing the amount of Zn until ~33 wt.%, coke formation upon Zn-Ni electrocatalyst increases.

Furthermore, as seen in Figure 11c, the microstructure of the Zn$_{35\%}$-Ni$_{65\%}$ electrocatalyst is semi-spherical, where carbon was deposited between the semi-spherical grains with needle-like microstructure. This high coke formation is due to changes in the microstructure and electrocatalytic activity due to the interaction between Zn and Ni with the ions present in the solution. By further reducing the amount of Zn up to 20 wt.% in the Zn-Ni coating, the coke formation (after 48 h of CO$_2$RR) on the electrocatalyst decreased. The microstructure of 20%Zn-80%Ni is a glossy spherical morphology where carbon is grown with a dark semi-spherical morphology about 22 wt.%.
Due to the results of gas chromatography, as shown in Figure 12, the Zn$_{85\%}$-Ni$_{15\%}$, Zn$_{65\%}$-Ni$_{35\%}$, Zn$_{55\%}$-Ni$_{45\%}$, and Zn$_{35\%}$-Ni$_{65\%}$ electrocatalysts have 63%, 55%, 25%, and 30% selectivity for CO and 37%, 45%, 75%, and 70% selectivity for H$_2$ products, respectively. Also, according to Table 2, the total efficiency for CO$_2$RR after 48 h of testing is 53%, 66%, 31%, and 57%, respectively. The Zn$_{65\%}$-Ni$_{35\%}$ electrocatalyst is appropriate in terms of morphology, stability, coke formation, product selectivity, and intensity of the electrochemical CO$_2$RR. The coke formation on the catalysts can influence the activity spots of the catalyst and have a negative impact on the efficiency and life cycle of the catalyst. Consequently, the chemical compositions, microstructure, and morphology of catalysts have a crucial role for the CO$_2$RR to produce gases with satisfactory ratio, desired product, least-coke formation, and suitable efficiency, activity, and stability.

4. Conclusions

The lower corrosion rate of coatings deposited at 25°C is mainly related to the role of nickel in zinc-nickel alloy and a higher corrosion rate at higher temperatures.
of 40°C, 60°C, and 70°C are related to the lower barrier properties such as uniformity, compactness and cracks in the alloy. Zinc-nickel alloy coatings with the highest corrosion resistance, within required composition of 12–15%, dense and compact morphology, better uniformity with less crack is achieved with coatings deposited at 25°C. CO₂RR on Znₓ-Ni₁₋ₓ electrocatalysts in 0.1 M KCl as the cathodic solution and 0.1 M H₂SO₄ as the anodic solution using cyclic voltammetry method demonstrated that the Zn₆₅%-Ni₃₅% electrode had the best performance for the CO₂RR with regarding the minimum coke formation (<10%) and optimal faradaic efficiencies of CO and H₂ (FE_CO = 55% and FE_H₂ = 45%). The coke formation on the catalysts can influence the activity spots of the catalyst and have a negative impact on the efficiency and life cycle of the catalyst. Consequently, the chemical compositions, microstructure, and morphology of catalysts have a crucial role for the CO₂RR to produce gases with satisfactory ratio, desired product, least-coke formation, and suitable efficiency, activity, and stability. Therefore, the Zn₆₅%-Ni₃₅% electrocatalyst with cluster microstructure had the best performance for CO₂RR among other electrocatalysts in this study.

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