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Electrocatalytic Activity of Nickel Zinc Selenide on Nickel Foam Towards Oxygen Evolution Reaction in the Production of Hydrogen

Ailyn L. Flaviano[a], Princess Rose O. Morente[a], Michael Buenly B. Owogowog[a], Joey D. Ocon[b], Jocelyn R. Balisnomo[a], Joseph R. Ortenero[b,*]

[a] Department of Chemical Engineering, Bicol University, Legazpi City 4500, Philippines
[b] Department of Chemical Engineering, De La Salle University, 2401 Taft Ave., Manila 0922, Philippines
joseph.ortenero@dlsu.edu.ph

The increasing demand for sustainable energy solutions and efficient conservation due to a mismatch in energy supply and demand has led to the development of various energy storage technologies, such as hydrogen storage systems (HSSs). The conversion back to electricity from HSS through reacting hydrogen gas (H_2) with air only produces heat and water, which can play a key role in reducing carbon emissions. However, the process of producing H_2 through water electrolysis faces challenges due to the high overpotential required for the oxygen evolution reaction (OER), which can be lowered by using an efficient electrocatalyst. In this study, NiZnSe particles are synthesized from inexpensive materials using a simple electrodeposition technique. The material is then characterized using SEM-EDS, FTIR, and Raman spectroscopy. The electrocatalytic activity is determined from the overpotential at 10 mA cm^{-2} using cyclic voltammetry (CV) with a scan rate of 20 mV s^{-1} in 1.0 M NaOH solution. The measured overpotential is 345.11 mV, which has a 0.92 % deviation from the predicted value. The stability of the catalyst in OER using chronoamperometry test shows stable current over 4.5 h. SEM results supported the findings that Ni : Zn ratio affects the morphology of the deposits. EDS confirmed the presence of Ni, Zn, and Se, indicating successful synthesis. Furthermore, Raman and FTIR spectra showed the presence of ZnSe and NiSe bonds.

1. Introduction

In the pursuit of reducing carbon emissions that contribute to greenhouse gases, renewable energy sources are increasingly a popular alternative. Renewable energy (RE) continues to be replenished making them a sustainable resource. However, RE sources such as solar energy, wind energy, and hydropower are constrained due to weather and seasonal variations leading to fluctuating energy supply (Mitali et al., 2022). These variable energy sources are managed by using efficient energy storage systems (ESS) that can store excess energy during peak production and release during energy scarcity (Ortenero et al., 2022). There are several general classification of ESS such as electrochemical (e. g. batteries), mechanical (e.g. flywheel), thermal, magnetic, and chemical (e.g. hydrogen) (Ortenero & Tan, 2021). A hydrogen storage system (HSS) has a promising potential, it has high energy density, versatile application, and long-term storage without significant energy losses. HSS stores chemical energy through the bonds in hydrogen molecule or its derivatives such as metal hydrides or ammonia.

According to the International Renewable Energy Agency (IRENA), as of 2021, the production of hydrogen globally is from natural gas, coal, oil, and electrolysis with corresponding share of 47 %, 27 %, 22 %, and 4 %, respectively. Currently, most of the hydrogen is generated from fossil fuels and only a small fraction is from a water electrolyzer integrated to a RE source. It shows how scarce is the focus on the production of green hydrogen due to challenges associated with electrode development. Out of all sources of hydrogen, hydrogen from the electrolysis of water known as green hydrogen is the purest and does not accompany the generation of carbon or greenhouse gases during the process. Water electrolysis uses external energy like electricity to

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initialize the splitting of water into oxygen gas and hydrogen gas (Awad et al., 2023). The splitting of hydrogen and oxygen happens in an electrolysis cell with two electrodes – the cathode and the anode. In the anode where the oxygen evolution reaction (OER) takes place, the water reacts producing oxygen gas, positively charged hydrogen ions, and electrons. Whereas in the cathode, hydrogen evolution reaction (HER) occurs, the ions of hydrogen react with the electrons to form hydrogen gas (Strathmann, 2004).

The process of OER is more energy-intensive than HER because of the complexity of the multiple proton/electron-coupled steps which means it has higher overpotential (Liu et. al., 2018). Since the reaction is an electrochemical process, the reduction (HER) or the gain of electrons will not happen without oxidation (OER) or the loss of electrons. The sluggish kinetics of OER is the bottleneck of the water-splitting reaction (Soriano et. al., 2023). Hence, improving the kinetics of the OER using an electrocatalyst to lower the overpotential will positively affect the production of oxygen gas and hydrogen gas through the coupled electrochemical reaction. An electrocatalyst facilitates the transfer of electrons between the electrode and the reactants by lowering the activation energy of the electrochemical reactions (Soriano et. al., 2024). For OER in acidic media, noble metals such as rutile-structured ruthenium oxide and iridium oxide are the state-of-the-art catalysts. RuO_2 has higher activity than IrO_2, but RuO_2 is less stable than IrO_2 (Lin et al., 2019). The activity of transitional metal catalyst is usually compared to these noble metals as benchmark.

Low-cost metal catalyst developed from transition metal chalcogenides have been demonstrated to reduce the overpotential. Nickel and zinc are particularly attractive due to the abundance of these metals compared to Pt. However, more research is still needed to establish the transition metal chalcogenides as an alternative to the noble metals. The effect of nickel to zinc ratio and catalyst loading on nickel are particularly important to elucidate the activity towards OER of varying ratios of these metals. Therefore, this work investigates the optimization of nickel zinc selenide on nickel foam (NF) as an inexpensive alternative OER electrocatalyst. Several studies have explored the activity of different Ni-, Zn-, and Se-based catalysts towards OER. However, the synthesis variables were fixed like precursor ratios and mass loadings. There is a growing literature on the use of nickel foam as a substrate for NiZnSe particle catalyst. The current study investigated the activity of NiZnSe using nickel foam as substrate and the effect of nickel to zinc ratio (0.1, 1, 10) and the mass loading (0.005 g, 0.01 g, 0.05 g) of the electrocatalyst particles on the substrate to its electrochemical behaviour.

2. Theory

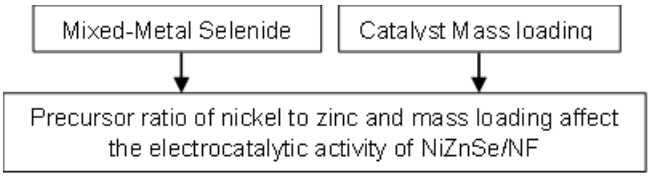

Figure 1: The theoretical paradigm of the study.

Mixed-metal catalysts may result in interaction that can influence the surface, structure, and electrochemical behavior of the material. The presence of additional transition metals like Mn and Ni in cobalt spinel effectively improved its electrochemical properties, resulting in a 482 mV overpotential at 100 mA cm^{-2} (Nozari-Asbemarz et al., 2022). The performance of transition metals as OER catalysts is inferior to noble metals but mixing with other compounds can enhance its activity (Soriano et al., 2023). Hence, in this study, the effect of nickel and zinc ratio to the electrocatalytic activity are considered by varying the weight fraction of the precursors. Nickel is known for its electrocatalytic properties, and zinc may influence its structure, stability, and electrochemical behavior. Moreover, combining NiZnSe with co-catalyst or support materials such as NF may also lead to improved performance. An iron hydrogen phosphate ($FeHPO_4$) has higher activity when drop-casted on NF compared to a glossy carbon electrode (Wang et al., 2021). The amount in grams of electrocatalyst particles bound to the backbone electrode or mass loading varies linearly with the electrochemically active surface area (ECSA) but has a non-linear relationship with the intrinsic electrocatalytic activity. The non-linear relationship is due to factors such as the distance of the electrons for mass transfer and changes in the accessibility of the electrolyte to the backbone electrode (Ortenero et. al., 2017). This study explores the optimal mass loading to increase the number of active sites without significantly blocking the NF pores for the electrolyte solution.

3. Methodology

All the reagent chemicals used in this study are analytical grade. The optimization study was carried out by varying the ratio of Ni to Zn and adjusting the loading of the catalyst on Ni foam substrate. The electrocatalyst activity was determined from the value of the overpotential at 10 mA cm^{-2} current density. After the optimized

electrocatalyst was determined, another set of a sample was prepared at the given Ni to Zn ratio and NiZnSe loading on Ni foam to validate the avtivity. Lastly, the optimized electrocatalyst underwent a stability testing using chronoamperometry.

Ni:Zn ratio of 0.1, 1, and 10 were prepared using zinc chloride and nickel (II) sulfate hexahydrate precursors with 0.025 M selenium dioxide and 9.318 g of potassium chloride. The resulting solutions were used as the electrolyte solution in the electrodeposition technique. To deposit NiZnSe on a nickel strip, a three-electrode set-up connected on a potentiostat was employed where a 6 cm-long nickel strip is the cathode, platinum is the anode, and the Ag/AgCl is the reference electrode. The nickel foam was cut into 0.2 cm × 1 cm × 4.5 cm. Then, it was chemically treated with ethanol for 15 min and washed with deionized water to remove any contaminants. After drying, at 1 cm from one end of the NF strip, an epoxy of 0.5 cm thick was applied to prevent capillary action during testing. A 100 mL of 7 : 3 deionized water to ethanol ratio was prepared and mixed with 0.5 wt. % PVP. The desired mass of NiZnSe was mixed with 5 mL of the PVP solution and then, drop-casted on NF. Lastly, the NiZnSe/NF was dried and tested.

4. Results and discussion

The optimized NiZnSe particles were characterized using SEM-EDS, FTIR, and Raman Spectroscopy to validate the presence of the nickel zinc selenide.

4.1 Characterization

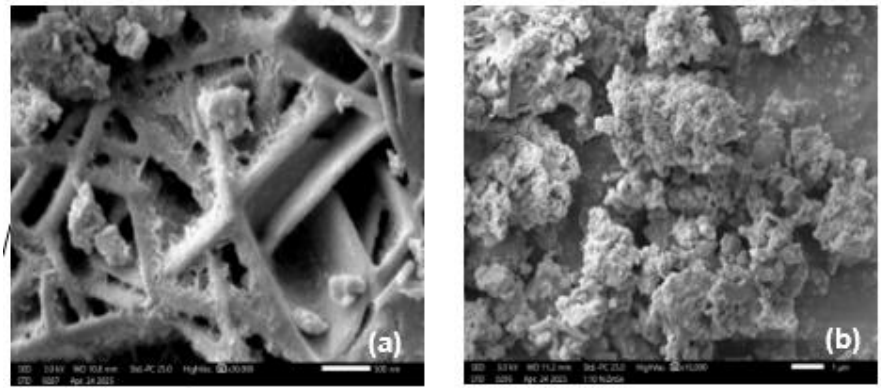

Figure 2: SEM images of NiZnSe particles at (a) 1:10 Ni:Zn ratio and (b) 1:1 Ni:Zn ratio using 30,000 magnification.

As shown in Figures 2a and 2b for the NiZnSe of different Ni to Zn ratio, the morphology of the two samples differs significantly, indicating that the proportion of Ni and Zn in the precursor solution influences crystal growth. As the nickel content increased, the particles became smaller from elongated branched rod-like structures with some flake-like crystals of 1:10 Ni:Zn ratio to clustered small irregular particles with porous surface of 1:1 Ni:Zn ratio. The smaller particles have a larger interfacial area that supports ion diffusion for faster reaction kinetics (Tang et al., 2019). The 1:1 ratio is more compacted because of the strong bonds between Ni and Se (covalent bonding). The shared electrons are trapped between the two atoms, providing a strong electrostatic attraction (Liu et al., 2023). The bond between Zn and Se typically generates structures in which the atoms are organized in sheets or layers. The bonding inside these layers may be stronger than between them, resulting in a weaker overall structure that allows the layers to be separated more easily (Archibald, 2003).

EDS result confirmed the presence of Ni, Zn, and Se on 1:1 Ni:Zn ratio with atomic percentages of 30.03 %, 31.79 %, and 38.18 %, respectively. The atomic ratio is 1:1.06 which is close to the theoretical ratio of 1:1. This minimal error can be caused by measuring errors during the synthesis of the electrocatalyst. For 1:10 Ni:Zn ratio, 4.22 % Ni, 39.73 % Zn and 56.05 % Se.

Raman Spectroscopy can provide extensive information on chemical structure and molecular interactions in a particle. Figure 3a shows the Raman spectra of the NiZnSe electrocatalyst having peaks at 254, 313, 532, and 564 cm^{-1}. The peak at 254, 532, and 564 cm^{-1} closely matched the reported peak of ZnSe (Nesheva et al., 2007). The peak at 313 cm^{-1} could be Se-Se (Vidhya et al., 2021) or Ni-Se bond (Imran et al., 2024). The Raman features of the NiZnSe show that ZnSe is more dominant than NiSe.

The FTIR result shown in Figure 3b has a medium broad peak at 690 cm^{-1} indicating an M-H bond (600-800 cm^{-1}, M = Ni, Zn) and the strong broad bending at 3,350 cm^{-1} corresponds to a single O-H bond (2500-3300 cm^{-1}) (Smith, 2024). A study of NiZnSe on nitrogen-doped carbon revealed that its small overpotential is caused by

the in-situ surface reconstructed nickel (oxy)-hydroxide (NiOOH) on the surface of the electrocatalyst which was assumed to be formed during the oxidative scan of the sample (Hu et al., 2023). The FTIR result of the current study also confirmed the presence of a single O-H bond which is a result of the anodic scanning during the oxidation reaction.

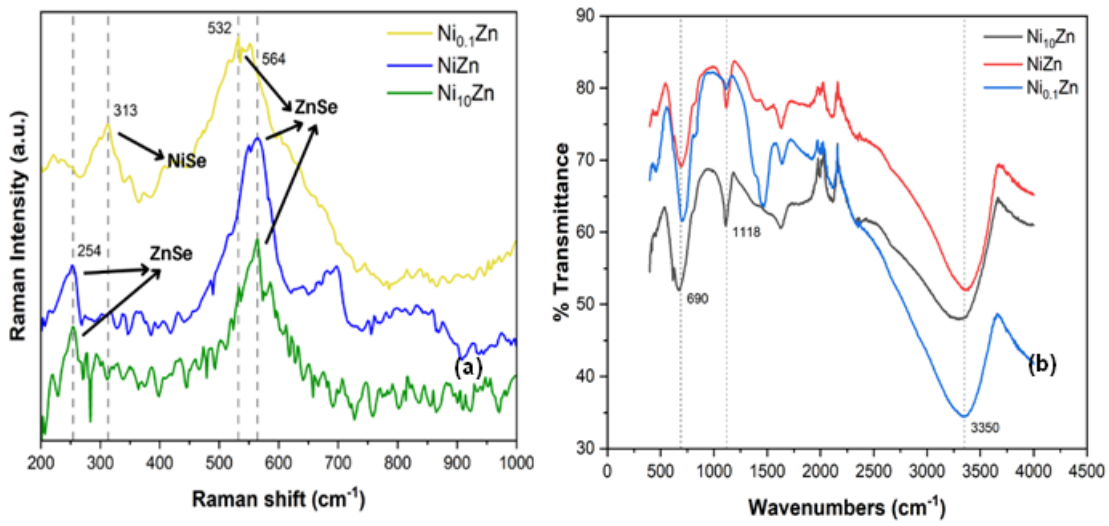

Figure 3: (a) Raman spectra (a) and (b) FTIR spectra of the optimized sample showing the formation of the Ni-Se and Zn-Se bonds.

4.2 Optimization

As shown in Figure 4a blue hues, low overpotential areas for high activity, are concentrated in the upper right which means high values of Ni:Zn ratio and mass loadings are preferred in the given range. As supported by the findings of Tang et al. (2019), as nickel content increases, the size of hierarchical urchin-like microspheres becomes smaller which is conducive to ion diffusion with a large interfacial area supporting faster reaction kinetics. This is also confirmed by the SEM image result that as the nickel ratio increases, the particle size decreases with more porosity and larger interfacial area for ion diffusion. For catalyst mass loading, as stated by Jiang et al. (2023), higher loadings significantly improved OER activity of nickel-based catalysts. However, too high mass loading can be too thick that electrolyte can't reach and wet all catalyst surfaces affecting the transport of electrons, ions, and thus kinetics (Yu et al., 2021). It can block the pores of nickel foam, which is the electrode that can also participate in the reaction, thus reducing activity. On the other hand, too low mass loading can result in insignificant improvement of the electrocatalytic activity. The balance between these two considerations results in optimal catalyst mass loading. In this study, the chosen range of 0.005 g to 0.05 g seems to capture the optimal value that was tested for validation. It was noted that during the process, gas generation forms bubbles blocking active sites that could also limit electrolysis efficiency.

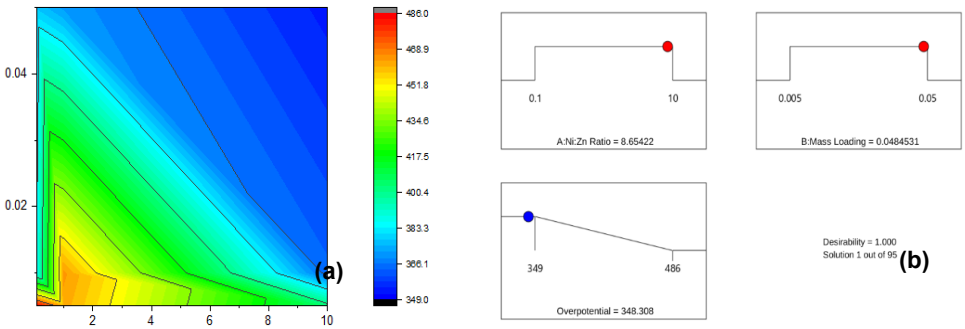

Figure 4: (a) Contour plot of the result of 11 samples and (b) optimal values for mass loading and Ni:Zn ratio.

4.3 Electrochemical Activity

The predicted optimal values are shown in Figure 5b, 8.65 for Ni:Zn ratio and 0.048 g for mass loading with a predicted overpotential of 348.308 mV at 10 mA cm^{-2}. The experimental result is 345.1068 mV at 10 mA cm^{-2} with a small deviation of 0.92 % from the predicted value. Furthermore, the overpotential of the bare nickel foam, which is 412 mV, was tested to be higher than with NiZnSe particles. This indicates that NiZnSe particles improved the activity of the nickel foam. The lower the overpotential the closer the OER value to the thermodynamic potential.

As shown in Figure 5b, the optimized catalyst is comparable to the activity of some of the catalyst reported in the literature. The activity is 32 mV more than that of RuO_2 (Lim et al., 2018) and superior to other reported Ni- and Zn-based OER catalysts such as $Ni_{0.8}Zn_{0.2}O$ with 473 mV (Agcali, 2020) and ZnO with 800 mV (Kwak et al., 2017) overpotential at 10 mA cm^{-2}.

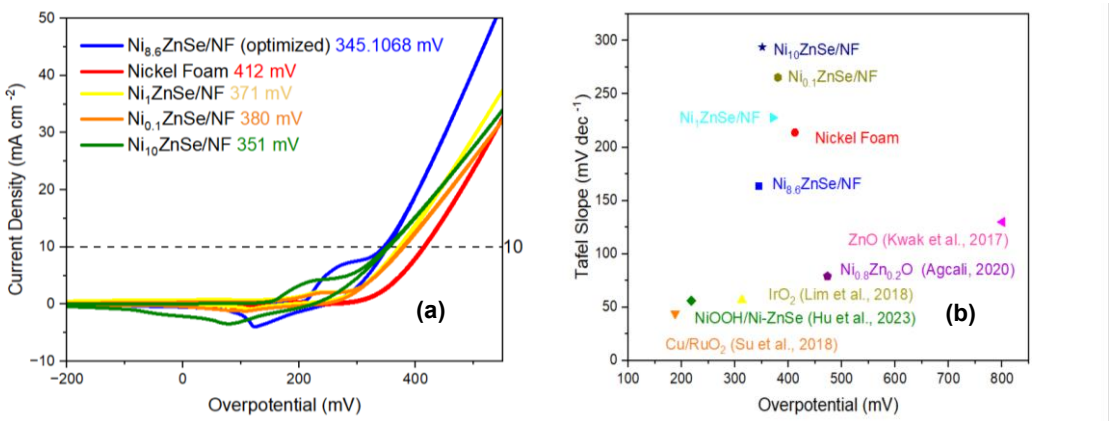

Figure 5. (a) Electrochemical activity of the NiZnSe on nickel foam at 20 mV s-1 sweep rate using 1.0 M KOH solution and (b) comparison of activities with other state-of-the-art OER catalysts.

5. Conclusions

In this study, a NiZnSe catalyst for the oxygen evolution reaction was synthesized via electrodeposition. The Ni:Zn ratio and mass loading were established as significant variables affecting the overpotential through ANOVA analysis. SEM results showed that Ni:Zn ratio affects the morphology of the electrodeposited particles. Raman spectra analysis showed the presence of ZnSe and NiSe bonds, while FTIR showed the presence of O-H bond which could be formed during the anodic scan of the sample. The optimal Ni:Zn ratio is 8.65, higher nickel content produces smaller particles that have larger interfacial area and more porous structure for ion diffusion. The optimal value of 0.049 g for mass loading balances two factors of increasing active site numbers through mass loadings and not too thick loading interfering with electrons and ions transport. The validation test closely matched the predicted overpotential with a 0.92 % deviation, confirming the accuracy of the model. When compared to bare nickel foam, the NiZnSe demonstrated a significantly lower overpotential of 19.42 % difference and a smaller Tafel slope highlighting its improved catalytic activity and reaction kinetics. These findings support the potential of the optimized NiZnSe catalyst as a promising and cost-effective electrocatalyst for OER.

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