

Iron-Nickel Alloy Oxygen Evolution Reaction Catalytic Activity Dependence on pH in Basic Solutions

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ABSTRACT: Oxygen Evolution Reaction is the oxidative counter reaction to Hydrogen Evolution Reaction used to produce Hydrogen gas which have potential to change the Energy and Chemical Industries. Two near-identical catalysts of Iron-Nickel alloy deposited on Glassy carbon were prepared by Bulk Electrolysis at -1.5V for 300s. The catalysts were tested at different Sodium Hydroxide (NaOH) concentrations to test the relation pH of and catalytic activity. An observed slope of the Tafel slope vs pH plot shows increase in activity at higher pH for the basic condition with a slope of -120 mV/dec/pH . However, later pH points suggest that around pH 14 the rate limiting step is not hydroxide dependent contrary to literature findings[1][4].

Oxygen Evolution Reaction (OER) serves the counterpart to Hydrogen Evolution Reaction (HER) in electrochemical water splitting via electrolysis. Hydrogen is projected to be a major energy storage component in the era of renewable energy. Currently the barrier to efficient electrolysis is sluggish OER mechanics which limit H_2 and O_2 production, and making less expensive catalysts for the OER reaction using earth abundant is important for making the hydrogen energy storage viable economically. [1][5]

Nickel-Iron alloys is an ORR catalyst used for its improved activity and lower overpotentials compared to Nickel, and in this paper we try to study the pH dependence as a descriptor of hydroxide concentration dependence of the Ni-Fe catalysts to serve as an intermediate in investigating the mechanics of the OER reaction in this catalyst compared to previous nickel and nickel-iron alloy mechanistic studies done in very basic conditions. This study carries tests around the 1M NaOH mark of pH 14 which in the lower end of the mechanistic studies scope. The measure used for the catalytic activity is Tafel slope instead of overpotential since the catalysts quality and structure is a major component of overpotential, but Tafel slopes are more indicative of the energetics of the catalyst's rate determining step. [4][3]

$$(1) \text{pH} = 14 - \text{pOH} = 14 - \log_{10}([\text{OH}^-]) = 14 - \log_{10}(1/[\text{OH}^-])$$

The catalyst prepared investigation is Nickel-Iron alloy deposited on Glassy Carbon Electrode. For the deposition a solution of 3mM of Iron(III) Nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$) and 3mM of Nickel Nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$) to be an electrolyte in an electrochemical cell. The cell of Glassy Carbon working electrode (0.07 cm^2), Silver/Silver Chloride reference electrode (A/AgCl 3M KCl) and Platinum wire as counter electrode. First, a Linear Sweep Voltammetry to decide the deposition voltage was carried and decided on deposition voltage. Then a deposition using Bulk Electrolysis applying a constant reductive -1.5V (versus Ag/AgCl) for 300s on the immersed Glassy Carbon Electrode was carried away with a measure of current. Two catalysts (1 and 2) were used for these tests.[1]

OER reaction is carried by making a cell with NaOH solution as electrolyte, catalyst on Glassy Carbon as working electrode, Ag/AgCl reference electrode, and platinum wire counter electrode. To test the characteristics of the OER reaction an LSV of 0 V – 1V (versus Ag/AgCl) at 100mV/s was carried, and a group of Chronopotentiometry (CP) measurements at 0.5mA, 1mA, 2mA, 3mA, 4mA, and 5mA for 60s to reach steady state conditions for use in Tafel slope analysis. When considerable bubbles form on the catalysts' surface during tests were carried with stirring bar at 1000 revolution per minute RPM or more stirring, and in general after each electrochemical test the solution was stirred for less than 10 s. [1][3][5]

To study the effects of hydroxide concentration described in pH, 6 aqueous solutions of Sodium Hydroxide (NaOH) with concentrations 2M, 1M, 0.5M, 0.2M, 0.1M, and 0.05M dissolved in milliQ deionized water corresponding to 14.3, 14.0, 13.59, 13.30, 13.0, and 12.69 pH respectively. Catalyst 1 tested pH 13 and 14 and was used to test the procedure. Then, Catalyst 2 was used for the rest of pH points 14.3, 13.69, 13.3, 12.69 and a second test of 13 for comparison of catalysts 1 and 2.[1][3]

A control cell of only Glassy carbon at 1M NaOH pH 14 ran a cyclic voltammetry (CV) from 0 V to 1.5 V to 0V (versus Ag/AgCl) at a scan rate 100mV/s, and CP was carried at 0.5, 1, 2, and 3 mA for 60s to carry Tafel analysis.

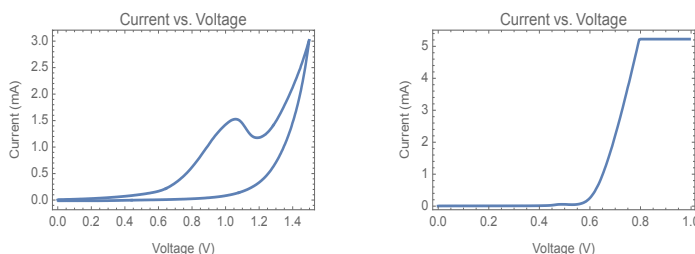


Figure 1: Current vs. Voltage (versus Ag/AgCl) of (left) CV of Glassy Carbon OER in pH 14 (right) LSV of Ni-Fe catalyst 1 at pH 14.

Nickel-Iron deposition was not equal between the two catalysts used, but the LSV characteristics in Alkaline solutions show similar catalytic activity but Catalyst 1 exhibited a higher current Catalyst 2 at similar voltage in LSV within the same pH of 13. This could be an issue when fitting the trend of Tafel slopes, but the difference in voltage might not be as big as the change due to pH. At $i = 0.5 \text{ mA}$ or $j = 7.14 \text{ mA/cm}^2$ the potential observed for catalyst 1 is 0.642 ± 0.001 and catalyst 2 is $0.709 \pm 0.001 \text{ V}$ showing lower overpotential for catalyst 1.

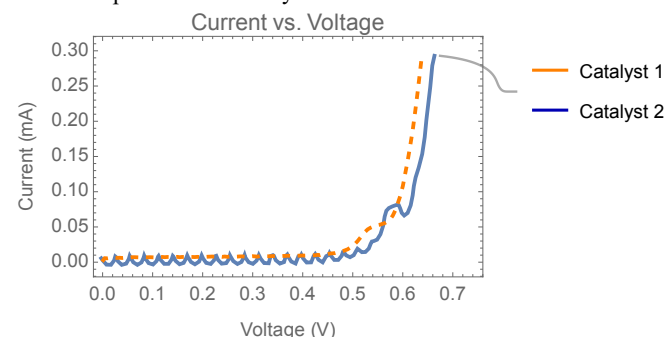


Figure 2: Current vs. Voltage (versus Ag/AgCl) of LSV of Catalysts 1 (orange and dashed) and 2 (blue and solid) LSV.

For Tafel analysis, the potential of each current state an average and standard deviation as error for the measurements for the 15s to 60s points of each CP was used as data. The uncertainty of the current applied was found to be minor compared to the uncertainty of the Voltage measured. Then plotting the voltage against the log of current density obtained by dividing measured current by the Glassy Carbon area. The resulting graph was then fitted to a linear model using the Leas-Square fit with the uncertainty as weights in the fit.[1][3]

The Tafel slope extraction was done to this equation.[3]

$$(1) \eta = b \times \log(j/j_0) = b \times \log(j) - \eta_0$$

Concentration NaOH (mol L ⁻¹)	pH	Tafel slope (mV/dec)	Onset potential (V)	R ²
0.05	12.69	356 \pm 2	1.5	0.956
0.1	13.0	339 \pm 4	1.37	0.916
0.2	13.3	271 \pm 3	1.23	0.893
0.5	13.69	172 \pm 1	0.99	0.939
1	14.0	179 \pm 1	0.96	0.953
2	14.3	180 \pm 2	0.96	0.935

The trend of Tafel slopes observed is descending Tafel slop as pH increase though not all the pH points had similar high confidence fit to the Tafel plot to the Tafel equation. This the weights of uncertainty alone in the Least-Square fit does not consider the difference in confidence for each data point.

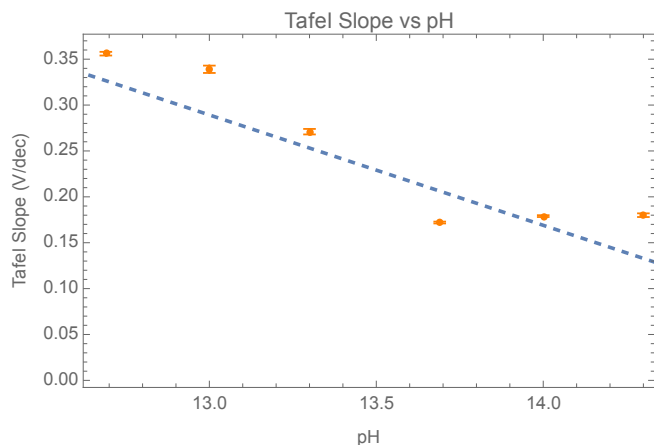


Figure 3: Tafel Slopes vs pH for both catalysts 1 and 2

$$(2) b = m \text{ pH} + b_0$$

When the Tafel slopes vs pH was fit to a liner model, slope of the fit is -120 \pm 1 (mV/dec)/pH with R²= 0.756 which shows that the data have a downward trend but not conclusively a linear fit.

This difference is within the range of difference in potential between catalyst 1 and 2 observed in LSVs shown in Figure 2 and during 0.5mA CP which suggest the inclusion of these data points negatively affected the confidence of the fit. A retrial with a single catalyst or 2 catalysts with better control for the catalysts activity should result in more conclusive results in regard to the

nature of the trend. At pH 13.69, 14, and 14.3 little change in Tafel slope and onset potential is observer which suggests at these concentrations the rate limiting step is not hydroxide dependent.

The pH dependence of the Ni-Fe alloy is not conclusively shown to be linear nor otherwise, but the data trend shows an increase in catalytic activity with higher pH and hydroxide. This is different form literature reports of nickel-iron alloy on steel in very concentrated KOH which indicates a different mechanism or competition by other paths. Hydroxide discharge followed by another hydroxide reacting to adsorbed [OH]_{ads} is shown to result in linear pH dependence in overpotential. The study was done with higher concentrations that done in that study on just nickel. Our study cannon conclude that the main mechanism does not involve water adsorption or water reacting with adsorbed intermediates. The path taking in these catalytic conditions might have routes with hydroxide dependence unlike solid nickel under very basic conditions. [3][4][5]

ASSOCIATED CONTENT

Supporting Information

Lab8SI2023Alasmari.docx

GitHub

<https://github.com/amasmari/LabMod8>

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ABBREVIATIONS

OER: Oxygen Evolution Reaction, CV: Cyclic Volumetry, LSV: Linear Sweep Voltammetry, CP: Chronopotentiometry

REFERENCE

(1)

Lu, X.; Zhao, C. Electrodeposition of Hierarchically Structured Three-Dimensional Nickel–Iron Electrodes for Efficient Oxygen Evolution at High Current Densities. *Nat Commun* **2015**, 6 (1), 6616. <https://doi.org/10.1038/ncomms7616>.

(2)

Fitting Data to Linear Models by Least-Squares Techniques. <https://reference.wolfram.com/applications/eda/FittingDataToLinearModelsByLeast-SquaresTechniques.html> (accessed 2023-10-17).

(3)

Shinagawa, T.; Garcia-Esparza, A. T.; Takanabe, K. Insight on Tafel Slopes from a Microkinetic Analysis of Aqueous Electrocatalysis for Energy Conversion. *Sci Rep* **2015**, 5 (1), 13801. <https://doi.org/10.1038/srep13801>.

(4)

Bronoel, G.; Reby, J. Mechanism of Oxygen Evolution in Basic Medium at a Nickel Electrode. *Electrochimica Acta* **1980**, 25 (7), 973–976. [https://doi.org/10.1016/0013-4686\(80\)87102-7](https://doi.org/10.1016/0013-4686(80)87102-7).

(5)

Singh, R. N.; Pandey, J. P.; Anitha, K. L. Preparation of Electrodeposited Thin Films of Nickel-Iron Alloys on Mild Steel for Alkaline Water Electrolysis. Part I: Studies on Oxygen Evolution. *International Journal of Hydrogen Energy* **1993**, 18 (6), 467–473. [https://doi.org/10.1016/0360-3199\(93\)90002-R](https://doi.org/10.1016/0360-3199(93)90002-R).