

# **Review of Determination Practices for the Electro-chemical Active Surface Area of Nickel-based Oxygen Evolution Reaction Catalysts in Alkaline Media**

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# 1. Introduction

Catalyst characterization is significant in the field of electrochemistry as it provides insights into the properties and performance of materials in catalytic reactions. This work focuses on the characterization of catalysts for the alkaline oxygen evolution reaction (OER). Due to the inherently slow kinetics of OER, extensive research has been conducted to develop precious high-efficiency metal-based catalysts such as Pt and IrO<sub>2</sub> [1]. Various techniques are used to evaluate catalysts, such as Tafel Analysis, Turnover Frequency, and Electrochemically Active Surface Area (ECSA) [2]. ECSA directly influences the catalyst performance, as it provides a means to normalize current density and isolate the activity of the catalyst, independent of surface roughness or material morphology. This ensures a more accurate comparison of electrocatalyst efficiencies across the different materials [3].

However, due to high cost and limit availability of precious metal, non-precious metal has come to consideration. Many of these metal-based oxides, such as Ni, Co, Mn, and Fe, have been explored as electrocatalysts to enhance OER performance, with nickel-based material as most promising materials among them [2,6]. Given the importance of ECSA in evaluating catalyst performance, continuous investigations are being carried out to refine measurement techniques. Many electrochemical techniques can be implemented to investigate ECSA characterization on Ni-based catalysts, including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV was utilized to evaluate the redox transitions and calculate the voltammetric charge, providing an estimate of active sites and oxide film thickness. Additionally, EIS was used to measure double-layer capacitance and adsorption pseudocapacitance, enabling the determination of ECSA and insight into the properties of the catalyst. The findings demonstrate that both methods offer consistent and reliable results for assessing the intrinsic activity of Ni-oxyhydroxide films in OER [3].

To better define oxygen and reduction peaks of those Nickel materials, a promising method for ECSA determination is the oxalate method. It has been deeply investigated by D. S. Hall [4], which involves adding oxalate salt to an alkaline electrolyte to create a controlled environment, forming an adsorbed oxalate layer on the nickel electrode. This layer stabilizes Ni(OH)<sub>2</sub> surface and limits its growth to a single monolayer, preventing the formation of multilayered oxide films. The faradaic oxidation and reduction of the stabilized Ni(OH)<sub>2</sub>/NiOOH layer are measured, and the Coulombic charge is used to calculate the active ESCA and provides a precise approach to surface determination

## 2. Motivation

Improving catalyst performance for OER in alkaline media remains a key challenge in electrochemical research. The overall efficiency of these catalysts is strongly influenced by the electrode's surface characteristics, which can be affected by various pretreatment processes. This study extends catalyst characterization to explore the effects of different surface modifications, mainly through pretreatment methods applied to bare nickel (Ni).

Pretreatment processes such as mechanical polishing, chemical etching, and pre-oxidation play a crucial role in modifying the surface morphology of bare nickel electrodes. These treatments influence surface roughness and create defects or active sites that might enhance electrochemical performance by increasing ECSA. The impact also affects the chemical composition and structure of the surface, particularly the formation and stability of nickel hydroxide ( $\text{Ni(OH)}_2$ ) and nickel oxyhydroxide ( $\text{NiOOH}$ ) layers. These oxide layers in OER are essential to dictate the availability and reactivity of catalytic sites.

The oxalate method is one of the promising methods for ESCA studies because it stabilizes the  $\text{Ni(OH)}_2$  layer, limits the growth of multilayered oxide films, and allows for precise measurements. Since different pretreatments alter both the surface morphology and oxide layer characteristics, they inevitably influence how effectively the oxalate method can perform by examining how various pretreatment strategies affect oxide formation and how these changes interact with oxalate adsorption. Moreover, insights into the mechanisms of surface stabilization and improving the accuracy of electrochemical measurements in OER studies are expected to be observed.

### 3. Theoretical Consideration

#### 3.1. Fundamental Electrochemistry of OER

OER will be the main electrochemical reaction discussed for this ESCA study. It is highly pH-dependent as it can occur in neutral, acidic, and alkaline conditions. In acidic and neutral solutions, water molecules ( $\text{H}_2\text{O}$ ) are oxidized to protons ( $\text{H}^+$ ) and oxygen molecules ( $\text{O}_2$ ). On the contrary, in an alkaline solution, the oxidation of hydroxyl groups ( $\text{OH}^-$ ) becomes  $\text{H}_2\text{O}$  and  $\text{O}_2$ . The half-cell potential ( $E$ ) for acidic and alkaline media at 1 atm and  $25^\circ\text{C}$  is 1.229 V and 0.401 V, respectively, and the reaction is as follows [5,6].



Generally, in alkaline solutions, the OER begins with the adsorption of  $\text{OH}^-$  from the electrolyte onto the active metal site (M) on the catalyst surface. The adsorbed  $\text{OH}^-$  reacts with another  $\text{OH}^-$  ion, forming adsorbed oxygen species, known as an oxygen intermediate ( $\text{O}^*$ ) formation, and releasing an electron. Then, the adsorbed  $\text{O}^*$  species reacts with another  $\text{OH}^-$ , forming  $\text{OOH}^*$  as a key intermediate. Lastly, the oxygen is released, by the further reaction of the  $\text{OOH}^*$  intermediate and regenerating the active catalyst site as illustrated in Figure 3.1 [8]. The kinetic of this mechanism is very sluggish because of the energy accumulation of this multistep reaction that requires electron transfer in each step. As a result, higher overpotentials are necessary to overcome the energy barrier. Therefore, parameters, for instance, faradaic efficiency, turn over frequency (TOF), and especially ESCA, are studied to analyze the performance of electrocatalysts toward the OER process [3,9].

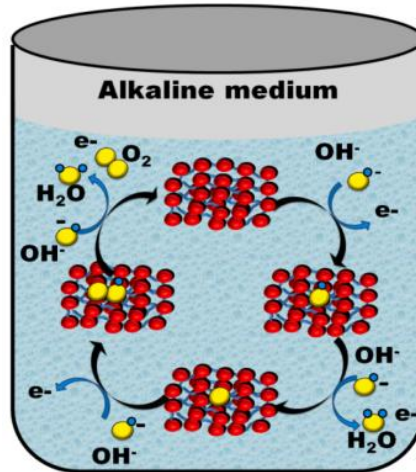


Figure 3.1: Schematic of the possible reaction mechanism for the electrochemical OER in an alkaline solution [2].

### 3.2. Nickel Surface Chemistry in OER

Non-noble-based metal oxide like nickel is widely used in OER catalysts because of its stability and corrosion resistance for OER. The reaction mechanism involves intermediate reactions, which can define the adsorption site on the catalyst surface. These reversible adsorption processes generate adsorption pseudo-capacitance, and the reaction occurs just on the active surface of the material at a given potential [2,7].

During the oxidation process in OER, two polymorphic nickel oxyhydroxides (NiOOH),  $\beta$ -NiOOH and  $\gamma$ -NiOOH, form and play a critical role.  $\beta$ -NiOOH transition from  $\beta$ -Ni(OH)<sub>2</sub> involves a relatively simple redox reaction and has a compact layer structure, whereas  $\gamma$ -NiOOH is formed through a more complex mechanism from  $\beta$ -NiOOH. It involves structural transformations and lattice expansion due to the incorporation of water molecules. In comparison, while  $\gamma$ -NiOOH is more electrochemically active,  $\beta$ -NiOOH is more stable during OER because of its structure and potential [3,9]. The Bode scheme is introduced to show this four-phase redox cycle, which illustrates the transformation of Ni(OH)<sub>2</sub> and NiOOH species, as shown in Figure 3.2.1 [10, 11].

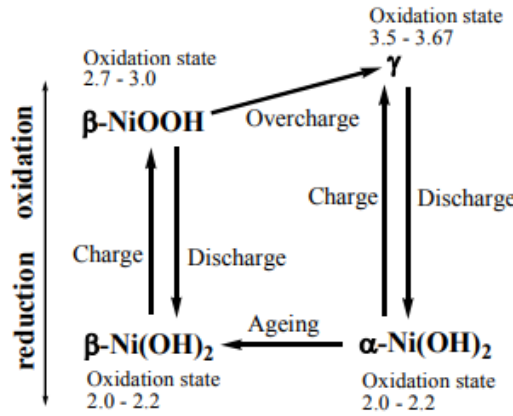


Figure 3.2.1: Ni(OH)<sub>2</sub>/NiOOH redox transformation scheme [10].

### 3.3. Definition of geometric surface area and ECSA

Geometric surface area (GSA) is the term that simply refers to the macroscopic area exposed to the electrolyte, determined by the electrode's shape and dimensions. It does not consider the electrode's microscopic surface roughness or porosity. In contrast, ECSA represents the area of the catalyst's surface that actively participates in electrochemical reactions. It is more relevant than GSA in evaluating catalyst performance because it excludes the inactive site of the catalyst. Moreover, ECSA plays a critical role in determining the number of active sites participating in the electrochemical reactions. A higher ECSA implies a greater density of active sites, leading to improved catalytic performance. The relation between GSA and ECSA can be shown as follows [3,4].

$$ECSA = GSA * f_r \quad (3)$$

Where  $f_r$  is a roughness factor

The roughness factor is a critical parameter. It accounts for surface irregularities, porosity, and structural defects, which influence catalytic activity. A higher roughness factor

indicates an increased ECSA, which enhances reaction kinetics. A process like applying anodic current can be used to define the roughness factor. However, estimating accurately can be challenging due to factors such as gas bubbles and changes in surface morphology over time.

## 3.4. Electrochemical Methods

### 3.4.1. Cyclic Voltammetry (CV)

CV is an electrochemical technique used to study molecules' oxidation and reduction processes by measuring the current response to a cyclically varying applied potential (E). The potential changes linearly over time, resulting in scan rate (v), indicating the experiment condition. CV relies on electron transfer reactions occurring at an electrode surface, and the Nernst equation (eq 4) explains the relationship between equilibrium potential, the concentration of redox species. Figure 3.4 shows the result of the CV, which can be used in estimating some key parameters. The commonly determined parameters are peak-to-peak separation ( $\Delta E_p$ ) and formal potential ( $E_0'$ ), which assess electron transfer reversibility and estimate the midpoint of the redox peak, respectively [13].

$$E = E^0 + \frac{RT}{nF} \ln \frac{(OX)}{(RE)} \quad (4)$$

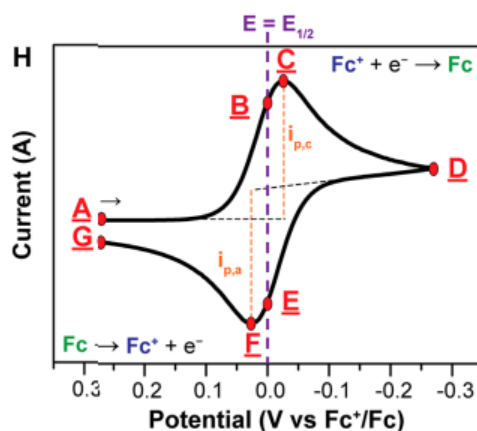


Figure 3.4.1: Voltammogram of the reversible reduction of a 1 mM Fc<sup>+</sup> solution to Fc, during the CV experiment [13].

#### 3.4.1.1 CV as electrochemical methods in practice

The common basic setup is proposed in Figure 3.4.2 when conducting CV experiments using three electrodes. Electrochemical Cell Components are composed of a Working Electrode (WE), Reference Electrode (RE), and Counter Electrode (CE) with different functions. The redox reaction occurs at WE, and a potentiostat is utilized to control the applied potential of the working electrode as a function of the potential at the RE. The purpose of CE is to complete the electrical circuit and counter the reaction at WE [13].

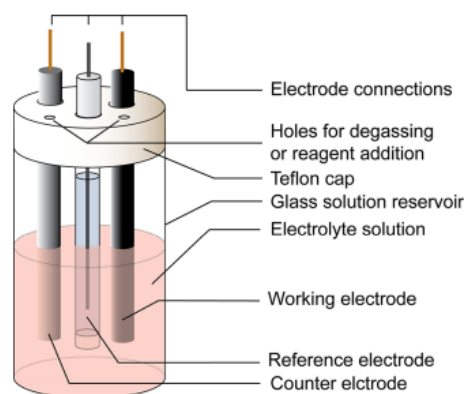


Figure 3.4.2: Schematic diagram of an electrochemical cell for CV Experiments [13].

CV has various applications, such as redox characterization, reaction mechanism studies, and catalysis research. Regarding evaluating electrocatalysts, it is one of the most widely used techniques, especially for determining the ECSA. In this study, investigating ESCA of non-noble metal catalysts like Ni, CV is well suited to the condition because a monolayer of  $\text{Ni}(\text{OH})_2$  is expected to form before oxidation. It can quantify the Ni redox transition, directly correlating with the number of active sites on the nickel electrode [3,12,13].

A number of cycles are crucial when it comes to repeated potential cycling in CV, as they affect electrode surface conditioning, reaction kinetics, and electroactive layer formation. The initial cycles stabilize the electrode surface, removing impurities and forming a consistent electrochemical layer. As it increases, the accumulation and structuring of electroactive species can affect charge transfer, leading to shifts in peak positions and intensity of current density. Figure 3.4.2 well demonstrates the impact of cycling on the Ni(II)/Ni(III) redox peaks considering Ni. A gradual positive oxidation peak shift suggests increasing resistance to oxidation. Peak width variations indicate surface homogenization, and current intensity growth confirms the formation of a more active electrochemical layer. However, repeated gradual conversion of Ni species might lead to unstable ones from excessive oxidation (see section 3.2). This will result in the ineffective use of CV in specific applications [4, 15].

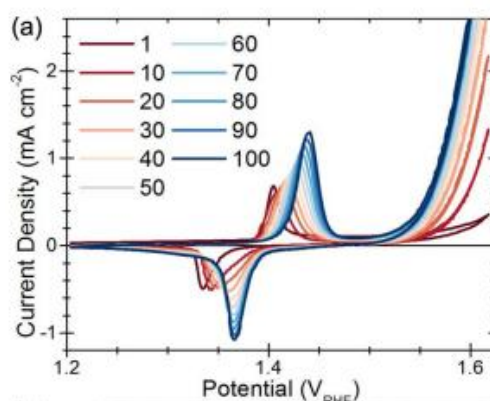


Figure 3.4.3: Schematic diagram of an electrochemical cell for CV Experiments [13].



### 3.4.2. Electrochemical Impedance Spectroscopy (EIS)

EIS is a technique for characterizing electrochemical systems by analyzing impedance responses over a range of frequencies and providing information of charge transfer, interfacial properties, and reaction kinetics. EIS distinguishes different electrochemical processes based on their characteristic time constants by applying a small alternating current (AC) perturbation and measuring the resulting voltage response. The technique is particularly effective in separating bulk resistance, charge transfer resistance, and diffusion-related processes. A key feature of EIS, shown in Figure 3.4.4, is its ability to model complex electrochemical behaviors using equivalent electrical circuits, which approximate the contributions of solution resistance, double-layer capacitance, and surface adsorption phenomena. It measures impedance as a function of frequency, and different systems of electrodes can be utilized. Figure 3.4.5 shows the simple setup of the 3-electrode system controlled by a potentiostat. The result is typically explained in the Nyquist plot, which is time constant and can ideally be visualized as a semicircle to represent the impedance data, as shown in Figure 3.4.5 [3,14].

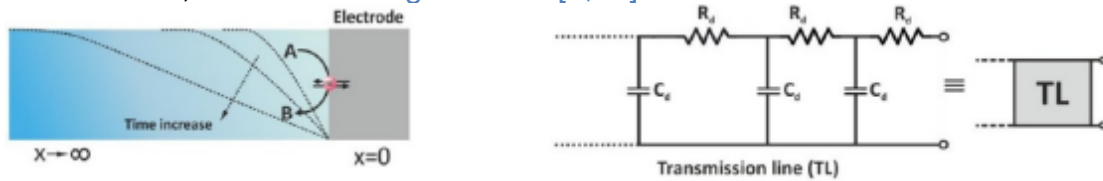


Figure 3.4.4: Equivalent electrical circuits for a semi-infinite regime of an electrochemical cell [14].

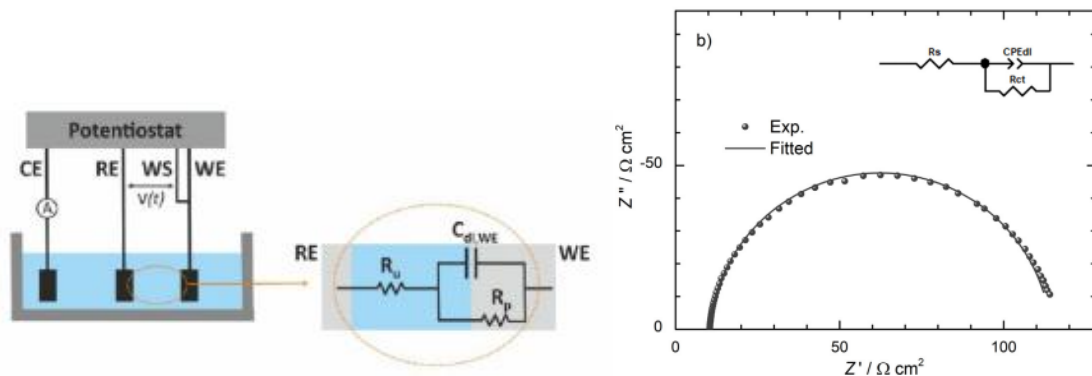


Figure 3.4.5: 3-electrodes system setup and its equivalent circuit modal (Left), and Example of Nyquist plots of Ni experiment in OER (Right) [3, 14].

## 4. ECSA Determination practices

### 4.1. Determination by adsorbates capacitance on layered double hydroxide (LDH)

Utilizing adsorption capacitance ( $C_a$ ) on layered double hydroxide (LDH) is one of the methods to determine ECSA using EIS at reactive OER potentials. It focuses on  $C_a$ , which directly correlates with the adsorption of OER intermediates ( $*O$ ,  $OH$ ,  $OOH^*$ ) on the catalyst surface. This approach provides a more accurate determination of the active sites to OER by analyzing the system under actual catalytic conditions and measuring the capacitance associated with OER intermediates, which is illustrated in Figure 4.1.1 [16].

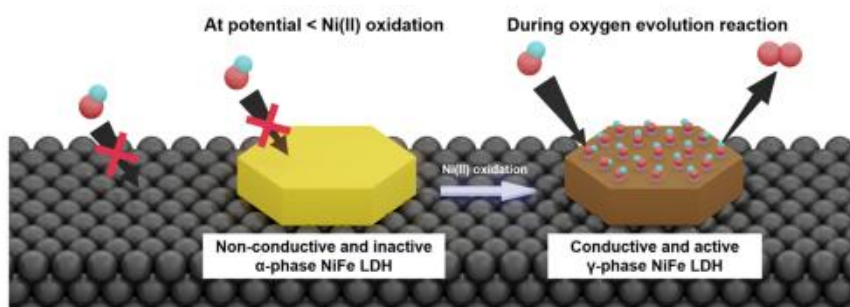


Figure 4.1.1: Schematic of OER intermediates ( $*OH$ ) on the surface of NiFe LDH during phase transition on glassy carbon electrode [16].

An investigation of ECSA using this method was conducted by S. S. Jeon [16] by utilizing NiFe LDH. It showed excellent catalytic activity due to interactions between Ni and Fe. The presence of Fe also enhances electric conductivity and reaction kinetics, lowering the overpotential for oxygen evolution.  $Ni(OH)_2$  undergoes oxidation to  $NiOOH$ , considered the primary active site for OER in alkaline environment. EIS is used to extract  $C_a$  at OER-relevant potentials, allowing precise ECSA calculations for NiFe LDH. As a result, it confirms a correlation between Ni redox peak integration and ECSA, offering a reliable approach to evaluate the intrinsic activity of NiFe LDH catalysts.

### 4.2. Determination by Oxalate method

The oxalate method is introduced as a promising approach to improve the accuracy and precision of identifying ECSA of nickel-based catalysts. It involves the addition of an oxalate salt to an alkaline electrolyte, which forms an adsorbed oxalate layer on the nickel electrode surface. As discussed regarding the formation of  $NiOOH$ , the oxalate method helps stabilize  $Ni(OH)_2$  and restricts its oxidation to  $\beta$ - $NiOOH$ , preventing excessive  $\gamma$ - $NiOOH$  formation. It ensures more reliable and repeatable ECSA measurements by limiting the growth of oxide films to a single monolayer [4].

D. S. Hall [4] experimented on ECSA measurement of nickel electrodes by preparing two different Ni electrodes. The electrode is mechanically polished by SiC paper and diamond suspensions, then an oxalate-containing alkaline electrolyte was freshly prepared to stabilize  $Ni(OH)_2$  formation. Electrochemical measurements were conducted in a three-electrode setup, with a Pt counter electrode and a saturated calomel (SCE), using Ar or  $H_2$

gas purging for potential calibration. CV was employed to analyze Ni oxidation behavior, and the effect of oxalate on the electrode was demonstrated. Initially, the addition of oxalate had little impact on the anodic scan up to approximately 1.35 V. However, above this potential, oxalate significantly affects the oxidation of  $\text{Ni}(\text{OH})_2$  to  $\text{NiOOH}$ , shifting the anodic peak potential leftward by approximately 80 mV. This results in a narrower peak width and a significant spike in peak current density, indicating an increased electrochemical response. These changes suggest that oxalate interacts with the nickel hydroxide layer, likely through adsorption and stabilization, leading to a modified oxidation process. Additionally, oxalate appears to have a minor effect on the OER, possibly enhancing its onset slightly. A similar reaction from the presence of oxalate can also be noticed in the hydrogen evolution reaction (HER).

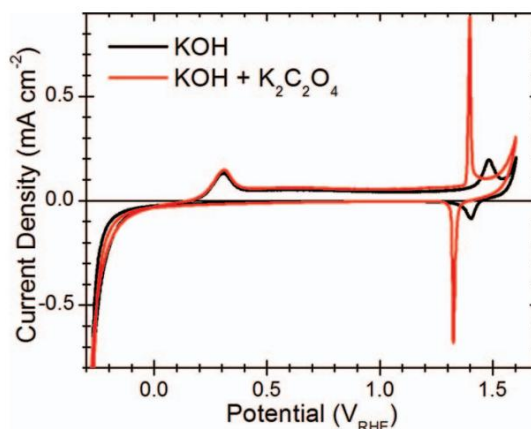


Figure 4.2.1: Experiment result of cyclic voltammetry measurement on polished nickel electrodes under KOH electrolyte and KOH with  $\text{K}_2\text{C}_2\text{O}_4$  electrolyte [4].

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