

TUNGSTEN BORIDES FOR HYDROGEN EVOLUTION REACTION AND OXYGEN EVOLUTION REACTION IN ALKALINE MEDIA

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DEDICATION/EPIGRAPH

To my Family.

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I would like to acknowledge my committee members for agreeing to serve on this committee. I would also like to thank the University of Houston for giving me the opportunity to be here and work towards my degree; U.H. is a very special place. I would like also to acknowledge Shaowei Song, Ph.D. for his assistance throughout the process of my research. Most important, I would to give a special thanks to my parents Sheppard P. Roubion, Sr. and Emily C. Roubion for their unwavering support throughout my life.

ABSTRACT

Hydrogen as a fuel source extracted from the correct sources could replace fossil fuels. Currently, most hydrogen is extracted from fossil fuels which as consequence releases carbon dioxide which is greenhouse gas. An alternative source for hydrogen is water. Several methods have been proposed and researched to extract hydrogen from water such as thermochemical or photocatalytic methods, but such methods have limitations which hinder their commercial viability. A more promising option is electrocatalytic water splitting. Currently, the ideal catalysts for water splitting are platinum-group metals which are scarce, and as consequence, limit the ubiquitous use of these electrocatalysts for water splitting. As an alternative to platinum-group metals, tungsten borides are investigated.

Hydrogen evolution reaction requires a Gibbs' free energy of 0 eV for water splitting, and tungsten borides were investigated to ascertain their overpotentials. Through methods such as ball-milling and hot-pressing, tungsten borides were synthesized. Testing revealed that tungsten borides in the composition of $W_2B_{5.25}$ exhibited performances and overpotentials that were comparable to platinum plate in overpotentials at current densities of 100 mA cm^{-2} , and were stable at those current densities for a twenty-four period.

Oxygen evolution reaction requires a Gibbs' free energy of 1.23 eV for the water splitting process. Tungsten borides were deposited on a nickel-foam substrate and investigated to ascertain their performances. A composition of $W_2B_5P_x/NF$, where phosphorous was also deposited on the substrate revealed that a 300 mV overpotential at a current density of 100 mA cm^{-2} was achieved, and were also stable at that current density for a twenty-four period.

Tungsten-boride compositions were physically analyzed with such techniques as microscopy, X-ray diffraction, X-ray photo-electron spectroscopy, and energy-dispersive X-ray spectroscopy to gain insight into reasons for their performances. Tungsten borides were also electrochemically analyzed, too, with such methods as cyclic voltammetry, linear sweep voltammetry, and electrical impedance spectroscopy. From the test performed, tungsten borides with abundant porosity, active sites, and low charge transfer resistance which all translate into the performances being comparable to platinum-group metals.

TABLE OF CONTENTS

DEDICATION	ii
ACKNOWLEDGMENTS	iii
ABSTRACT	iv
LIST OF TABLES	vii
LIST OF FIGURES	x
1 THE PROBLEM AND ITS BACKGROUND	1
1.1 Hydrogen from Fossil Fuels	2
1.2 Hydrogen from Photocatlytic Water Splitting	3
1.3 Hydrogen from Thermochemical Water Splitting	4
1.4 Hydrogen from Photocatalytic Water Splitting	5
2 EXPERIMENTAL METHODS	8
2.1 Glovebox	8
2.2 Ball-Milling	9
2.3 Hot-Press	9
2.4 Linear Sweep Voltammetry (LSV)	11
2.5 Cyclic Voltammetry(CV)	14
2.6 Electrical Impedance Spectroscopy (EIS)	16
2.7 X-Ray Diffraction (XRD)	17
2.8 X-Ray Photo-Electron Spectroscopy (XPS)	18
2.9 Scanning Electron Microscopy (SEM)	20
2.10 Energy Dispersive X-Ray Spectroscopy (EDS)	20
3 HYDROGEN EVOLUTION REACTION SAMPLES	22
3.1 Introduction	22
3.2 Tungsten Boride Materials Preparation	22
3.3 Electrochemical Sample Testing	24
3.4 Electrochemical Analysis	26
3.5 Sample Analysis	32
3.6 Sample Morphology	36
3.7 Summary	40
4 OXYGEN EVOLUTION REACTION SAMPLES	44
4.1 Introduction	44
4.2 Material Synthesis	45
4.3 Electrochemical Sample Testing and Results	46
4.4 Electrochemical Analysis	50
4.5 Sample Analysis	51
4.6 Sample Morphology	53
4.7 Summary	56

5	OVERALL PERFORMANCE	63
5.1	Introduction	63
5.2	Electrochemical Sample Testing and Results	63
5.3	Summary	63
A	Derivation for Impedance Curve Equations for Randles Circuit	65
	BIBLIOGRAPHY	67

LIST OF TABLES

1	Hydrogen production processes and their enthalpies.	3
2	Chemical steps for thermochemical water splitting.	5
3	The densities and masses of the synthesized compounds. The masses for the compounds are for an eight-gram composition.	23
4	The overpotentials for the catalysts' performances at current densities of -10 mA cm^{-2} and -100 mA cm^{-2} . The overpotentials for the for catalysts at -100 mA cm^{-2} with no iR compensation.	25
5	The double-layer capacitance can be used to acquire the electrochemical surface area (ECSA).	28
6	The resistivity values of the samples	29
7	The results are a from using Equations 12–14 and data from above tables and figures	31
8	Active site calculation from using 6a.	32
9	Area EDS on sample $\text{W}_2\text{B}_{5.25}$ before testing.	35
10	Area of EDS on sample $\text{W}_2\text{B}_{5.25}$ after testing.	37
11	Comparison of Pt plate and $\text{W}_2\text{B}_{5.25}$ with other metal borides in 1M KOH.	42
12	The performances of other HER electrocatalysts with reported low overpotentials. .	43
13	The overpotentials for the catalysts' performances at current densities of 10 mA cm^{-2} and 100 mA cm^{-2} . The overpotentials for the for catalysts at 100 mA cm^{-2} with no iR compensation.	47
14	The overpotentials for the catalysts' performances at current densities of 10 mA cm^{-2} and 100 mA cm^{-2} . The overpotentials for the for catalysts at 100 mA cm^{-2} with no iR compensation.	49
15	The results are a from using Equations 12–14 and data from above tables and figures	50
16	Charge and specific capacitance of the samples.	51
17	Active site calculation from using 6b.	51
18	Comparison of $\text{W}_2\text{B}_{5.25}/\text{NF}$ and $\text{W}_2\text{B}_{5.25}\text{P}_x/\text{NF}$ with other metal borides in 1M KOH.	61
19	The performances of other OER electrocatalysts with reported low overpotentials. .	62

LIST OF FIGURES

1	Carbon dioxide (CO_2) in the Earth's atmosphere measured in parts per million (ppm) for the past 800, 000 years. (Source: www.climate.gov)	1
2	Global average temperatures and carbon dioxide concentration in the atmosphere. (Source: www.globalchange.gov)	2
3	Schematic of the photocatalytic water splitting bandgap.	4
4	In photocatalytic water splitting, oxidation occurs at the valance band and reduction occurs at the conduction band.	4
5	Schematic of the iodine-sulfur reactions.	5
6	The current flows from the cathode to the anode. The electrons flow the positively-charge anode to the negatively-charge cathode. The membrane allows protons (H^+) to pass through, where combine with electrons (e^-) and form hydrogen gas (H_2). . .	6
7	The HER is the reduction process and the OER is the oxidation process.	6
8	Pourbaix diagram for water splitting, where the vertical axis is the hydrogen/oxygen bonding energy and the horizontal axis is the pH. (Source: en.wikimedia.org)	12
9	Chemical steps for the hydrogen desorption and absorption for an acidic (low-pH), basic (high-pH), and neutral ($\text{pH} \approx 7$) medium.	12
10	Three-electrode configuration for LSV testing.	13
11	Chemical steps for the absorption of hydrogen.	14
12	Randles circuit	17
13	Bragg plane diffraction.	18
14	(a) Linear sweep voltammograms indicating the HER performance in relation to platinum plate with iR compensation with 1M of KOH as the electrolyte. (b) Uncompensated data for $\text{W}_2\text{B}_{5.25}$ and $\text{W}_2\text{B}_{5.5}$, two best performing catalysts. Test are in 1M KOH electrolyte.	24
15	The Tafel slopes for the measured catalysts.	25
16	Long-term stability test for twenty-four hours for a current density 100 mA cm^{-2} . .	26
17	(a) CV curves for the W_2B_5 where the voltages range is between -0.92 V to -0.84 V. (b) W_2B_5 sample plot of the current density versus the scan rate. (c) CV curves for the $\text{W}_2\text{B}_{5.25}$ where the voltages range is between -0.95 V to -0.81 V. (d) $\text{W}_2\text{B}_{5.25}$ sample plot of the current density versus the scan rate. (e) CV curves for the $\text{W}_2\text{B}_{5.25}$ where the voltages range is between -0.96 V to -0.86 V. (f) $\text{W}_2\text{B}_{5.5}$ sample plot of the current density versus the scan rate.	27
18	EIS plots of the impedance curves.	29
19	(a) CV curve of W_2B_5 in 1M of PBS. (b) CV curve of $\text{W}_2\text{B}_{5.25}$ in 1M PBS. (c) CV curve of $\text{W}_2\text{B}_{5.5}$ in 1M of PBS.	30
20	XRD for the samples.	32
21	(a) The top plot is before long-term stability testing of $\text{W}_2\text{B}_{5.25}$, and bottom plot is the $\text{W}_2\text{B}_{5.25}$ after long-term stability testing. (b) The top plot is before long-term stability testing of $\text{W}_2\text{B}_{5.25}$, and bottom plot is the $\text{W}_2\text{B}_{5.25}$ after long-term stability testing.	33
22	SEM image of $\text{W}_2\text{B}_{5.25}$ before testing at a working distance of 15 mm for EDS. A rectangle encloses the region where the EDS was measured.	34

23	The (a) image is the area of the sample that was mapped. The (b) image is the mapping overlay of the elements in $W_2B_{5.25}$ before testing. $W_2B_{5.25}$ before testing. Image (c) is the tungsten. Image (d) is the boron.	35
24	Sum spectrum of the mapping. Of the $W_2B_{5.25}$ sample before testing. Vertical axis represents the intensity count and horizontal axis in kV each element's characteristic energy.	36
25	SEM image of $W_2B_{5.25}$ after testing at a working distance of 15mm for EDS.	37
26	The (a) image is the area of the sample that was mapped in the rectangle. The (b) image is the mapping overlay of the elements in $W_2B_{5.25}$ after testing. $W_2B_{5.25}$ after testing. Image (c) is the boron. Image (d) is the tungsten.	38
27	Sum spectrum of the mapping. Of the $W_2B_{5.25}$ sample after testing. Vertical axis represents the intensity count and horizontal axis in kV each element's characteristic energy.	38
28	(a) Image of a diameter of a hot-pressed sample. (b) Image of a gauge of a hot-pressed sample. (c) Image of the length and width of a machined sample. (d) Image of the gauge of a machined sample.	39
29	$W_2B_{5.25}$ sample at various magnifications before testing.	40
30	$W_2B_{5.25}$ sample at various magnifications after testing.	41
31	Tungsten borides on Ni foam iR compensated samples.	47
32	Tafel slopes of the tungsten borides.	48
33	P boosted tungsten borides on Ni foam LSV curves with iR compensation.	48
34	Tafel slopes of the P boosted tungsten borides on Ni foam.	49
35	Twenty-four-hour test of $W_2B_5P_x/NF$ at a current density of 100 mA cm^{-2}	50
36	(a) CV curves for the $W_2B_5P_x/NF$ where the voltages range is between -0.15 V to -0.15 V . (b) $W_2B_5P_x/NF$ sample plot of the current density versus the scan rate. (c) CV curves for the $W_2B_{5.25}P_x/NF$ where the voltages range is between -0.15 V to -0.15 V . (d) $W_2B_{5.25}P_x/NF$ sample plot of the current density versus the scan rate. (e) CV curves for the $W_2B_{5.5}P_x/NF$ where the voltages range is between -0.1 V to -0.1 V . (f) $W_2B_{5.5}P_x/NF$ sample plot of the current density versus the scan rate.	52
37	EIS plots of the impedance curves.	53
38	(a) CV curve of $W_2B_5P_x/NF$ in 1M of PBS. (b) CV curve of $W_2B_{5.25}P_x/NF$ in 1M PBS. (c) CV curve of $W_2B_{5.5}P_x/NF$ in 1M of PBS.	54
39	The (a) image is the area of the $W_2B_5P_x/NF$ sample before testing that was mapped. The (b) image is the mapping overlay of the elements. The (c) image is the B. The (d) image is the W. The (e) image is the P. The (f) image is the Ni,	55
40	Sum spectrum of the mapping. Of the $W_2B_5P_x/NF$ sample before testing. Vertical axis represents the intensity count and horizontal axis in kV each element's characteristic energy.	56
41	The (a) image is the area of the $W_2B_5P_x/NF$ sample after testing that was mapped. The (b) image is the mapping overlay of the elements. The (c) image is the B. The (d) image is the W. The (e) image is the P. The (f) image is the Ni.	57
42	Sum spectrum of the mapping. Of the $W_2B_5P_x/NF$ sample after testing. Vertical axis represents the intensity count and horizontal axis in kV each element's characteristic energy.	58

43	Image (a) is of the length width of the Ni foam sample. Image (b) is of the gauge of the Ni foam sample.	58
44	W_2B_5/NF before testing.	59
45	Ni foam before testing with P deposited on the surface.	59
46	$W_2B_5P_x/NF$ before testing.	60
47	$W_2B_5P_x/NF$ after testing.	60
48	Overall water splitting performance with iR compensation	64
49	Overall water splitting performance without iR compensation	64

1 THE PROBLEM AND ITS BACKGROUND

The incessant consumption of fossil fuels is causing deleterious effects to the planet's climate. Greenhouse gas emission resulting from human activity, such as the burning of fossil fuels, is causing a rise in global average temperatures. Carbon dioxide (CO₂) is the primary greenhouse gas emitted by humans, and its role as a greenhouse gas has been known for more than one century [1]. Figure 1 shows the average CO₂ in the planet's atmosphere in parts per million (ppm). Current CO₂ levels are the highest in modern human history and are significantly in a higher concentration than the previous record of about 300 ppm.

CARBON DIOXIDE OVER 800,000 YEARS

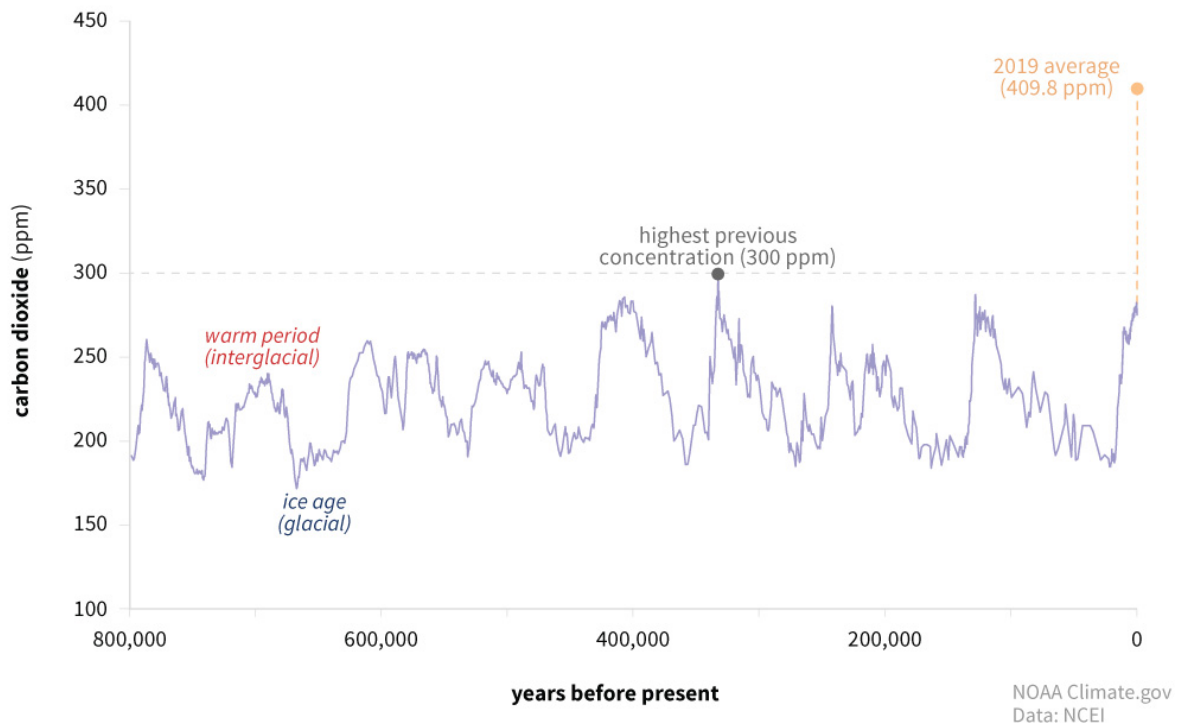


Figure 1: Carbon dioxide (CO₂) in the Earth's atmosphere measured in parts per million (ppm) for the past 800, 000 years. (Source: www.climate.gov)

Figure 2 shows direct correlation between the increase of CO₂ in the atmosphere and the rise in global average temperature. According to the 2019 report by the Intergovernmental Panel on Climate Change, global average temperature is likely to rise 1.5°C above pre-industrial levels by

years between 2030 and 2052. Therefore, finding a sustainable strategy to mitigate the rise in global average temperature has become a crucial issue.

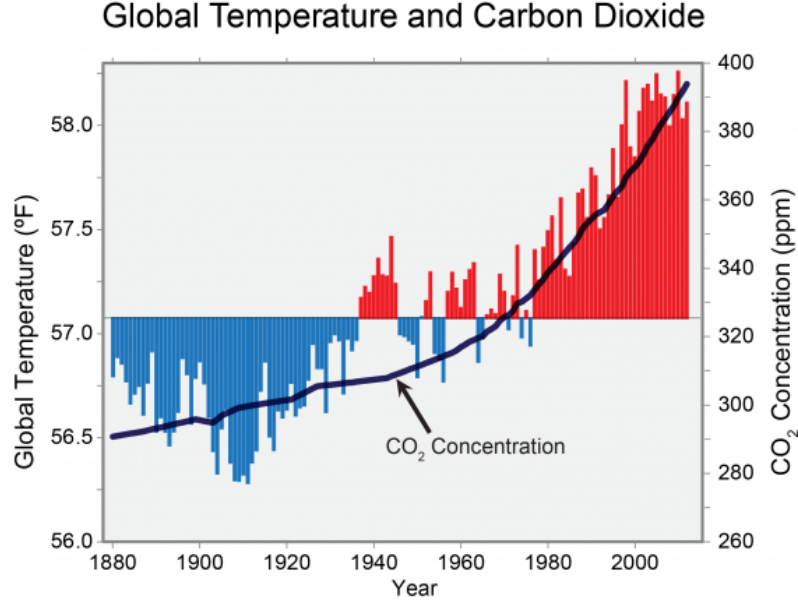


Figure 2: Global average temperatures and carbon dioxide concentration in the atmosphere. (Source: www.globalchange.gov)

1.1 Hydrogen from Fossil Fuels

One potential and sustainable alternative to fossil fuels is hydrogen (H_2). H_2 has a specific energy density that is eighteen times greater than a lithium-ion battery [2]. In addition, hydrogen composes 75% [3] of the visible universe making it an attractive and, in principle, a limitless energy source. However, H_2 on Earth is mostly derived from fossil fuels, [4] primarily methane (CH_4). For example, in the United States, about 95% of all H_2 is produced from the steam methane reforming process (SMR) [5]. The SMR process is an endothermic process [6]. An alternative to SMR is partial oxidation of methane (POM). The POM is an exothermic reaction which uses oxygen instead of water to facilitate the reaction [7]. Another method that is exothermic is CO_2 reforming of CH_4 . Each method has its advantages depending several economic factors [8]. The reactions are chemically expressed in Table 1. When extracting H_2 from CH_4 using either of the methods, the

water gas shift (WGS) reaction must be used so that the H_2 can be separated. The WGS reaction will produce CO_2 as a consequence. To avoid producing CO_2 , other methods have been proposed to completely remove the CO_2 emission from any of the processes.

Table 1: Hydrogen production processes and their enthalpies.

Reaction Type	Reaction Formula	$\Delta H_{298\text{K}}$ [kJ/mol]
Steam-Methane Reforming Reaction	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	206.6
Partial Oxidation Reaction	$\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 + \text{CO}$	-36.0
CO_2 Reforming Process	$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$	216.0
Water Gas Shift (WGS) Equilibrium	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	-41.2

1.2 Hydrogen from Photocatalytic Water Splitting

One alternative to non- CO_2 -producing H_2 production is photocatalytic water splitting. Photocatalytic water splitting takes advantage of the concept that the hydrogen-oxygen bond of water (H_2O) can be broken with a photocatalytic semiconductor when interacting with photons. Photocatalytic water splitting reaction starts with a photon striking a semiconductor that collides with the semiconductor’s electron and causing it to escape and creating a positive hole in its place. To replace the lost electron, an electron is pulled from the water and fills in the hole. To accomplish water splitting via a photocatalyst, a semiconductor with a band gap energy of 1.23 eV or greater is required. The conduction band must be greater than the reduction potential of water, 0 eV, and the valence band must be greater than the oxidation potential of water, 1.23 eV. Figure 3 gives an illustration of this process, and Figure 4 shows the chemical steps of the processes of oxidation and reduction reactions.

H_2 generation from light has its environmental advantages, but it also has its disadvantages which makes it difficult to be used ubiquitously. Photocatalytic water splitting is extremely inefficient and therefore is not commercially viable [9]. Given that the bandgap energies are very large for the non-platinum group metals, [10] this also limits their commercial viability. Since the catalysts made of non-platinum group have high overpotentials, they can only absorb a narrow amount

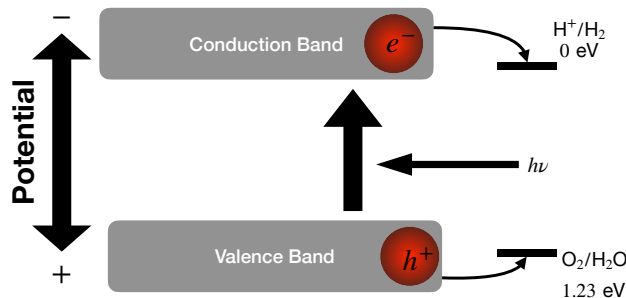


Figure 3: Schematic of the photocatalytic water splitting bandgap.

of sunlight, such as the ultraviolet spectrum, instead of the wider visible light spectrum [11]. The electrocatalysts must be free of surface defects as to not have the problem electron and hole recombination [12]. The recombination of electrons and holes can prevent the redox reaction and generate heat [13].

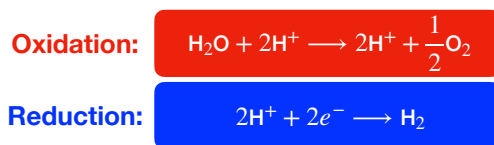


Figure 4: In photocatalytic water splitting, oxidation occurs at the valence band and reduction occurs at the conduction band.

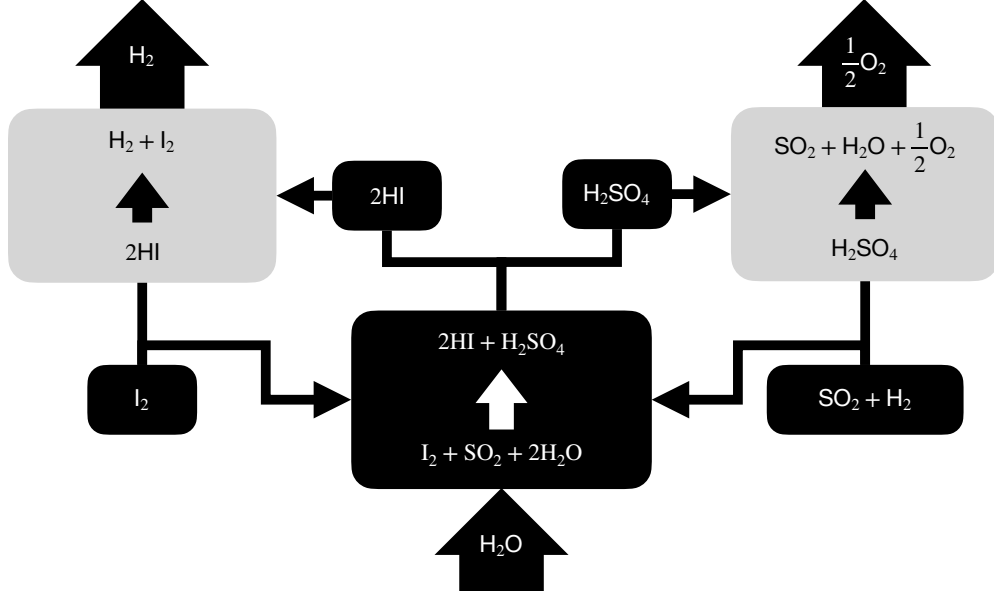
1.3 Hydrogen from Thermochemical Water Splitting

Another non-CO₂-producing alternative is to split water with heat. Thermochemical process of water splitting produces no CO₂ in the chemical breakdown. In this process, three-step endothermic and exothermic reactions are required as shown in Table 2. The hydrolysis step starts the reaction which is known as the Bunsen reaction which is exothermic, and it produces hydriodic acid (HI) and sulfuric acid (H₂SO₄). In the second endothermic step, the sulfuric acid is disassociated. In the final endothermic step, the hydriodic acid is disassociated to acquire the hydrogen. Each of these reactions occur in a compartmental section of a reactor as illustrated in Figure 5.

As the state of field currently stands, there are no commercially working iodine-sulfur reactors. Though, pilot programs have been conducted showing its feasibility [14]. The high temperatures

Table 2: Chemical steps for thermochemical water splitting.

Step	Reaction Formula	Temperature and Type
Hydrolysis	$\text{I}_2(l + g) + \text{SO}_2(g) \rightarrow 2\text{HI}(g) + \text{H}_2\text{SO}_4$	Exothermic at 120°C
Oxygen production	$\text{H}_2\text{SO}_4(g) \rightarrow \text{SO}_2(g) + \text{H}_2\text{O}(g) + 0.5\text{O}_2(g)$	Endothermic at 850°C
Hydrogen production	$2\text{HI}(g) \rightarrow \text{I}_2(g) + \text{H}_2(g)$	Endothermic at 450°C

**Figure 5:** Schematic of the iodine-sulfur reactions.

required also puts it at a disadvantage. Chemicals such H_2SO_4 are corrosive to the chambers [15]. A high-temperature gas reactor has to be helium (He) cooled [16]. He is a very expensive and scarce gas which would limit the wide-spread use of this technology.

1.4 Hydrogen from Photocatalytic Water Splitting

For water splitting to be commercially viable, it has to be able to fit into the current industrial infrastructure. Other than hydrocarbon sources for H_2 , the only current commercially viable source is water splitting via electrolysis. Compared to the other non- CO_2 -producing methods, water electrolysis is a mature and well-researched field with industrial electrolyzers reporting very high nominal efficiencies [17]. Water splitting via electrolysis is a two-electrode configuration with a

cathode and an anode as shown in Figure 6.

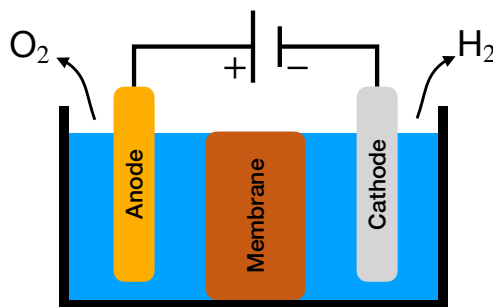


Figure 6: The current flows from the cathode to the anode. The electrons flow the positively-charge anode to the negatively-charge cathode. The membrane allows protons (H^+) to pass through, where combine with electrons (e^-) and form hydrogen gas (H_2).

It is at the anode where the oxygen evolution reaction (OER) occurs. At the cathode is where the hydrogen evolution reaction (HER) occurs. Of the two reactions, the OER is the more complex reaction given the fact that it is a four-electron oxidation reaction, whereas the HER is a two-electron reduction reaction process. Figure 7 shows the chemical steps involved in the water-splitting process. An ideal and critical energy of 1.23 eV is required for OER to occur at the anode. For the HER to occur at the cathode, an ideal energy is 0 eV.

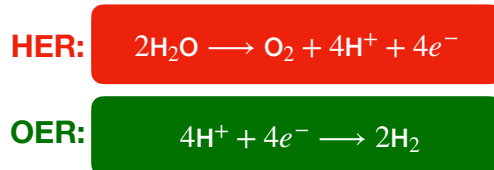


Figure 7: The HER is the reduction process and the OER is the oxidation process.

Characteristics of efficient electrocatalysts have low overpotentials which can be achieved by proper Gibbs' free energy of absorption and desorption, [18] [19] low charge-transfer resistance which allows for efficient charge transfer, [20] and large surface area with abundant active sites [21]. Platinum group metals (Pt, Ir, and Rh) [22] and their oxides (PtO_2 , IrO_2 , and RhO_2) [23] are the ideal candidates to be used for HER and OER, respectively, but their ubiquitous use is not possible

due to their rarity and high cost. The search for non-platinum group alternatives that are earth-abundant and low-cost is a requirement for massive-scale water splitting. Nanoscale materials in the form of nanowires, [24] nanoribbons, [25] or nanosheets [26] have been used to enhance the performances of electrocatalysts with significant success. It has been done by such methods as hydrothermal or chemical vapor deposition which deposits nanomaterials on substrates, such as fiber sheets, metal foams, or metal sheets. A disadvantage of the substrate approach is degradation of the nanomaterials at high current densities in part due to the weak adherence of the nanomaterials to the applied substrates [27] To improve the adherence of materials to substrates, and the research of cheap and abundant non-precious-metal alternatives, is an area of active research.

2 EXPERIMENTAL METHODS

2.1 Glovebox

Pyrophoric materials when exposed to air (or moisture) are susceptible to combustion. Elements like Fe, and other metals, have the physical inclination to transfer electrons [28]. This loss of electrons can occur through the process of oxidation when metals react with the oxygen in the air or moisture in the atmosphere [29]. During this oxidation process, a large amount of heat can be generated, which can result in a fire under the right conditions [30]. When elements are milled into a powder, their surface areas increase, along with the exposure of active reaction sites, makes combustion that much more likely [31]. As a solution to prevent this from happening, these sensitive materials are kept in a glovebox. A glovebox is a chamber with an atmosphere inside of it that minimizes oxidation of these pyrophoric materials. For manipulation of material inside the glovebox, the handler must wear gloves as a way to protect the hands and the box's gloves from any damage. When using sharp objects inside the glovebox, an additional glove covers the box's gloves to prevent damage to the box's gloves. Any puncture to the box's gloves could result in a loss of pressure, atmosphere, and moisture levels inside the glovebox. The conditions inside the glovebox must be kept at specific moisture, pressure, and stoichiometric levels to ensure that oxidation is kept to a minimum.

The first thing that must be checked before opening the transfer chamber is that the vacuum pump is turned on. At this point of the material transfer, an inert gas is filled in the transfer chamber and opened and then the material is placed in the transfer chamber and closed. A vacuum is pulled inside the chamber and refilled. This process is repeated three times as way to ensure that transfer chamber is removed of impurities. The transfer chamber is now opened into the glove box and the material is transferred from inside the transfer chamber and into the glovebox. When one is finished with the glovebox, the pump is turned off and a vacuum is pulled inside the transfer chamber.

2.2 Ball-Milling

The use of a ball-mill is an effective method to control the microstructure of particles [32]. The ball-milling process also has the advantage to achieve the synthesis of compounds that would otherwise have to be done with more intensive techniques such as melting [33]. Another effective feature of the ball-mill process is that it can be used to achieve phase transitions in the compounds from the elements that are in ball-mill process [34]. To achieve the phase transition and desired particle size, a sufficient time in which the particles are in the ball-milling process is required. If ball-milling time is too short or too long, the acquisition of phase transitions will not be achieved [35].

For ball-milling of elements to be done, a steel jar with steel ball bearings is used as the container for elements. The sample's elements are placed inside the ball-milling jar while it is contained in a glovebox. While in the glovebox, the jar is in an atmosphere of an inert gas. After the elements are placed inside the jar, the jar is then sealed while still inside the glovebox which will have the ball-milling process take place in an inert gas. The ball-milling jar is then placed in a vise of the ball-milling machine. A time is set and then the ball-milling machine is activated. Once the ball-milling process is complete, the jar is then immediately moved into the glovebox as to prevent any possible introduction of oxygen into the ball-milling jar.

2.3 Hot-Press

A simple and cost-effective method to convert a powder into a bulk material involves using the hot-press [36]. The hot-pressing technique has been extensively used as method to synthesize materials and enhance their conductive properties [37]. The hot-press works by taking materials, placing them into a die, and subjecting them to high temperatures and pressures so that the materials weaken and combine. When the materials emerge from the hot-press after cooling, bulk samples exhibit properties that make them mechanically stronger and chemically stable versus the materials in their powder states [38].

The hot-pressing procedure starts with a clean graphite die, plunger, and spacer so that current can flow with little resistance. The powder will be put inside the die. However, as a preceding

step, the die must be prepared to go into the glovebox. This requires applying insulation paper around the die. The insulation paper will be used to insulate the die from the heat that will be generated during hot-pressing. In addition, graphite foil is applied between the plunger and the spacer. This prevents the sample from sticking to the plunger and spacer when the sample is cooled and removed.

As the name suggests, hot-pressing is a technique where samples are subjected to significant amounts of heat and similarly large pressures. The heat generated in the hot-press is produced from a large amount of electrical current that can reach about 12,000 A. For these experiments, currents of only a fraction ($\sim 6\%$) of this upper limit were used. Along with the heat, the sample will also be under pressure. The force for these experiments were about one metric ton. The die has a half-inch-diameter hole in the middle of the die where the sample powder is placed. There is also a small hole on the side of the die to allow for a thermocouple to be placed inside the die during the hot-press to read the temperature. Two graphite blocks are put at the top and bottom of the die so that it does not make contact with the metal plates inside the press. The press is jacked to a force below a metric ton. While the sample in the die is heated, thermal expansion occurs, which will cause the force to increase to about a metric ton and will also increase the pressure. Only when the safety door is closed and the coolant is checked to make sure it is working, is then the current turned on.

The sample is quickly brought from room temperature to a temperature where the material mechanically weakens by adjusting the current with the rheostat. The indication that the sample is mechanically weakened is when there is a drop in force. The sample is jacked up and held at a constant force and temperature for a set period of time. After that period of time, the current is switched off. The sample is left in the press and allowed to cool to a temperature where it can be safely removed from the press and allowed to cool to a temperature where it could be safely removed from the die. At this point, the sample is now in bulk form and can be removed from the die.

2.4 Linear Sweep Voltammetry (LSV)

To study the performance of electrocatalysts, an analysis of the current over a fixed voltage range is used to analyze the samples. Linear sweep Voltammetry is an effective way to measure and investigate the electrocatalytic activity of electrocatalysts [39]. With linear sweep voltammetry, one can measure the onset potential of the reaction [40]. The onset potential is the point in the reaction where the current starts to increase from zero. From the onset potential, the overpotential of the electrocatalyst can be measured for a given current density. For the reduction process of the hydrogen evolution reaction (HER), the overpotential is measured and should be as close to the Gibbs' free energy of hydrogen absorption which is 0 eV [41]. For the oxidation process of the oxygen evolution reaction (OER), the Gibbs' free energy of hydrogen desorption should have an overpotential measured as the difference from 1.23 eV [42].

To measure the performance of a sample, the physical and chemical properties of the sample must be considered. The physical properties such as the dimensions have to be considered for the samples and will vary depending on how each sample is synthesized. If a sample is on a very thin substrate, then only two physical sides will have to be considered for the surface area, and only the part of the sample that is immersed in the electrolyte will be considered. If the sample is a bulk material, then all sides will have to be considered that are in the electrolyte, and this is because the sample will have a gauge to it which is an area where activity can occur which must be measured, too. The chemical properties that have to be considered will largely depend on the pH of the electrolyte and if the measurement is for an HER or OER catalyst. Figure 8 is the Pourbaix diagram which gives information about pH versus the voltage and illustrates what range the voltage must be in for water splitting to occur.

Hydrogen evolution reactions are a two-electron reduction process which is a cathodic type of electrocatalyst. The oxygen evolution reactions are four-electron oxidation processes, which require anodic electrocatalysts. The chemical steps for the HER or OER processes will vary based on whether electrocatalysts are tested in a low-pH or high-pH electrolyte as illustrated in Figure 9 [43].

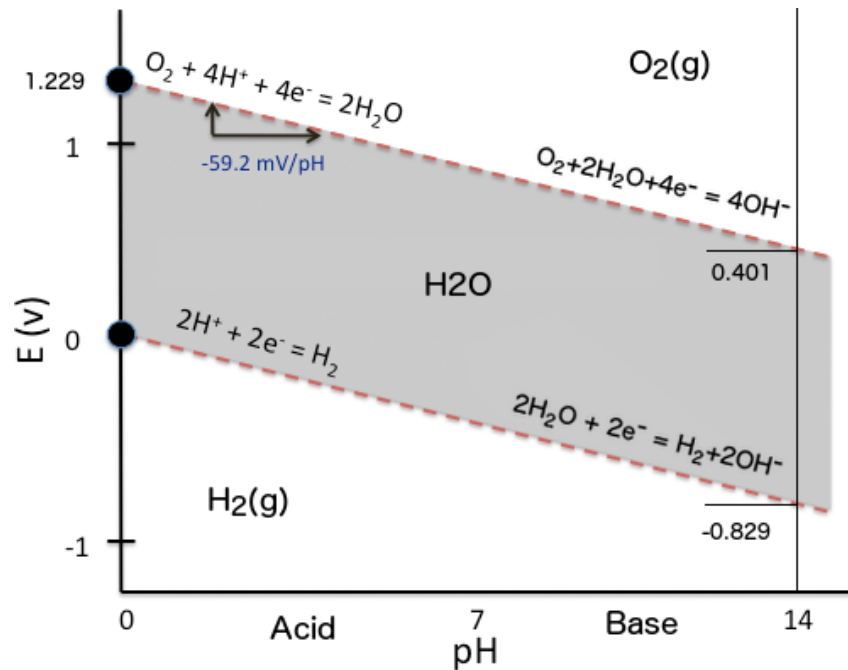
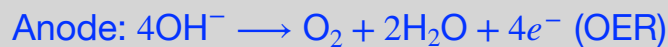


Figure 8: Pourbaix diagram for water splitting, where the vertical axis is the hydrogen/oxygen bonding energy and the horizontal axis is the pH. (Source: en.wikipedia.org)

In acidic medium



In basic medium



In neutral medium



Figure 9: Chemical steps for the hydrogen desorption and absorption for an acidic (low-pH), basic (high-pH), and neutral ($\text{pH} \approx 7$) medium.

The experimental configuration for testing samples is illustrated in Figure 10. A reference electrode in the setup is used to provide a stable reference voltage, which is used to convert to the reversible hydrogen electrode (RHE) via the Nernst equation [44]. The sample is used as the working electrode while the counter electrode completes the three-electrode system. This configuration is known to facilitate the flow of current [45]. Counter electrodes are made of materials such as platinum or carbon. When testing a sample, one must consider if the reaction is HER or OER because this will determine the proper counter electrode. In HER conditions, platinum would not be an appropriate choice as a counter electrode because the HER is an attractive potential which could cause platinum atoms to plate the working electrode and give false performance data [46].

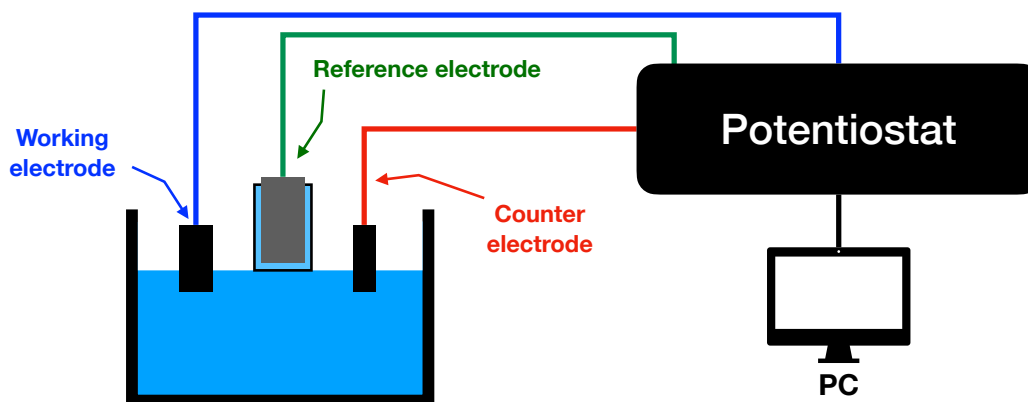


Figure 10: Three-electrode configuration for LSV testing.

The measurements from the electrode configuration are measured by a potentiostat, which is then outputted by a computer. From the LSV measurements, one can acquire the polarization curves. The polarization curves are a plot of the current density value for a given voltage. From the polarization curves, the overpotentials can be computed. The overpotential is a measurement of the kinetic barriers that are intrinsic to an electrocatalyst [47]. Overpotentials are a product of the internal resistances that are present in the reactions. Resistance could be from charge transfer resistance or uncompensated resistance [48]. The uncompensated resistances are a product of the sample in contact with the electrolyte which can cause a drop in voltage. The following set of

equations (Equations 1a and 1b) show when the iR is compensated for in the overpotentials η [49].

$$\eta_{OER} = E_{RHE} - 1.23V - E_{iR} \quad (1a)$$

$$\eta_{HER} = E_{RHE} - 0V - E_{iR} \quad (1b)$$

The LSV curves for HER are used to assess the efficiencies of the reactions' release of hydrogen at the sites of the electrocatalysts. The internal kinetics that determines the efficiencies is given by the Tafel slope which is Equation 2, where η is the overpotential, b is the Tafel slope, j is the current density, and a is the exchange current density [50]. The information that the Tafel slope can reveal is how much of the overpotential increment is required to raise the current density by a factor of ten [51]. Lower Tafel slopes are indicative of more efficient electrocatalysts. Tafel slopes are given in units of mV dec^{-1} . Depending on the value of the Tafel slopes, one can determine what steps are occurring in the HER, where the Tafel step is 30 mV dec^{-1} , the Heyrovsky step is 40 mV dec^{-1} , and the Volmer step is 120 mV dec^{-1} [52]. Figure 11 shows the chemical steps for the absorption of hydrogen H_2 [53].

$$\eta = a + b \log(j). \quad (2)$$

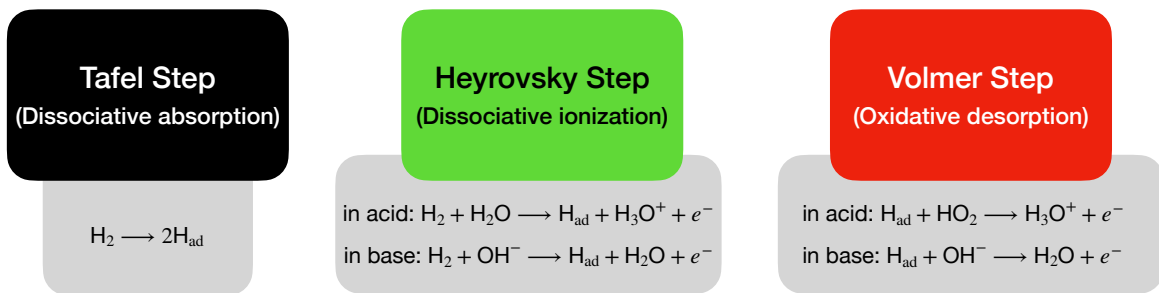


Figure 11: Chemical steps for the absorption of hydrogen.

2.5 Cyclic Voltammetry(CV)

A method to investigate the oxidation and reduction process that an electrocatalyst will exhibit is with cyclic voltammetry. Just as LSV, the CV is measured as a current versus a fixed voltage range.

Cyclic voltammetry is a method used to study the electron transfer within the electrode [54]. For the purposes of OER, CV can also be used to activate the electrocatalysts [55]. CV activation for OER electrocatalysts can occur by taking a metal and converting it to a metal oxide which could improve its OER performance [56].

The cyclic voltammetry is also a method used to measure the electrochemical double-layer capacitance (EDLC), C_{dl} , where the double layer refers to the layers formed by the surface of the electrocatalyst in contact with the electrolyte [57]. The C_{dl} is determined from the CV curves by plotting the current densities versus the scan rates and doing a linear fit to acquire the C_{dl} [58]. The C_{dl} is linearly proportional to the electrochemical active surface area (ECSA) [59]. The cyclic voltammetry also gives the specific capacitance, C_p , where the C_p can be used to measure the ability of a material to store charge. From the C_{dl} and C_p , one can acquire the ECSA by using Equation 3 [60].

$$\text{ECSA} = \frac{C_{dl}}{C_p} \quad (3)$$

Equation 4 is the calculation for the C_{dl} , where $\Delta j = |j_a - j_c|/2$ is the difference between the anodic and cathodic current density measured from the center of the CV curve. V_b is the scan rates of the CV which are in units of mV^{-1} [61]. From measuring the Δj at given scan rates, one can plot the results as current density versus the scan rates and do a linear fit to acquire the C_{dl} , which will be in units of Farads per unit area. For the calculation of the C_p , Equation 5 gives a method of how to acquire it [62], [63]. For Equation 5, ΔV is the voltage range, m is the mass, I is the current, and t is time. To acquire the Q value, one integrates the CV curve to acquire area which will be the charge of sample.

$$C_{dl} = \frac{d(\Delta j)}{dV_b} \quad (4)$$

$$C_p = \frac{\frac{\int_{V_1}^{V_2} I(V) dV}{V_b}}{\Delta V_m} = \frac{I_t}{\Delta V_m} = \frac{Q}{\Delta V_m} \quad (5)$$

The CV curves gives insight into the active site that an electrocatalysts may have. Active sites are important to measure because active sites are a measurement of the overall efficiency of the overall activity on the surface of an electrocatalyst [64]. The more active sites that an OER electrocatalyst has; the more sites on the surface of the electrocatalyst has to facilitate the oxygen evolution reaction [65]. The more active sites that an HER electrocatalysts has; the more sites on the surface of the electrocatalyst has to facilitate the hydrogen evolution reaction [42]. Equation 6a is used to calculate the number of active sites an HER electrocatalyst has [66]. In Equation 6a, F is the Faraday constant and $1/2$ represents the two-electron reaction that is required to form one hydrogen molecule [30]. Equation 6b is used to calculate the active sites for OER electrocatalyst, [67], $1/4$ is used instead of $1/2$ because OER is a four-electron process. From measuring the number of active sites, one can acquire the turn over frequencies. The turnover frequency (TOF) is a measure of the intrinsic catalyst's performance [68]. Equation 6c explicitly shows how to calculate the TOF for the OER process [69], and Equation 6d shows the TOF for the HER process [70], where A is the geometric surface area of the electrode.

$$N = \frac{Q}{2F} \quad \text{for HER} \quad (6a)$$

$$N = \frac{Q}{4F} \quad \text{for OER} \quad (6b)$$

$$TOF = \frac{jA}{4Fn} \quad \text{for OER} \quad (6c)$$

$$TOF = \frac{jA}{2Fn} \quad \text{for HER} \quad (6d)$$

2.6 Electrical Impedance Spectroscopy (EIS)

To acquire a better understanding of the electrocatalyst's performance, the EIS technique is employed to analyzed the kinetics of the sample. The charge transfer resistance (R_{ct}) is associated with the sample's kinetics [71]. EIS reveals the intrinsic properties of the electrocatalyst that determines the internal conductivity. The EIS analysis is an alternating current (AC) procedure as opposed

to a direct current (DC) procedure [72]. The EIS measurement is a complex plot of resistance measurements in the form of Nyquist plots.

The EIS measurements are interpreted through RC circuits [73]. When measuring the Nyquist plots, a curve fitting is done with an equivalent circuit. There are many circuit-equivalent models, but the two-resistor circuit is the one utilized in these experiments [74]. Figure 12, which is known as the simplified Randles cell, is a demonstrative of the RC circuit that is used these experiments. The two resistors are R_s and R_{ct} , where R_s is the solution resistance. A full and complete derivation of the equations for the Nyquist plots are given the appendix.

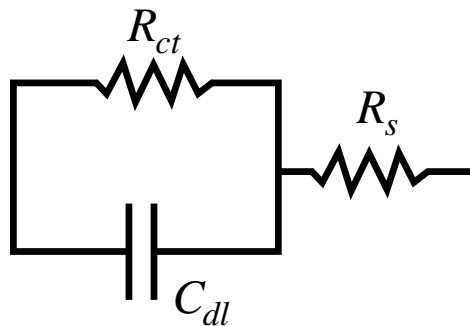


Figure 12: Randles circuit

2.7 X-Ray Diffraction (XRD)

To determine the crystallinity of a sample, X-ray diffraction is utilized [75]. The Miller indices and space groups can also be determined from XRD [76]. By studying the shift peaks and angles, XRD can be used to determine the cell volume and oxygen vacancies in a sample [77]. Stoichiometry for a prepared composition could also be verified by XRD [78]. For XRD to detect the elements in a compound, it must be of significant quantity; otherwise, it may not be detected [79].

X-rays are produced when high-speed electrons collide with a metal. The electrons are produced from a metal filament, which is usually made of tungsten, that is heated and is used as a cathode. A target metal, which is used as an anode, usually made of copper, that is water-cooled, is stricken with the electrons that have been accelerated by a high-voltage between the cathode and the anode. From the collisions of the electrons with the target metal, X-rays are produced. The X-rays are

emitted through a window, usually made of beryllium, and collide with a static sample. The X-rays are scattered at different angles off of the sample which is detected and recorded.

Bragg's law is used to interpret the X-ray scattering. Figure 13 shows how an incident wave and reflective wave impact and scatter off the sample. Equation 7 is the explicit description of Bragg's law. In Equation 7, n represents the wave number which is one because X-ray beams scattered from successive planes in the crystal (as shown in Figure 13) and will travel distances differing by exactly one wavelength, d_{hkl} represents the interplanar spacing, where hkl are the Miller indices, and θ is the orientation of the atomic positions. Equation 8 shows explicitly how to acquire the Miller indices, where a is the value that is determine for the given crystal orientations. For the experiments that were performed, data such as the Miller indices were determined with the help of computer software and literature references.

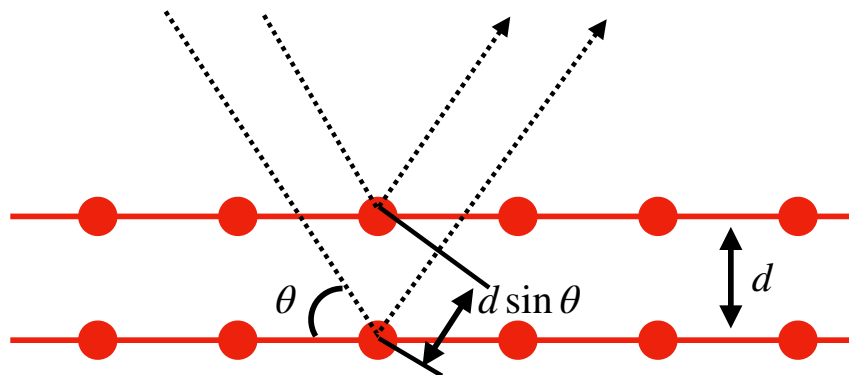


Figure 13: Bragg plane diffraction.

$$n\lambda = 2d_{hkl} \sin(\theta), \quad (7)$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (8)$$

2.8 X-Ray Photo-Electron Spectroscopy (XPS)

To study in greater detail the dynamic changes and chemical reactions of electrocatalysts, XPS is utilized [80]. The chemical states of the sample can be identified through XPS [81]. For many

samples that are made, XPS can reveal the surface-oxide layer which is present on samples when exposed to air [82]. The way XPS determines the chemical composition of a sample is by measuring the electron-orbital energy [83]. XPS is a surface probing technique which probes only a few nanometers below the surface [84].

XPS works on the concept of the photo-electric effect, where the photo-electric effect is the release of electrons from a material when exposed to electromagnetic radiation such as X-rays. The phenomenon that is measured from this effect can then be used to determine the binding energy of the electrons which can then be used to determine the electron-orbital states. The energies involved in XPS is stated in Equations 9a and 9b, where 9a is the overall kinetic energy, KE , and 9b is a re-arrangement of Equation 9a to acquire the binding energy, E_B . Variables hf are the Planck's constant and frequency of the photon, respectively, which is the product of the energy of the photon, and φ is the work function of the element which is the energy that required to release an electron from the atom. All variables are controlled for in XPS except the E_B ; the other variables are measured from the X-ray source or spectrometer. Based on the binding energies, the spin-orbit couplings can be determined based on the Fermi energy levels.

$$KE = hf - (E_B + \varphi) \quad (9a)$$

$$E_B = hf - KE - \varphi \quad (9b)$$

Split-orbit coupling peaks are produced from XPS. For total angular momentum J , where $J = l + s$. Couplings will usually come in doublets for all l greater than zero; that is when there is quantum degeneracy. Chemical shifts can be observed by peaks which could be caused by interactions with other elements. To analyze the XPS peaks, the deconvolution technique is employed. The deconvolution process takes data and curve fits it with gaussian functions. In other words, the output given by XPS peaks is deconvolved with a known function so that the input functions can be extracted. The deconvolution process is executed by software programs.

2.9 Scanning Electron Microscopy (SEM)

To visually see the morphology of a sample, the scanning electron microscope is employed [85]. One way that an SEM analysis can help improve the performance of a sample is by showing the defects on the surface of the sample [86]. For OER samples, SEM can reveal how the surface morphology changes before and after CV activation [87]. For HER samples, SEM can also reveal how the surface morphology changes before and after LSV [88]. SEM works on the concept that back-scattered electrons can be detected from a sample to form an image. SEM can reveal details up to about one-hundred thousand times in magnification. Particles' sizes will determine how much magnification is required.

Electrons, which are known as primary electrons, are usually thermionically generated from a tungsten filament. The number of electrons generated is controlled by the emission current. The primary electrons are then accelerated from the cathode with a high voltage to the anode which takes place all inside a vacuum chamber. The electrons are then focused by magnetic lenses. With magnetic lenses, one can adjust the probe current. The probe current determines how many electrons are focused onto the sample. If the probe current is high, the image is bright but the resolution is low and vice versa [89]. For use of the SEM, a proper working distance is required, where working distance is the vertical distance that the lens is from the sample. The shorter the working distance; the higher the resolution of the image will be. The image detected by SEM is composed of secondary electrons, where secondary electron are electrons that are not detected as having backscatter.

2.10 Energy Dispersive X-Ray Spectroscopy (EDS)

To evaluate the elemental composition of the sample, EDS measurements are used [90]. EDS can be employed to find impurities in a sample which can impede charge transfer [91]. EDS has the ability to give insight into the elemental distribution on a sample by mapping the surface [92]. Along with elemental distribution, elemental concentration can also be determined via EDS [93]. EDS has limitations to what it can detect: it is unable to detect very low-atomic-number elements

such as hydrogen [94].

EDS works by primary electrons colliding with the sample's core-shell electrons and valance electron fills that core's vacancy. The energy that is released from this process subsequently causes a release of an X-ray. These X-rays are characteristic X-rays. Characteristic X-rays are X-rays that have a certain energy value that corresponds to a certain element. To interpret the characteristic X-ray, software programs are used to determine which energies correspond to which elements.

3 HYDROGEN EVOLUTION REACTION SAMPLES

3.1 Introduction

Tungsten boride was theoretically predicted to be an efficient Hydrogen evolution reaction (HER) electrocatalyst due to its electronic transport properties [95]. Arc melting has been shown as a way to synthesize metal borides and that the manipulation of the boron content is key to improving the performance; but, the performance from arc melting preparation has low current density with high overpotential [96]. A method involving ball-milling and hot-pressing electrocatalytic materials is an alternative to the substrate deposition method or arc melting, which produces materials which are more structurally stable under higher current densities [38]. Today, Tungsten borides have not been studied extensively [97]. Therefore, there is a potential for research progress to be made in the study of tungsten borides.

3.2 Tungsten Boride Materials Preparation

The preparation of tungsten boride starts with the precursors of tungsten (W) powder and boron (B) crystals. Tungsten powder particles are about 12 microns in size while the boron crystals are about 99.95% pure. The molar ratio for W was two and the B was five, which has the formula symbol W_2B_5 . Other preparations were made with the W ratio held at two while the B ratio was manipulated, giving ratios of $W_2B_{5.25}$ and $W_2B_{5.5}$. Each preparation was made in batches of eight grams. The required amount of W and B were found using:

$$\text{Element Mass} = \frac{(\text{Molar ratio})(\text{Atomic Mass})}{\sum(\text{Molar Ratio})(\text{Atomic Mass})}. \quad (10)$$

The atomic mass of W and B are $184.840 \text{ g mol}^{-1}$ and $10.811 \text{ g mol}^{-1}$, respectively. Table 3 lists the molar ratios of the B and W compounds as well as their densities and masses. As indicated by the values listed, as the ratio of B is increased, the density of the compounds increases. The masses are a result the samples size after machining.

The precursors are assembled in the glovebox, where the samples are in an inert gas environment.

The precursors are placed in a steel jar and sealed while inside the glovebox with two steel ball bearings. The sealed jar is removed from the glovebox and placed in the ball-milling machine. Next, the samples are mixed inside the ball-milling machine for twelve hours to ensure that they combine properly. Although the ball milling can be done for longer periods of time, one must factor in that W and B are hard elements. W has a Mohs hardness of 9 [98] and B is even harder, with a Mohs hardness of 9.3 [99], while steel’s hardness is considerably less. Therefore, an amount of steel particles can be introduced into the compounds the longer ball-milling continues.

Table 3: The densities and masses of the synthesized compounds. The masses for the compounds are for an eight-gram composition.

Compound	Mass of B [g]	Mass of W [g]	Mass of Compound [g]	Density [g/cc]
W_2B_5	6.980	1.020	0.2230	4.877
$W_2B_{5.25}$	6.940	1.060	0.2358	5.381
$W_2B_{5.5}$	6.890	1.110	0.2356	6.415

After the ball-milling process, the jar is transferred back to the glovebox. Once in the glovebox, the sample is placed into a graphite die and subsequently placed into the hot-press, where it is placed under a tonnage of eight-tenths of a metric ton. As a current heats up the sample, thermal expansion of the sample causes the tonnage to rise to about one metric ton. Additionally, the temperature of the sample rises from room temperature to between 1000°C - 1050°C. The sample’s temperature is kept in this range for five minutes and then cooled to about 600°C. Once the sample undergoes this first cooling stage, it is removed from the hot-press and allowed to cool to room temperature. This is followed by the removal from the graphite die. After removal from the die, the sample is taken to be polished with sand paper and machined with a diamond-blade saw into geometric shapes with straight edges so that the dimensions can be measured and the sample is prepared for testing.

3.3 Electrochemical Sample Testing

The samples were tested in a three-electrode configuration with a Gamry Reference 600 Potentiostat/Galvonstat/ZRA. The electrolyte used for testing is 1M potassium hydroxide (KOH). The scanning for test is 2 mV sec^{-1} . The linear sweep potentials were converted to the potential (V) versus reversible hydrogen electrode (RHE) using the Nernst equation [100]:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.0591\text{pH} + 0.098, \quad (11)$$

where $E_{\text{Hg/HgO}}$ is the readout of voltage from the potentiostat and the pH is approximately 14 for 1M KOH.

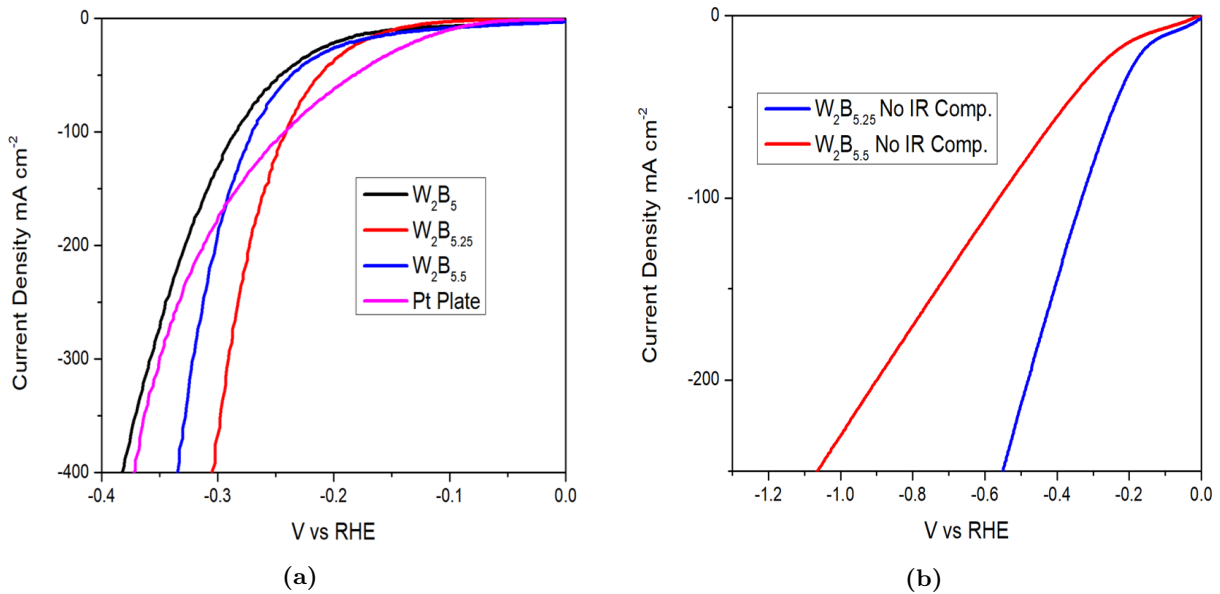


Figure 14: (a) Linear sweep voltammograms indicating the HER performance in relation to platinum plate with iR compensation with 1M of KOH as the electrolyte. (b) Uncompensated data for $W_2B_{5.25}$ and $W_2B_{5.5}$, two best performing catalysts. Test are in 1M KOH electrolyte.

Figure 14 summarizes the results of the analysis. In particular, the samples' performances with iR compensation is plotted in Figure 14a with their performances compared to Pt plate. The performances when the contact resistances between the samples and electrolyte is not compensated are shown in Figure 14b. From the samples, the composition of $W_2B_{5.25}$ showed the lowest

overpotential at current densities of 100 mA cm^{-2} or greater.

Table 4 shows the results of all of the samples for current densities of 10 and 100 mA cm^{-2} with and without iR compensation. Note that the Pt Plate and W_2B_5 were not analyzed without compensating for iR.

Table 4: The overpotentials for the catalysts' performances at current densities of -10 mA cm^{-2} and -100 mA cm^{-2} . The overpotentials for the for catalysts at -100 mA cm^{-2} with no iR compensation.

Sample	$j = -10 \text{ mA cm}^{-2}$ iR Compensated	$j = -100 \text{ mA cm}^{-2}$ iR Compensated	$j = -100 \text{ mA cm}^{-2}$ No iR Compensation
Pt Plate	100 mV	242 mV	N/A
W_2B_5	150 mV	285 mV	N/A
$\text{W}_2\text{B}_{5.25}$	119 mV	241 mV	326 mV
$\text{W}_2\text{B}_{5.5}$	150 mV	270 mV	563 mV

The Tafel slopes of the samples are given in Figure 15. The Pt plate shows the lowest slope of the compared samples. The lower Tafel slope is an indication that at lower current densities the Pt plate has lower onset potential.

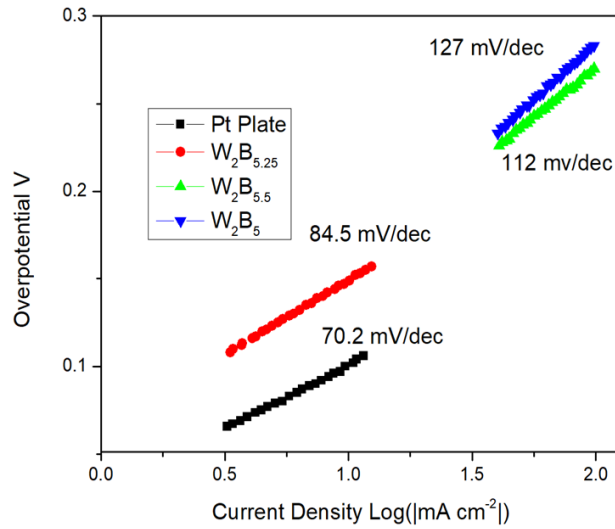


Figure 15: The Tafel slopes for the measured catalysts.

Figure 16 gives the stability test of the $\text{W}_2\text{B}_{5.25}$ sample in 1M of KOH over a 24 hour period. The stability test is a chronopotentiometry scan is that configured to measure at a current density

of 100 mA cm^{-2} . The stability test revealed that the difference in voltage changes only slightly in 24 hours; the voltage change was 6 mV from the second hour to the twenty-fourth hour. The stability test also revealed that once impurities were removed from the surface, the performance stabilized.

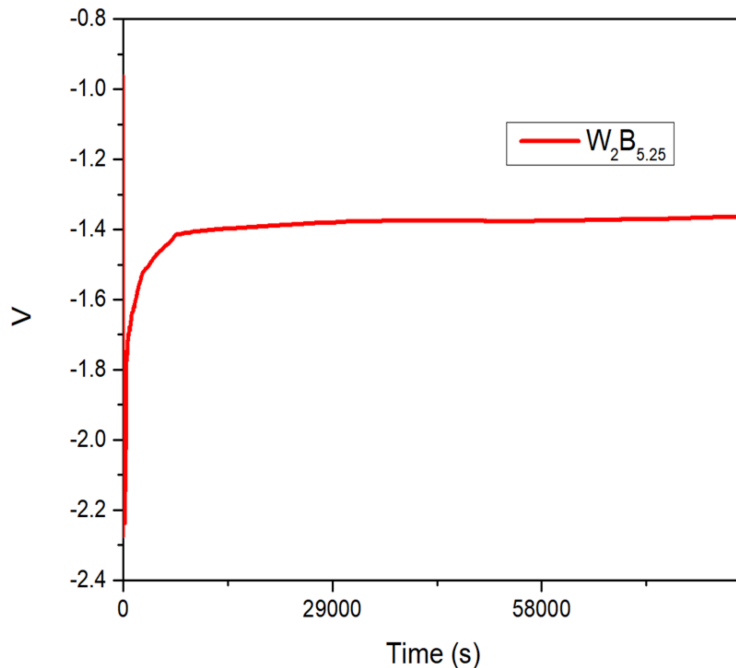


Figure 16: Long-term stability test for twenty-four hours for a current density 100 mA cm^{-2} .

3.4 Electrochemical Analysis

To gain insight into the internal workings of the samples, a series of tests (i.e. cyclic voltammetry (CV), resistivity analysis, and electrical impedance spectroscopy(EIS)) were carried out to understand the differences in performance. Figures 17a through Figures 17f show the CV curves of the three samples along with their corresponding “current densities versus scan rate” plots. To acquire the CV plots, cyclic voltammetry was done at declining scan rates in 1M of KOH. A measurement of current versus voltage was acquired and the geometric surface area of the sample was used to obtain the current densities.

To acquire the “current density versus scan rate” plots shown in Figure 17, the difference

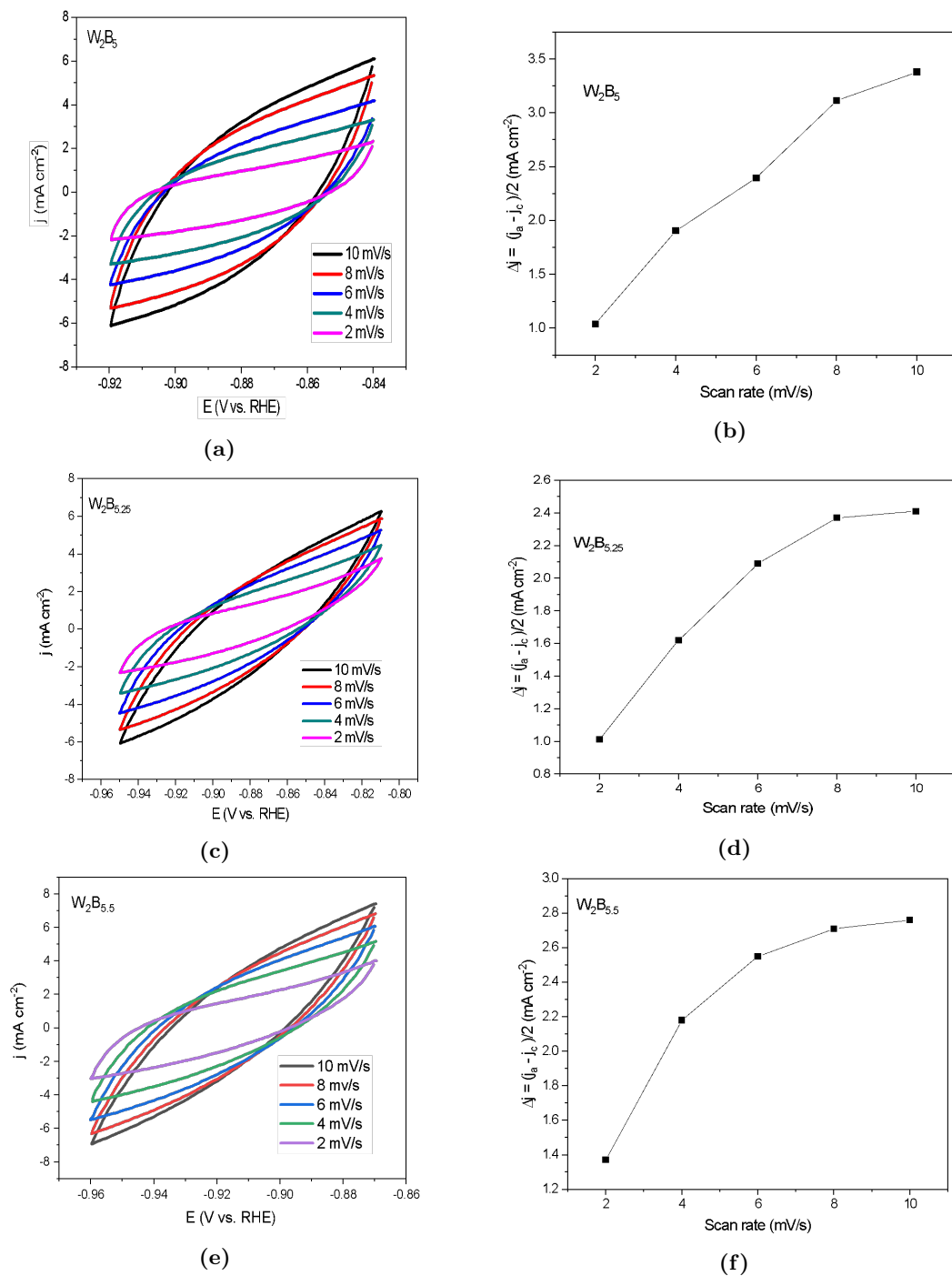


Figure 17: (a) CV curves for the W_2B_5 where the voltages range is between -0.92 V to -0.84 V. (b) W_2B_5 sample plot of the current density versus the scan rate. (c) CV curves for the $W_2B_{5.25}$ where the voltages range is between -0.95 V to -0.81 V. (d) $W_2B_{5.25}$ sample plot of the current density versus the scan rate. (e) CV curves for the $W_2B_{5.5}$ where the voltages range is between -0.96 V to -0.86 V. (f) $W_2B_{5.5}$ sample plot of the current density versus the scan rate.

between the anodic current density (j_a) and cathodic current density (j_c) were taken at the center of the CV curves and, subsequently, divided in half for the different scan rates. The j_a is the oxidation part of the curve which is the top part of the CV curve. The j_c is the reduction part of the curve which is the bottom part of the CV curve. From doing a linear fit of the of the current density versus scan rate plots, double-layer capacitance (C_{dl}) can be acquired. The resulting double-layer capacitance for each sample are given in Table 5. The W_2B_5 had the greatest C_{dl} , but its performance was the least of the samples in the HER process. To gain a greater insight into why certain samples performed better than others, subsequent tests would need to be performed to ascertain reasons.

Table 5: The double-layer capacitance can be used to acquire the electrochemical surface area (ECSA).

Sample	Double-Layer Capacitance [mF cm ⁻²]
W_2B_5	0.2946
$W_2B_{5.25}$	0.1774
$W_2B_{5.5}$	0.1654

Electrical impedance spectroscopy tests were done to acquire the charge transfer resistances (R_{ct}) and contact resistances with the solution (R_s). From the EIS tests and the resulting plots, $W_2B_{5.25}$ has found to yield the smallest impedance curve of three samples. A smaller impedance curves is indicative of a smaller R_{ct} . Furthermore, a smaller R_{ct} is indicative of better performance. Figure 18 gives the impedance curves of the three samples. Since the samples are bulk materials with flat geometric edges, an analogous and effective analysis that can be performed is to test the resistivities of the samples. To obtain this property, the samples were tested in a ULVAC-RIKO ZEM-3 machine and the resistivities of the samples were measured.

Table 6 shows the results of the resistivity tests. For all three samples the resistivities were quite low. This indicated that the samples are conductors. In addition, the resistivity values of the samples are in the neighborhood for what has been reported by others [101].

Active sites (N) and specific capacitance (C_p) measurements were done to see how the samples

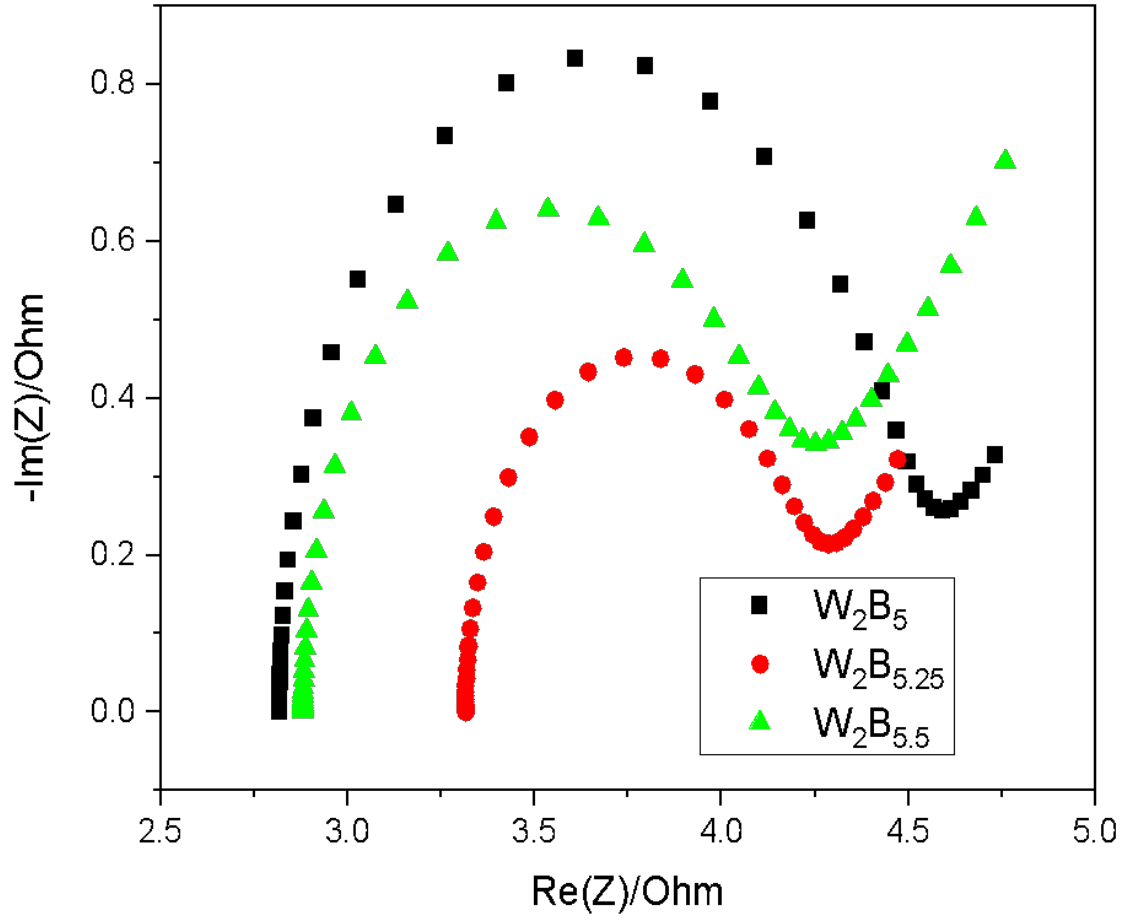


Figure 18: EIS plots of the impedance curves.

Table 6: The resistivity values of the samples

Sample	Resistivity ($\Omega \cdot \text{m}$)
W_2B_5	1.156×10^{-7}
$\text{W}_2\text{B}_{5.25}$	2.166×10^{-5}
$\text{W}_2\text{B}_{5.5}$	1.045×10^{-5}

compare to each other. To measure the active sites, CV curves of the samples, Figure 19, were measured in phosphate buffered saline (PBS) which has a pH of around seven. The area of the CV curves is then measured. With the area of the CV curve, one can use it to get the specific capacitance and the number of active sites of each sample. The areas of the CV curves are the charges (Q) of each sample, and is acquired using Equation 12. The scan rate of each sample was 50 mV/sec, and voltage range is -0.2 V to 0.6 V for each sample. The parameters were kept the same for all samples to ensure the conditions were the same for each sample and for continuity.

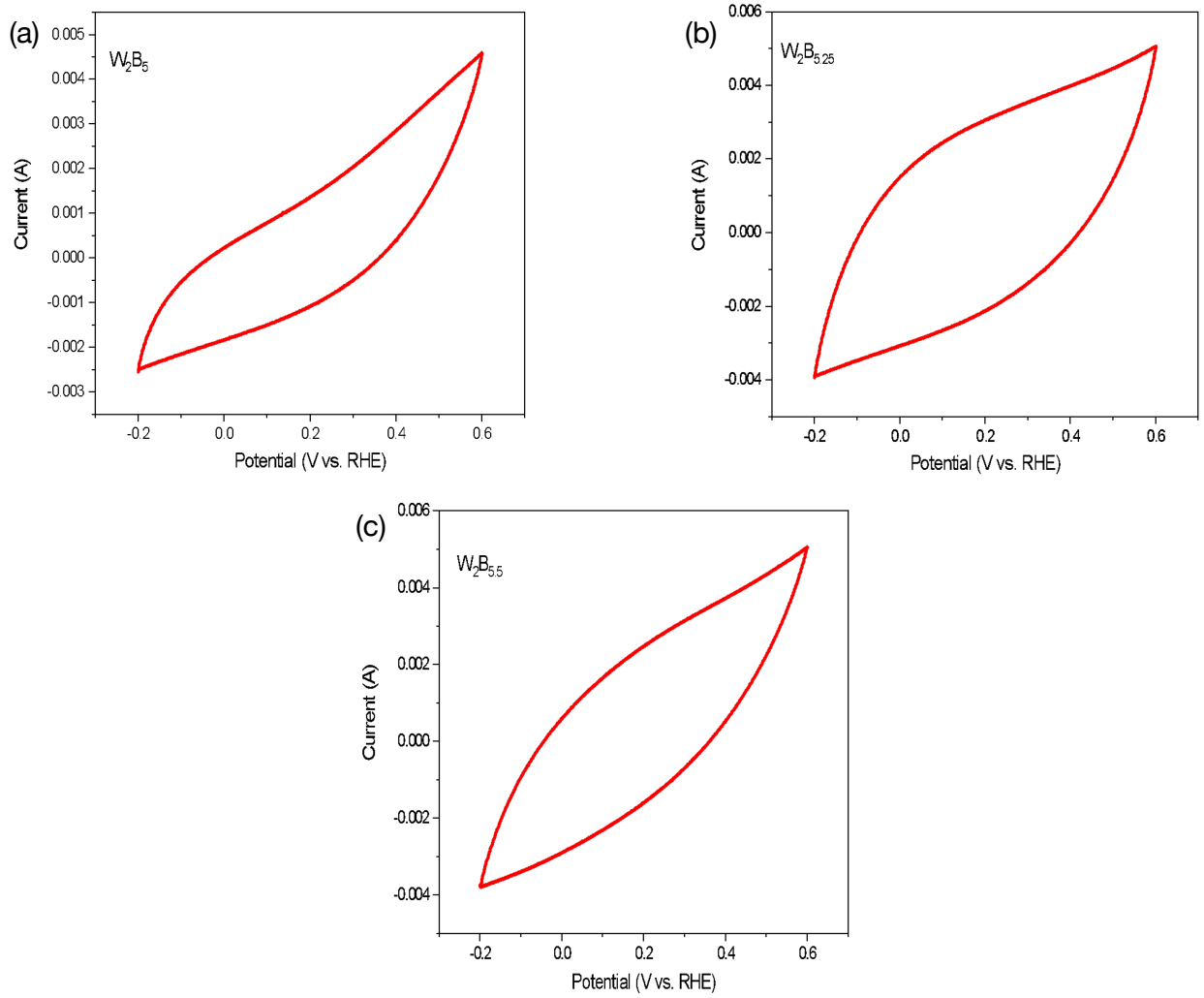


Figure 19: (a) CV curve of W_2B_5 in 1M of PBS. (b) CV curve of $W_2B_{5.25}$ in 1M PBS. (c) CV curve of $W_2B_{5.5}$ in 1M of PBS.

An explicit derivation of Q from the area of the CV curve is given below:

$$Q = \text{Area} = C_p m k \int_{V_1}^{V_2} -C_p m k \int_{V_2}^{V_1} dV = C_p m k [(V_2 - V_1) - (V_1 - V_2)] \quad (12)$$

$$Q = \text{Area} = \text{Area}_1 - \text{Area}_2 = 2(V_2 - V_1)C_p m k \quad (13)$$

$$C_p = \frac{Q}{2(V_2 - V_1)mk}. \quad (14)$$

In Equation 13, Area_1 represents all the area below the curve and Area_2 represents all the area below the CV curve that is not inside the CV curve. Subtracting these two areas will give the area inside the CV curve and therefore, the Q , where m is the mass of the sample and k is the scan rate. Re-arranging Equation 13 will give the C_p , Equation 14. The units of the area are given amperes seconds (A s) or 1 coulomb per volt (C/V) which is equivalent to 1 Farad (F), and C_p units are given Farads per gram (F/g). Results that are shown in Table 7 gives the charge and specific capacitance.

Table 7: The results are a from using Equations 12–14 and data from above tables and figures

Sample	Charge (Q) [A s]	Specific Capacitance (C_p) [F/g]
W ₂ B ₅	0.001584	0.08879
W ₂ B _{5.25}	0.003134	0.1688
W ₂ B _{5.5}	0.002375	0.1260

Another important measurement that can be taken is the number of active sites (N). The active sites calculation is very simple since the Q has already been ascertained. Equation 6a is used for the HER active site calculation. Using the known values, the calculated number of active sites results are given in Table 8. The W₂B_{5.25} sample has the greatest number of actives sites which is correlative to its performance in having the lowest overpotential of the measured samples.

Table 8: Active site calculation from using 6a.

Sample	Active Sites (N) [mol]
W_2B_5	8.2×10^{-9}
$\text{W}_2\text{B}_{5.25}$	1.6×10^{-8}
$\text{W}_2\text{B}_{5.5}$	1.2×10^{-8}

3.5 Sample Analysis

The physical characteristics can give insight into how a material will perform under HER conditions. XRD analysis was done on the three samples to find out the atomic structure of samples. Figure 20 shows the XRD results of the three samples. The indexing below is for W_2B_5 , and given where the peaks are, they are all closely related to the compound. The peaks for the samples are within the neighborhood of results of tungsten borides that has been reported by others [102,103].

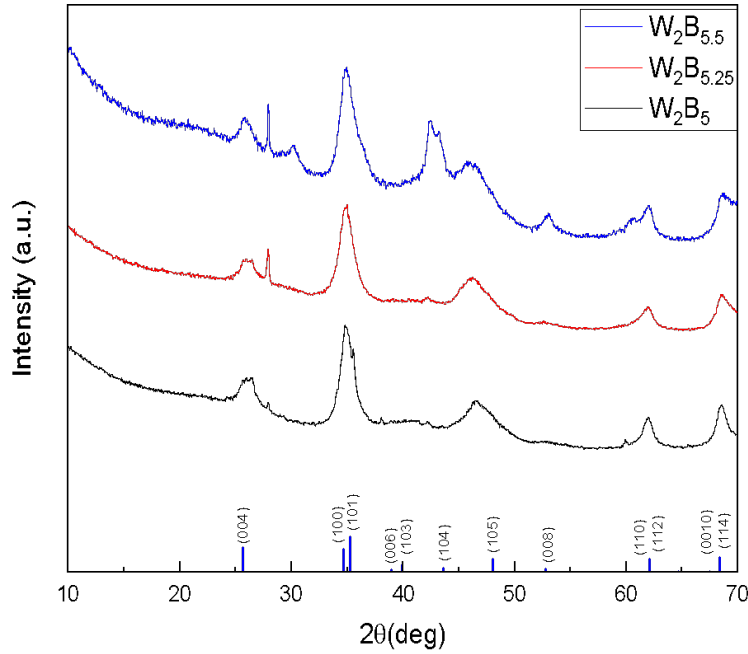


Figure 20: XRD for the samples.

The $\text{W}_2\text{B}_{5.25}$ was the best performing sample, and XRD patterns of the other samples show they are closely related; given those facts, it is the only sample that was used for further analysis.

XPS testing was done on the $W_2B_{5.25}$ sample to ascertain the elemental phases of the sample before and after testing and the results are shown in Figure 21. W has energies of 31.8 eV and 33.9 eV which are the metallic phases [104]. The bonding energy of 31.8 eV could also be W-B bonding based on what some researchers have reported [105]. The metallic oxide phases have energies of 35.6 eV and 38.1 eV. The oxide phases are similar to what others have reported [106]. Figure 21(b) gives the binding energies for the B before and after testing. Boron has the binding energies of 186.1 eV and 189.1 eV, and the boron oxides have the energies 191.6 eV and 192.7 eV. The binding energies of the B and B-O are consistent with other reported data [107, 108].

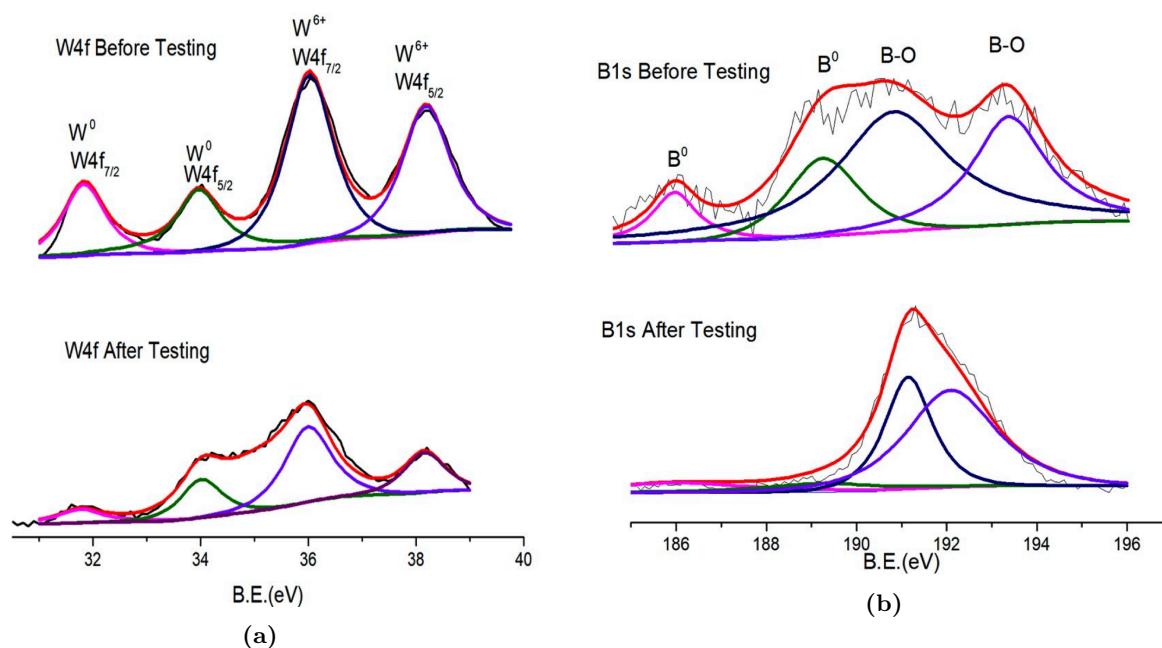


Figure 21: (a) The top plot is before long-term stability testing of $W_2B_{5.25}$, and bottom plot is the $W_2B_{5.25}$ after long-term stability testing. (b) The top plot is before long-term stability testing of $W_2B_{5.25}$, and bottom plot is the $W_2B_{5.25}$ after long-term stability testing.

Another surface test that was done on the $W_2B_{5.25}$ was EDS. The EDS tests were done with the help of a EDAX TEAM EDS system. During EDS testing, sample that were not electrochemically tested were used. This was done to avoid introducing additional elements. To further ensure this, the sample was cleaned in a sonicated bath of ethanol for about five minutes and allowed to dry in a drying oven at a of temperature of 80°C for twenty-four hours. Figure 22 shows the selected

area in the rectangle where the EDS was measured for the $W_2B_{5.25}$. The area was selected based on the contrasts of its morphologies. Due to the working distance that is required to do EDS, the image is not of high-resolution.

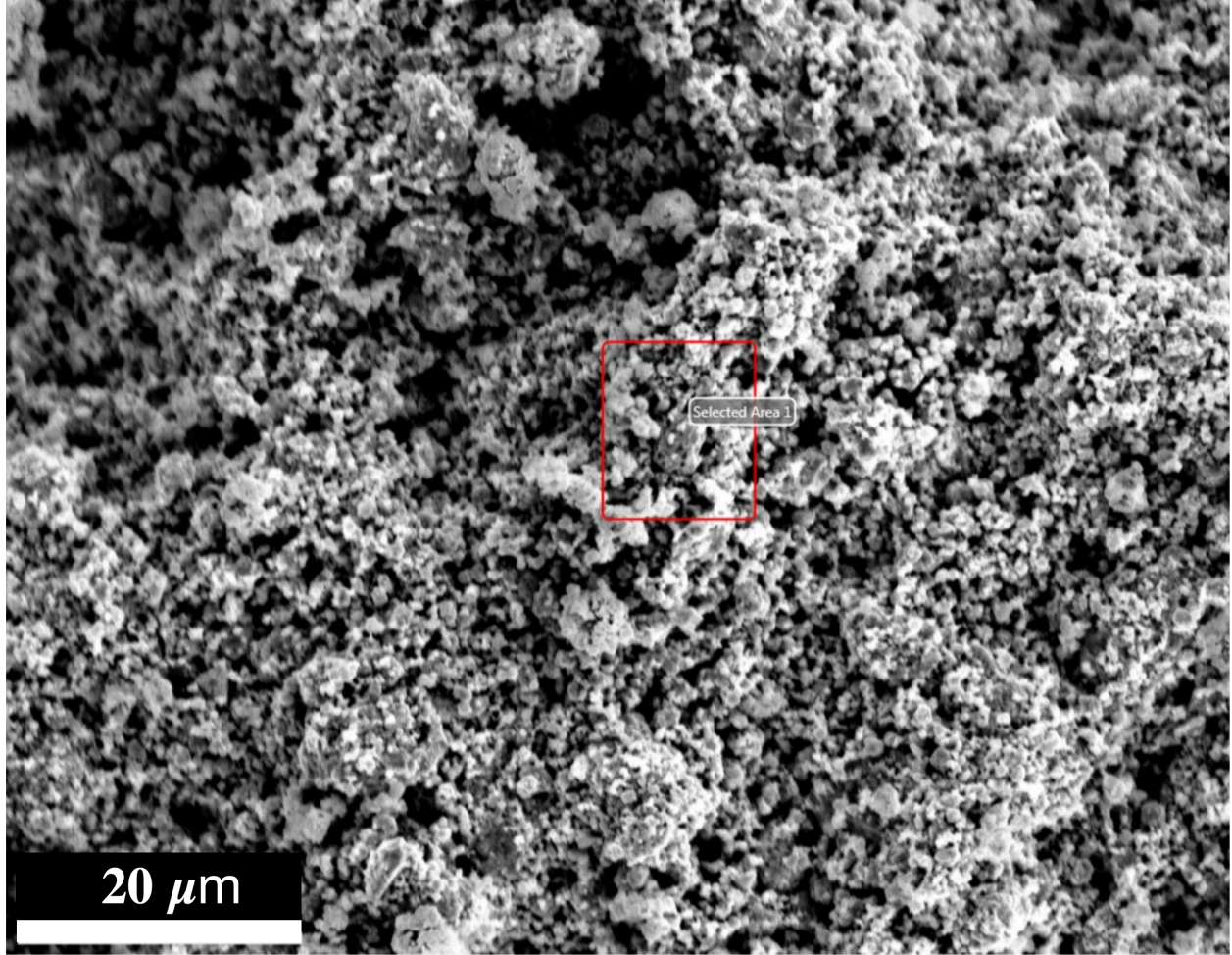


Figure 22: SEM image of $W_2B_{5.25}$ before testing at a working distance of 15 mm for EDS. A rectangle encloses the region where the EDS was measured.

Figure 23 shows the mapping overlays of elements of $W_2B_{5.25}$ before testing of elements B and W. Elements B and W are the primary elements of the $W_2B_{5.25}$ sample, and that is the reason why they were selected to be measured. Table 9 represents the weights and atomic percentages of $W_2B_{5.25}$ before testing of the selected area. The weight and atomic percentage represent the atomic weight and the number of atoms, respectively.

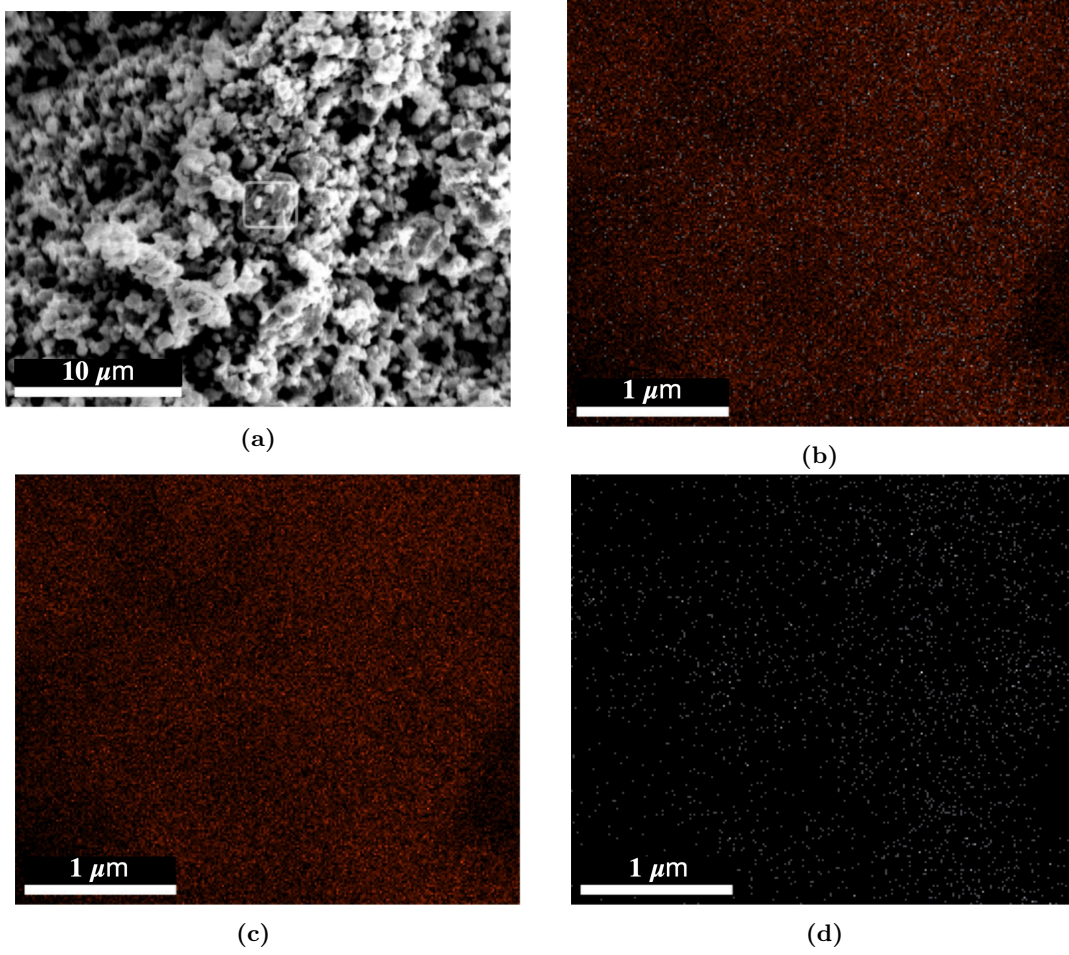


Figure 23: The (a) image is the area of the sample that was mapped. The (b) image is the mapping overlay of the elements in $W_2B_{5.25}$ before testing. $W_2B_{5.25}$ before testing. Image (c) is the tungsten. Image (d) is the boron.

Table 9: Area EDS on sample $W_2B_{5.25}$ before testing.

Element	Weight Percentage	Atomic Percentage
W	11.74	62.69
B	88.26	37.31

The sum spectrum of the $W_2B_{5.25}$ sample before testing is shown in Figure 24. The resulting peaks, which characterize the elements of the sample, indicate the presence of W and B. Boron is near the lower-limit of detection of the EDS method, which is not effective for light elements. On the other hand, the presence of W is clearly indicated by a prominent peak at its characteristic energy.

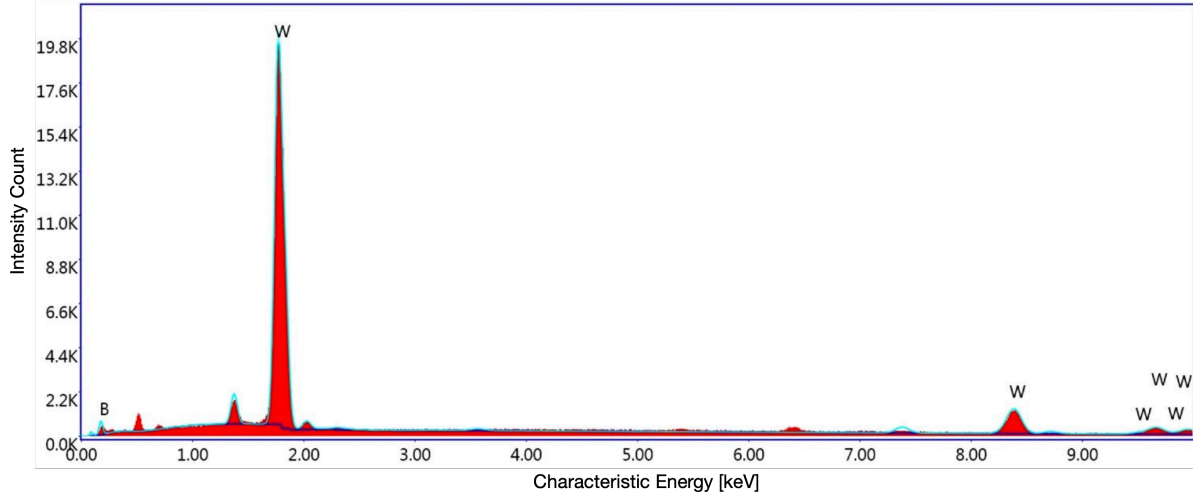


Figure 24: Sum spectrum of the mapping. Of the $W_2B_{5.25}$ sample before testing. Vertical axis represents the intensity count and horizontal axis in keV each element's characteristic energy.

EDS for the $W_2B_{5.25}$ sample was done after the sample was tested in an electrolyte of 1M of KOH. Figure 25 shows the area where the EDS measurements were taken inside the rectangle. Table 10 gives the weight and atomic percentages after testing. Figure 26 shows the area in the rectangle where the mapping was done. The area in the rectangle was chosen as a way shorten the duration of the mapping time. Figure 26 also shows the individual distribution of each element. Figure 27 shows the sum spectrum of the mapping. Other elements were detected which are introduced from the testing process.

3.6 Sample Morphology

To understand the surface morphology of the samples, scanning electron microscopy (SEM) analysis was done on the samples. The best performing sample, $W_2B_{5.25}$, was analyzed for further analysis to

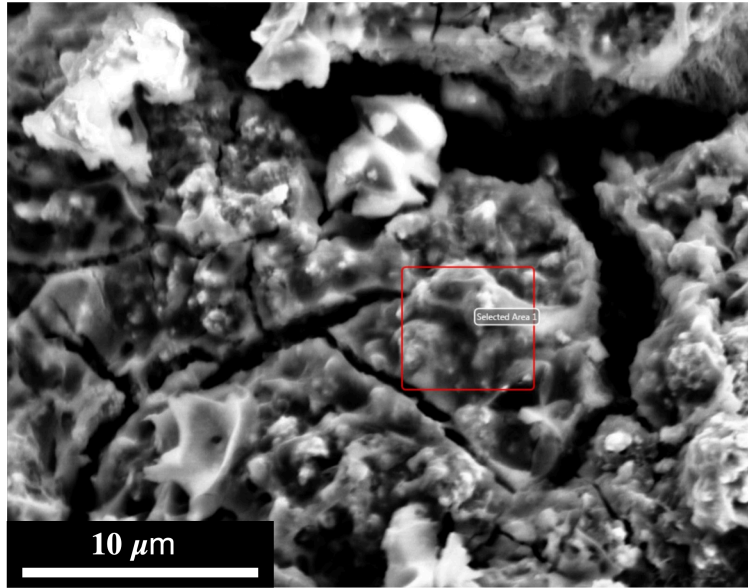


Figure 25: SEM image of $W_2B_{5.25}$ after testing at a working distance of 15mm for EDS.

Table 10: Area of EDS on sample $W_2B_{5.25}$ after testing.

Element	Weight Percentage	Atomic Percentage
W	12.14	51.29
B	87.86	48.7

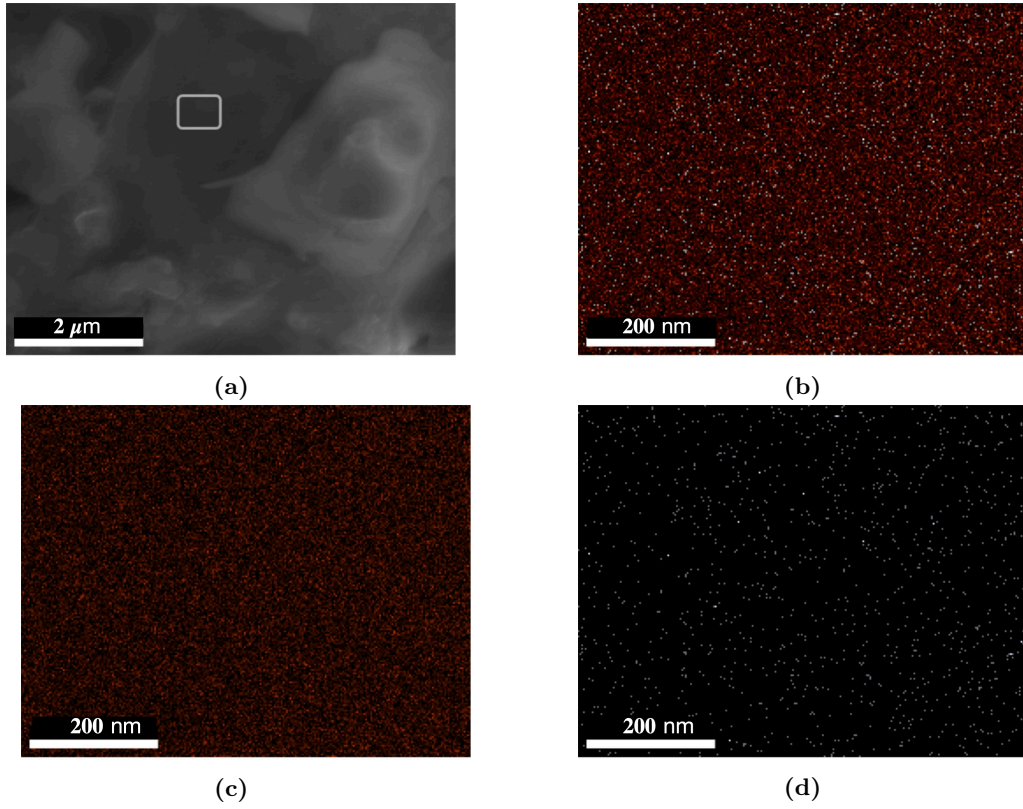


Figure 26: The (a) image is the area of the sample that was mapped in the rectangle. The (b) image is the mapping overlay of the elements in $W_2B_{5.25}$ after testing. $W_2B_{5.25}$ after testing. Image (c) is the boron. Image (d) is the tungsten.

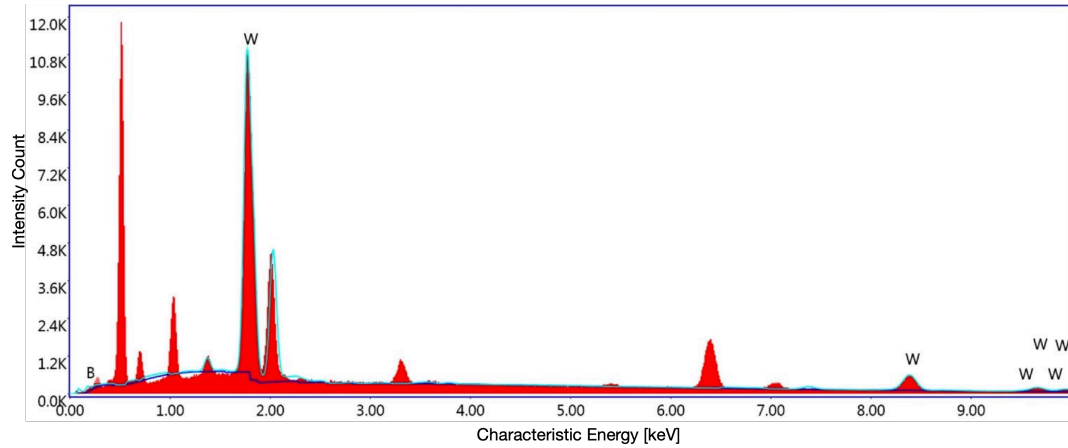


Figure 27: Sum spectrum of the mapping. Of the $W_2B_{5.25}$ sample after testing. Vertical axis represents the intensity count and horizontal axis in keV each element's characteristic energy.

understand how the surface morphology before and after testing. Figures 28a-28b and Figures 28c-28d show the sample after hot-press and after machining, respectively. Figure 29 shows the SEM images before testing. On the surface of the $W_2B_{5.25}$, the surface is very porous and rough. This porosity contributes the performance of the sample. Figure 30 shows the SEM images after testing. On the surface of the $W_2B_{5.25}$ after testing, the surface is smoother and has changed significantly. This change in morphology strongly suggests that the sample has great number of reactive activities occurring on its surface.

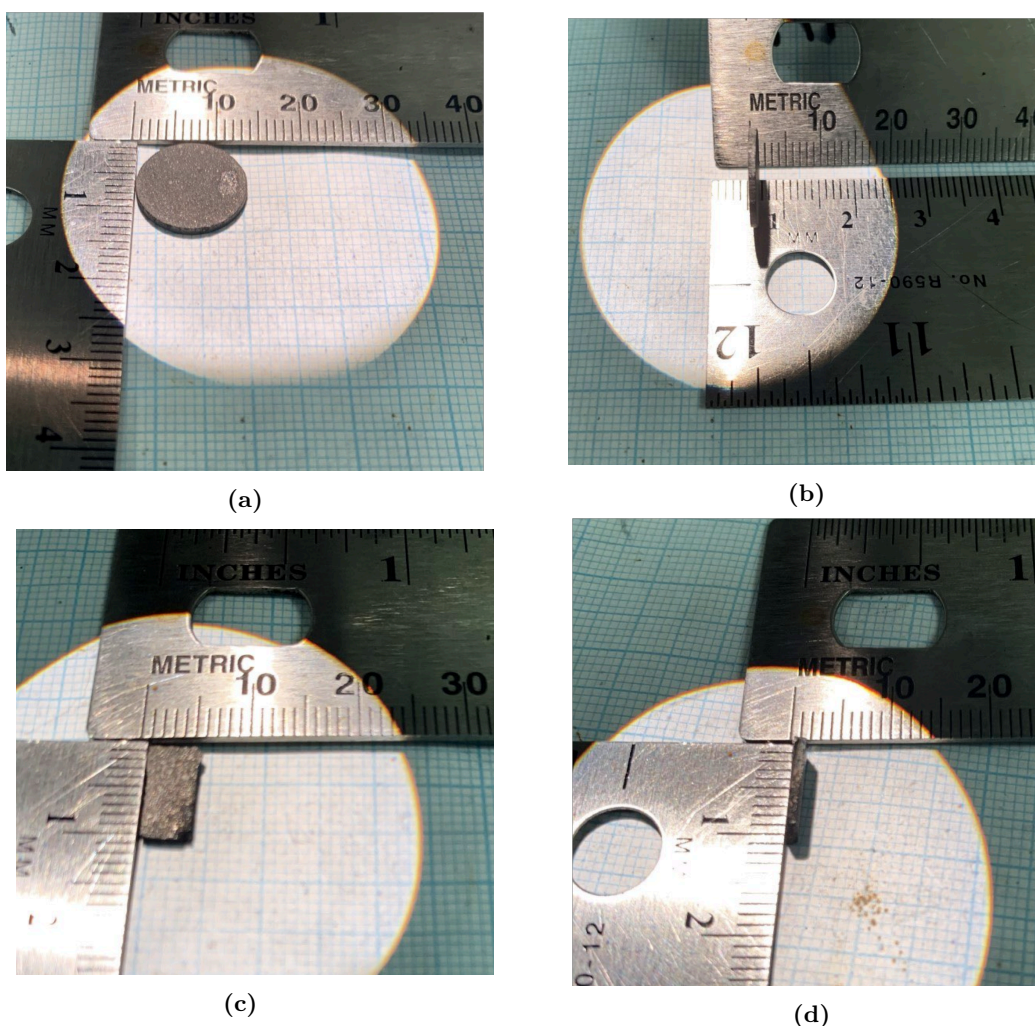


Figure 28: (a) Image of a diameter of a hot-pressed sample. (b) Image of a gauge of a hot-pressed sample. (c) Image of the length and width of a machined sample. (d) Image of the gauge of a machined sample.

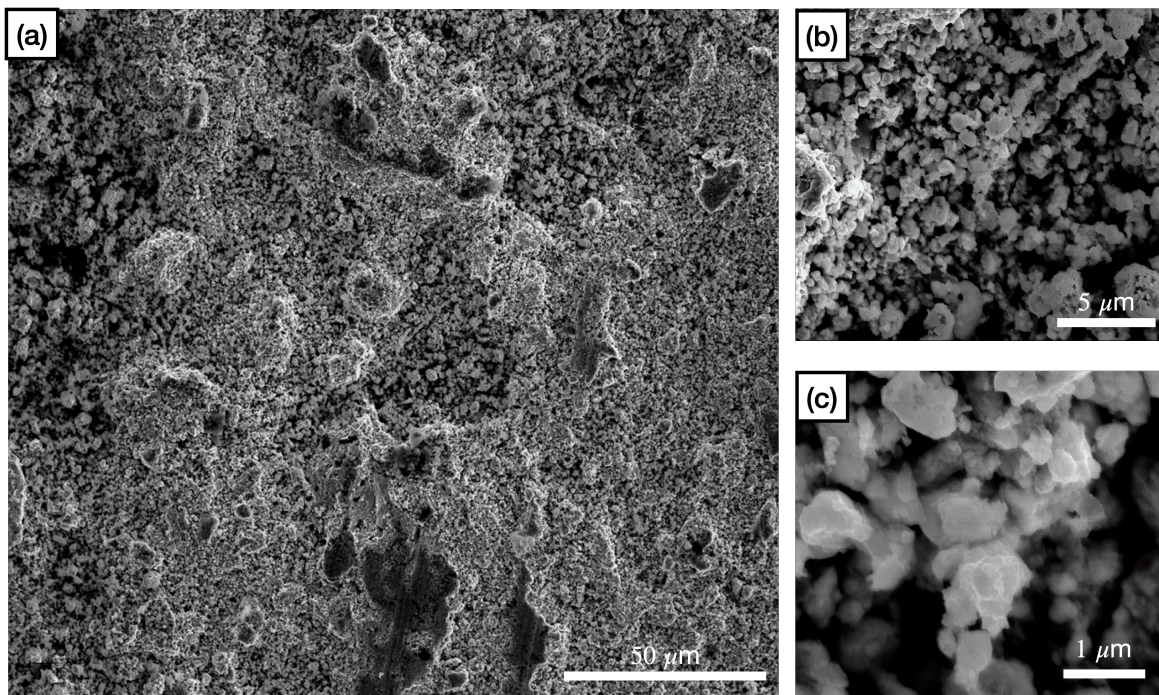


Figure 29: $W_2B_{5.25}$ sample at various magnifications before testing.

3.7 Summary

Tungsten borides for the use of hydrogen evolution reaction has been shown to have very low overpotentials and can be comparable to platinum plate at very high current densities. The synthesis of the tungsten and boron by others have been done through chemical synthesis and substrate deposition and the performance has only been reported at very low current densities. The ball-milling and hot-pressing techniques are ideal for the synthesis of tungsten and boron because they generate the chemical phases of the tungsten boron compounds. Table 11 gives a comparison $W_2B_{5.25}$ and Pt plate performances to other reported metal borides and Table 12 gives the reported performances of some the best reported HER catalyst. The overpotentials that are given are for low current densities because not all samples have data reported for high current densities. When comparing these catalysts to the tungsten borides, it needs to be considered that the other catalyst are supported on a substrate which can greatly increase the surface area and improve the performance, where the tungsten borides in this work have no such support. The tungsten boride samples made

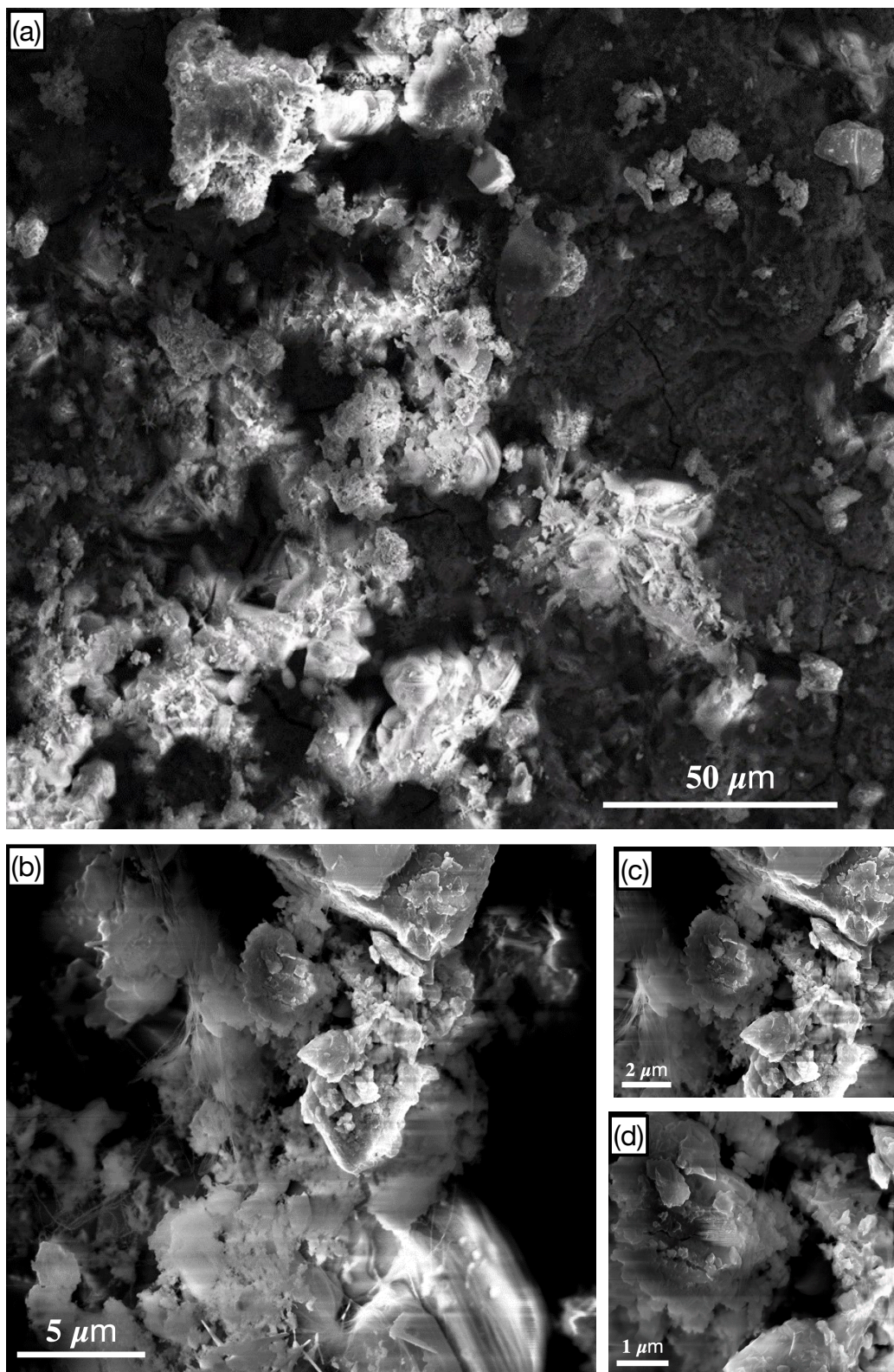


Figure 30: $W_2B_{5.25}$ sample at various magnifications after testing.

for this work also have more geometric surfaces sides (length, width, and gauge) because they are bulk samples. The larger geometric surfaces can decrease the performance when compared to other catalysts supported on substrates.

From all the test that were performed, some conclusions can be made about tungsten borides to explain how and why they work as HER catalysts. The low resistivity of the samples are indicative of the low electrical resistances of the samples. Of the three samples, the $W_2B_{5.25}$ has the lowest charge transfer resistance which is reflected in the fact that it has the best performance. The $W_2B_{5.25}$ also had the greatest number of active sites. With greatest number of active sites of the samples, $W_2B_{5.25}$ can have more activity on its surface to facilitate reactions, and this fact was demonstrated in its better performance than the other samples.

Table 11: Comparison of Pt plate and $W_2B_{5.25}$ with other metal borides in 1M KOH.

Sample	Support	Electrolyte	Overpotential	Reference
Mo-B	Carbon Paste	1M KOH	$\eta_{20} = 240$	[109]
Ni-B	Glass Carbon	1M KOH	$\eta_{20} = 194$	[110]
Ni-B _x film	Cu Foil	1M KOH	$\eta_{10} = 135$	[111]
Co ₂ B-CoSe ₂	Glass Carbon	1M KOH	$\eta_{10} = 300$	[112]
Co-W-B	Ni Foam	1M KOH	$\eta_{10} = 98$	[113]
FeB ₂	Glass Carbon	1M KOH	$\eta_{10} = 61$	[114]
Co-B	Ni Foam	1M KOH	$\eta_{10} = 110$	[108]
Co-B Nanosheets	Ni Foam	1M KOH	$\eta_{10} = 42$	[115]
Co-Ni-B	Carbon Cloth	1M KOH	$\eta_{10} = 80$	[116]
Ni _x B-f-MWCNT	Glass Carbon	1M KOH	$\eta_{10} = 116$	[117]
Pt Plate	N/A	1M KOH	$\eta_{10} = 100$	This Work
$W_2B_{5.25}$	N/A	1M KOH	$\eta_{10} = 119$	This Work

Table 12: The performances of other HER electrocatalysts with reported low overpotentials.

Sample	Support	Electrolyte	Overpotential	Reference
N@MoPC _x	Carbon Cloth	1M KOH	$\eta_{10} = 139$	[58]
NiMo	Ni Foam	1M KOH	$\eta_{10} = 18$	[118]
Cu _x Ni _{4-x} N/NF	Ni Foam	1M KOH	$\eta_{10} = 12$	[119]
NiMo ₃ S ₄ /Ni ₃ S ₂	Ni Foam	1M KOH	$\eta_{10} = 23$	[46]
Ni ₃ N-NiMoN	Ni Foam	1M KOH	$\eta_{10} = 31$	[120]
Ni ₅ P ₄	Ti Foil	1M KOH	$\eta_{10} = 47$	[121]
Ni ₃ S ₂	Ni Foam	1M KOH	$\eta_{10} = 48$	[122]
SN-MoP/G	Graphene	1M KOH	$\eta_{10} = 49$	[123]
NiCo ₂ P _x NW	Carbon Felt	1M KOH	$\eta_{10} = 58$	[124]
CoP NWs/CoO _x	Carbon Cloth	1M KOH	$\eta_{10} = 100$	[125]

4 OXYGEN EVOLUTION REACTION SAMPLES

4.1 Introduction

The thermodynamic threshold to split water into H_2 and O_2 is 1.23 V, but thermodynamic barriers require additional potential energy, and therefore to facilitate the kinetic process, efficient catalysts are required to lower the thermodynamic barriers [126]. The multiple-electron steps of the OER process is reason for the thermodynamic barriers [127]. IrO_2 and RuO_2 are the ideal catalysts material, but their rarity and high cost hinder their ubiquitous applications [128]. Progress has been made to demonstrate that there are non-noble metal alternatives that will outperform noble metals in alkaline electrolyte [38]. The search for alternatives to non-noble metal alternatives is not only a requirement for massive-scale water splitting; but given the success in the discovery of non-noble alternatives, it is research that needs to be expanded.

Metal borides are an area of research where the performances of oxygen evolution reaction (OER) catalysts have been limited to very high overpotentials at very low current densities [129]. The best OER performances so far reported when tungsten (W) and boron (B) are used as an electrocatalyst is moderate [113]. The synthesis methods of metal borides have been achieved through such techniques as electroless plating [130] or hydrothermal methods [131], where B sources are sodium borohydride ($NaBH_4$) [132] or Potassium tetraborate ($K_2B_4O_7$) [133]. With the use of use of such chemicals, the B manipulation is much more difficult to control and determine how B content facilitates the reaction. To optimize the performances the of electrocatalysts, it is essential that each element content be manipulated at the molar scale.

An alternative method to synthesize metal borides is with ball-milling and hot-pressing [134]. With precursors of W powder and B crystals, the molar ratios can be controlled and determined how each element contributes to the reaction. Based on phase diagrams, tungsten borides have only a few stable phases [135]. The stability phases of W and B are dependent on their enthalpies at a given pressure [136]. Based on theoretical calculations, WB_4 is predicted to have excellent transport properties; but given its positive enthalpy, it is not phase stable. WB_4 is also very difficult

to synthesize and requires tungsten-boron ratios of 1:9 in the arc-melting process [137]. The next phase closest in enthalpy to WB_4 is W_2B_5 .

4.2 Material Synthesis

A ball-milled and hot-pressed sample of W_2B_5 is crushed with a mortar and pedestal into a fine powder. Other compositions such as $W_2B_{5.25}$ and $W_2B_{5.5}$ were also crushed into powder. A .150 ml of nafion is mixed with 1 ml of de-ionized water and 1.35 ml of ethanol. The nafion is a bonding agent and the de-ionized water and ethanol are used to help disperse the nafion onto a substrate. At this point, the fine powder combined with nafion, de-ionized water, and ethanol. The combined mixture is then mixed in a sonicated bath for about one hour in thirty-minute intervals. The thirty-minute intervals are done as to ensure that mixture does not overheat. From here, the mixture is now ready to be applied to a nickel (Ni) foam substrate. The Ni foam is immersed into the mixture for about ten seconds and is then ready to be placed into a tube furnace.

The tube furnace is used to heat the mixture and deposit it onto the substrate and ensure that it bonds to the substrate. Before going into the tube furnace, the samples are placed on a cradle as to assist in the insertion into the tube furnace. While the samples are on the cradle, the samples are inserted into the tube furnace and placed in the middle. At this point, if no other chemicals are going to be deposited, the tube is sealed. Argon (Ar) gas is pumped through the tube from holes in the seal. The Ar purges the tube and ensures that an inert environment is created. While in the inert environment, the furnace is heated to a temperature of 120°C for sixty minutes. This temperature is sufficient to allow the mixture to bond to the substrate. If additional elements are used, higher temperatures may be required. Phosphorous (P) was deposited on a set of samples. The temperature that is used to vaporize the P is 420°C and the time is sixty minutes. To get the P deposited onto the substrate, the P is placed up tube and is blown on the sample, which are down tube, by the Ar gas. As the P vaporizes, it is deposited onto the samples. After the samples have cooled to room temperature, they are removed from the tube furnace, and the samples are ready to be tested.

4.3 Electrochemical Sample Testing and Results

The samples were tested in a three-electrode configuration, where carbon (C) is the counter electrode and mercury/mercury oxide (Hg/HgO) is the reference electrode, where the electrolyte is potassium hydroxide (KOH). The samples are the working electrodes and the samples are immersed into the electrolyte. To measure the current density, the samples' geometric surface area is measured. For the geometric surface area measurement, the length, width, and gauge of the sample is factored into the measurement. Normally, gauge is not considered when a sample is on a substrate. But given that the gauge is thick, it is factored into the measurements. The linear sweep voltammetry (LSV) test is a measurement of voltage versus current. The LSV output data is then converted to the reversible hydrogen electrode (RHE). Via the Nernst equation, the OER performances of the samples can be derived. The Nernst equation is derived from the Gibbs' free energy equation. The Nernst equation for Hg/HgO [138]:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + \frac{RT}{nF} + E_{\text{Hg/HgO}}^0 \quad (15a)$$

$$= E_{\text{Hg/HgO}} + \frac{RT}{nF} \log_e \log_{10}(q) + E_{\text{Hg/HgO}}^0 \quad (15b)$$

$$= E_{\text{Hg/HgO}} + \frac{RT}{nF} (2.303) \log_{10}(q) + E_{\text{Hg/HgO}}^0 \quad (15c)$$

$$= E_{\text{Hg/HgO}} + 0.598pH + E_{\text{Hg/HgO}}^0. \quad (15d)$$

In Equation 15a is the read out from the potentiostat, R is the universal gas constant, n is the number of electrons per reaction which is one, T is the temperature with a value of 298.15 K, F is Faraday's constant, q is the concentration quotient, and $E_{\text{Hg/HgO}}^0$ is the equilibrium electrode potential [139] with a value of 0.098 V. In Equation 15b, $\ln(q)$ can be converted to logarithm base ten, and in Equation 15c, $\ln(10)$ is 2.303. In Equation 15d, $\log(q)$ can be converted into the pH of the electrolyte. Here the value of E_{RHE} is added to 1.23 V.

The LSV curves for the samples are given in Figure 31. Table 13 gives the samples' overpotentials for the given current densities. $\text{W}_2\text{B}_{5.25}/\text{NF}$ has the lowest overpotentials of the three

samples. The lowest overpotentials of $W_2B_{5.25}/NF$ is reflected in the lowest Tafel slopes, too, as shown in Figure 32. Figure 33 is the iR compensated LSV performance of the P boosted tungsten borides. Table 14 gives the performances of the P boosted tungsten borides at certain current densities, and $W_2B_5P_x/NF$ had the lowest overpotential. Figure 34 gives the Tafel slopes of the P boosted tungsten borides and $W_2B_5P_x/NF$ had the lowest slope which correlates to its low overpotential in comparison to the other tested samples. Figure 35 shows a twenty-four-hour OER test of $W_2B_5P_x/NF$ at a current density of 100 mA cm^{-2} . The first fifteen hours of the test show variances, thereafter, the performance stabilizes.

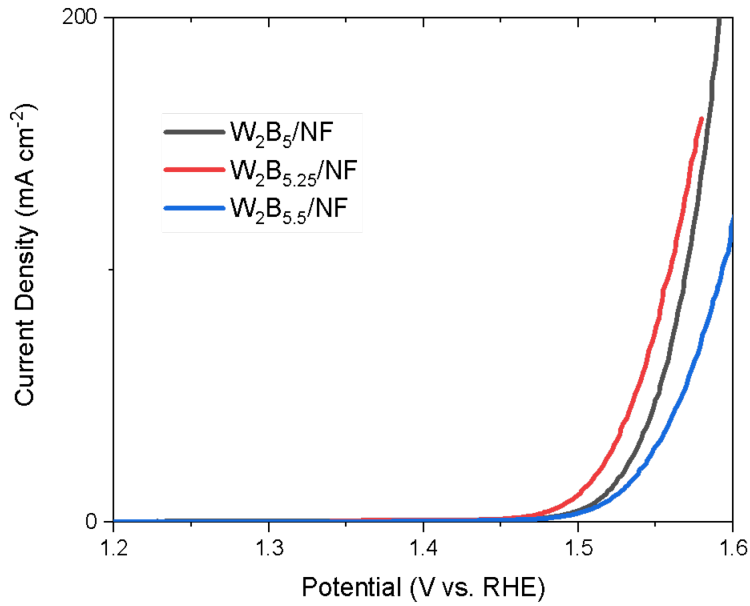


Figure 31: Tungsten borides on Ni foam iR compensated samples.

Table 13: The overpotentials for the catalysts' performances at current densities of 10 mA cm^{-2} and 100 mA cm^{-2} . The overpotentials for the for catalysts at 100 mA cm^{-2} with no iR compensation.

Sample	$j = 10 \text{ mA cm}^{-2}$	$j = 100 \text{ mA cm}^{-2}$
W_2B_5/NF	280 mV	340 mV
$W_2B_{5.25}/NF$	260 mV	320 mV
$W_2B_{5.5}/NF$	290 mV	360 mV

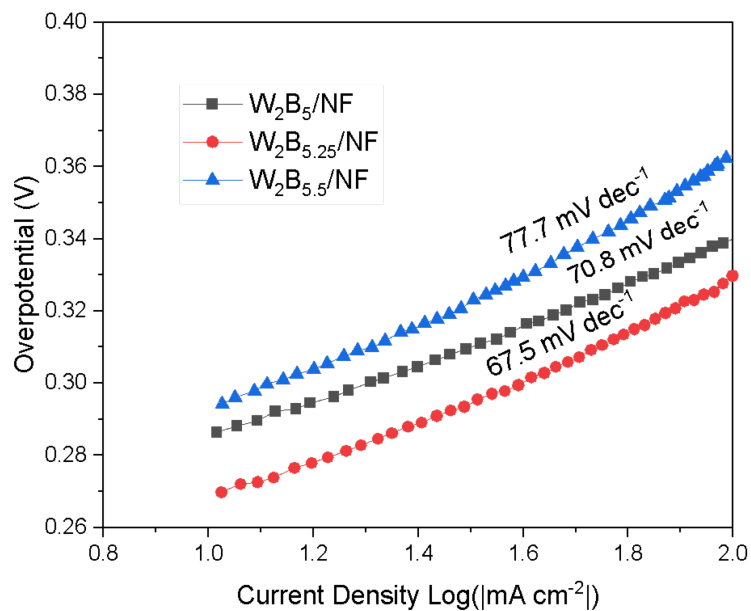


Figure 32: Tafel slopes of the tungsten borides.

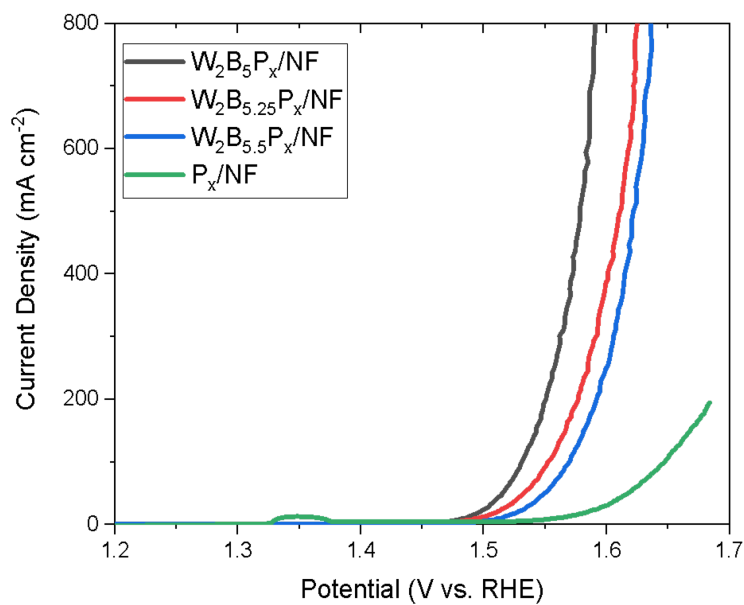


Figure 33: P boosted tungsten borides on Ni foam LSV curves with iR compensation.

Table 14: The overpotentials for the catalysts' performances at current densities of 10 mA cm^{-2} and 100 mA cm^{-2} . The overpotentials for the for catalysts at 100 mA cm^{-2} with no iR compensation.

Sample	$j = 10 \text{ mA cm}^{-2}$	$j = 100 \text{ mA cm}^{-2}$	$j = 500 \text{ mA cm}^{-2}$
$\text{W}_2\text{B}_5\text{P}_x/\text{NF}$	250 mV	300 mV	340 mV
$\text{W}_2\text{B}_{5.25}\text{P}_x/\text{NF}$	260 mV	320 mV	380 mV
$\text{W}_2\text{B}_{5.5}\text{P}_x/\text{NF}$	280 mV	340 mV	390 mV
P_x/NF	330 mV	410 mV	N/A

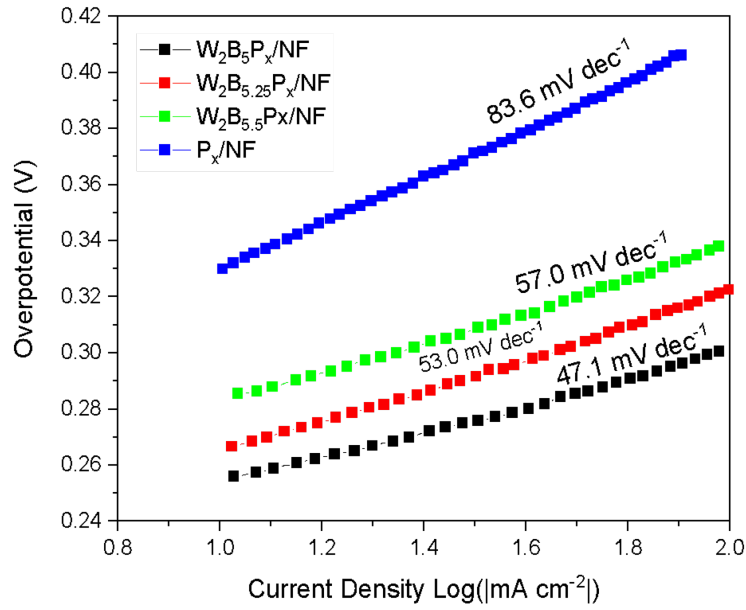


Figure 34: Tafel slopes of the P boosted tungsten borides on Ni foam.

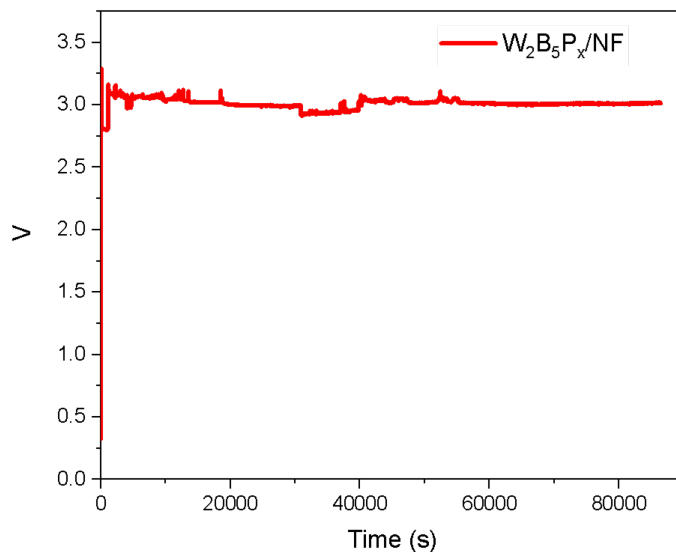


Figure 35: Twenty-four-hour test of $W_2B_5P_x/NF$ at a current density of 100 mA cm^{-2} .

4.4 Electrochemical Analysis

Cyclic Voltammetry (CV) was done on the samples to determine their double-layer capacitances (C_{dl}). Figures 36a, 36c, and 36e give the CV curves of the samples at different scan rates in 1M KOH. Figures 36b, 36d, and 36f give the plot of the anodic current density (j_a) and cathodic current density (j_c), where the difference is taken between them and is halved. The j_a and j_c are measured from the center of the CV curve. From the doing a linear fit, the C_{dl} is acquired, and the results of the linear fits are shown in Table 15 with $W_2B_{5.25}P_x/NF$ having the highest C_{dl} .

Table 15: The results are a from using Equations 12–14 and data from above tables and figures

Sample	Double-Layer Capacitance (C_{dl}) [mF cm^{-2}]
$W_2B_5P_x/NF$	.000430
$W_2B_{5.25}P_x/NF$	.00114
$W_2B_{5.55}P_x/NF$	.000804

Another test that was done is electrical impedance spectroscopy (EIS). EIS test can give the charge transfer resistances (R_{ct}) of the samples. The results of the EIS are shown in Figure 37.

The EIS tests indicate that $W_2B_5P_x/NF$ has the lowest R_{ct} . The EIS plots are a set of impedance curves. In the figure, the width of the curves give the R_{ct} , whereas the left side of the curves give the resistances of the solution (R_s).

The active sites of the samples were calculated as part of the internal analysis. Figures 38a, 38b, and 38c are CV curves of the samples in 1M of phosphate buffered saline (PBS). PBS has a pH of about seven. The CV curves were conducted at a scan rate of 50 mV/s. The area of the CV curve is integrated to acquire the area which is the charge (Q), and from the Q , the specific capacitance (C_p) can also be acquired. Table 16 gives the results for Q and C_p . With knowing the Q , one can also acquire the number of actives sites. Table 17 gives the active sites results, and it shows that $W_2B_{5.25}P_x/NF$ has greatest number of active sites.

Table 16: Charge and specific capacitance of the samples.

Sample	Charge (Q) [A s]	Specific Capacitance (C_p) [F/g]
$W_2B_5P_x/NF$	.000383	.0127
$W_2B_{5.25}P_x/NF$	.000141	.0469
$W_2B_{5.55}P_x/NF$	.000680	.0311

Table 17: Active site calculation from using 6b.

Sample	Active Sites (N) [mol]
$W_2B_5P_x$	9.19×10^{-10}
$W_2B_{5.25}P_x$	4.0×10^{-9}
$W_2B_{5.5}P_x$	2.0×10^{-9}

4.5 Sample Analysis

To ascertain the chemical composition of the samples, X-ray diffraction (XRD) was attempted, but it was abandoned. XRD could not detect the P that was deposited on the Ni foam. The reason for this is because of the detection limits of XRD. If the material is in very low concentrations, then XRD cannot detect it [140]. A solution to the problem was to use energy dispersive spectroscopy

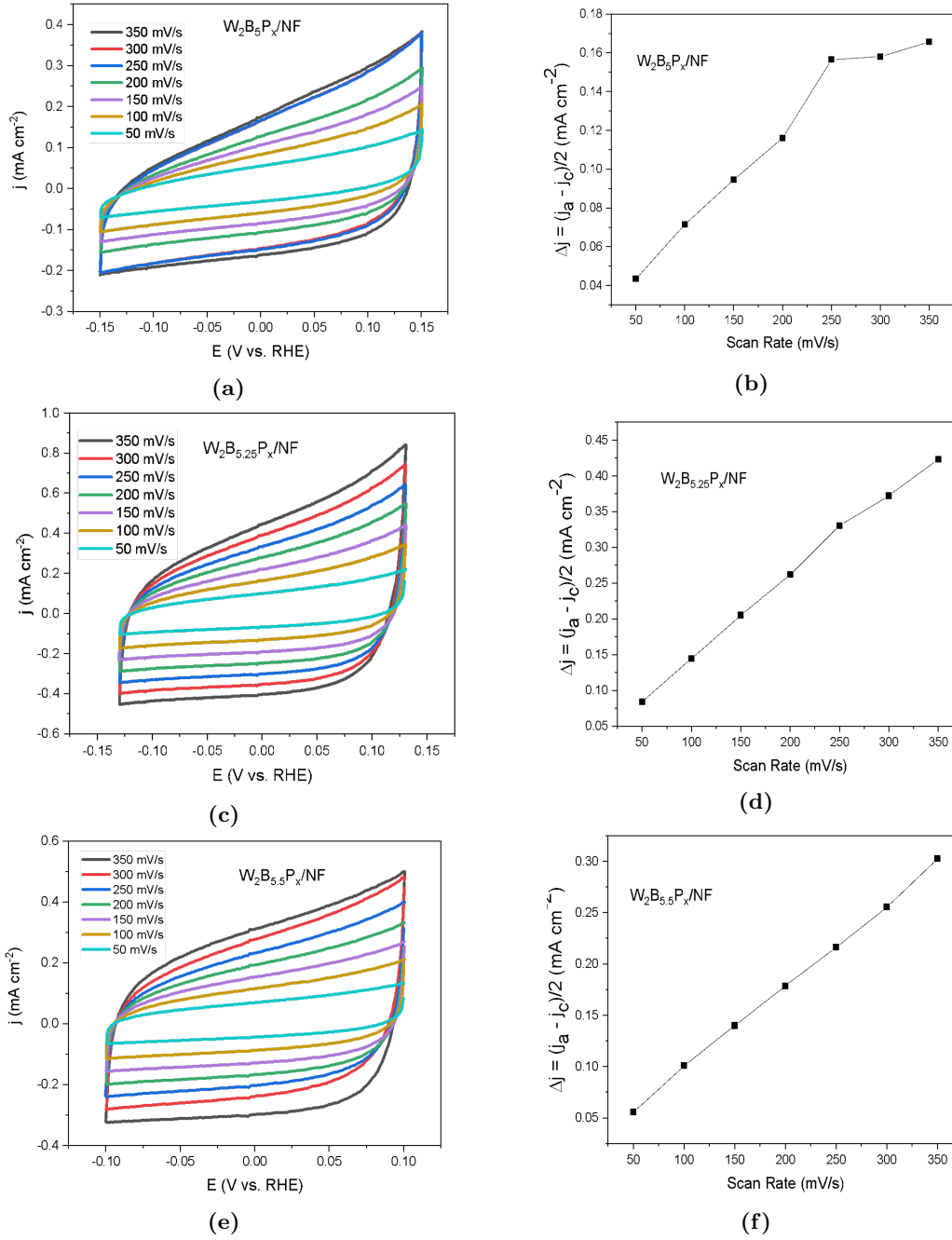


Figure 36: (a) CV curves for the $W_2B_5P_x/NF$ where the voltages range is between -0.15 V to 0.15 V. (b) $W_2B_5P_x/NF$ sample plot of the current density versus the scan rate. (c) CV curves for the $W_2B_{5.25}P_x/NF$ where the voltages range is between -0.15 V to 0.15 V. (d) $W_2B_{5.25}P_x/NF$ sample plot of the current density versus the scan rate. (e) CV curves for the $W_2B_{5.5}P_x/NF$ where the voltages range is between -0.1 V to 0.1 V. (f) $W_2B_{5.5}P_x/NF$ sample plot of the current density versus the scan rate.

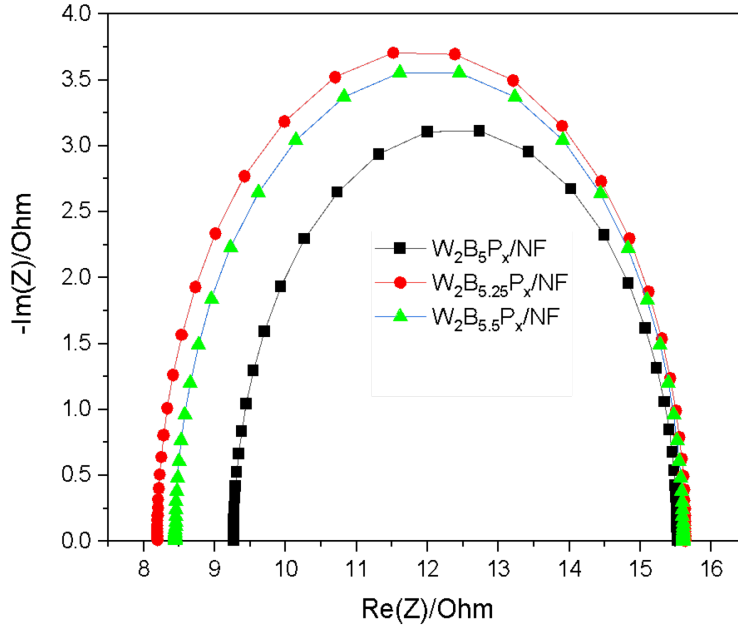


Figure 37: EIS plots of the impedance curves.

(EDS) mapping techniques. For the EDS mapping measurement, a sample of $W_2B_5P_x/NF$ was used to administer the EDS. Figure 39 shows a series mapping images for the main elements in the sample before it was tested in an electrolyte of KOH. From the area that was mapped, it shows that the W is dominant element, along with traces B and P on the Ni foam. In the sum spectrum of Figure 40, W intensity is also clearly dominant. Figure 41 shows the $W_2B_5P_x/NF$ after testing in KOH, and the area that was selected is an area with smother contour where Ni is the dominant element and the sum spectrum of Figure 42, and it also shows the deposited elements are in significantly less intensity as compared to the Ni foam.

4.6 Sample Morphology

To see how the samples were deposited on the Ni foam substrate, scanning electron microscopy (SEM) was performed on the samples. Figure 43 gives an image with the length, width, and gauge of the Ni foam with material deposited onto it. The samples were examined to see how W_2B_5 and P was deposited, distributed, and changed from testing. Figure 44 shows a sample of W_2B_5/NF , and it shows the tungsten boride particles deposited on Ni foam. Figure 45 shows a sample of Ni

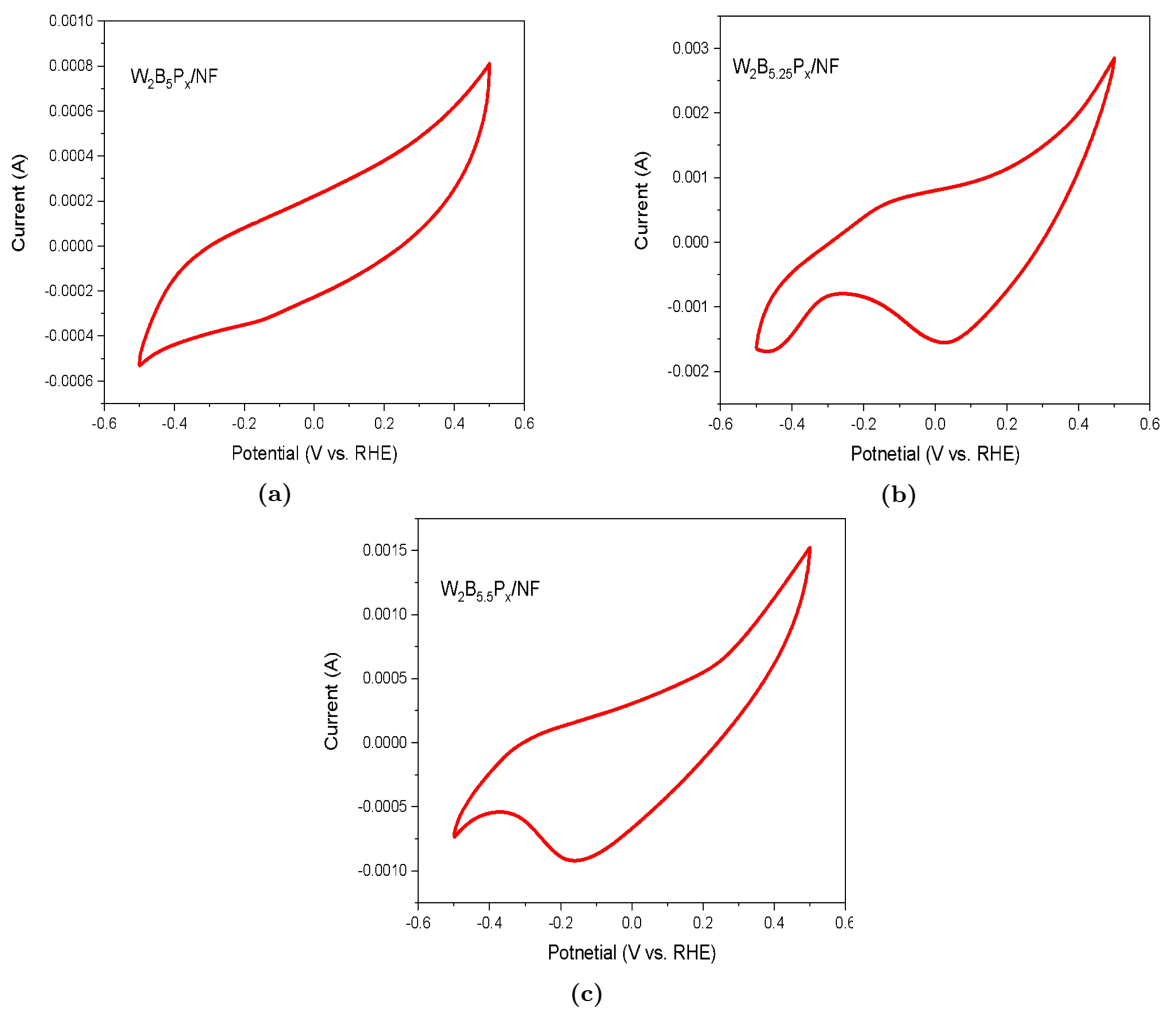


Figure 38: (a) CV curve of $W_2B_5P_x/NF$ in 1M of PBS. (b) CV curve of $W_2B_{5.25}P_x/NF$ in 1M PBS. (c) CV curve of $W_2B_{5.5}P_x/NF$ in 1M of PBS.

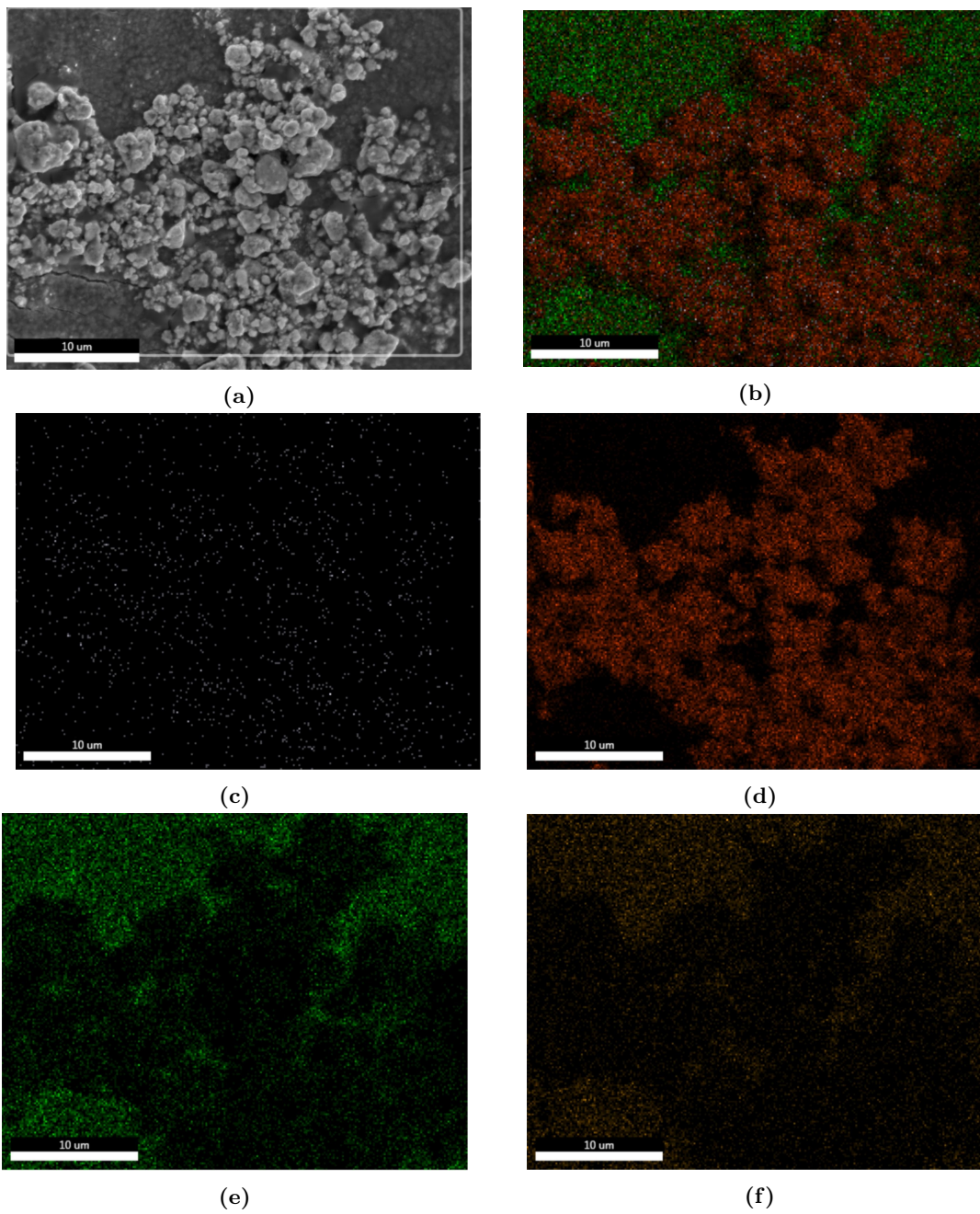


Figure 39: The (a) image is the area of the $W_2B_5P_x/NF$ sample before testing that was mapped. The (b) image is the mapping overlay of the elements. The (c) image is the B. The (d) image is the W. The (e) image is the P. The (f) image is the Ni,

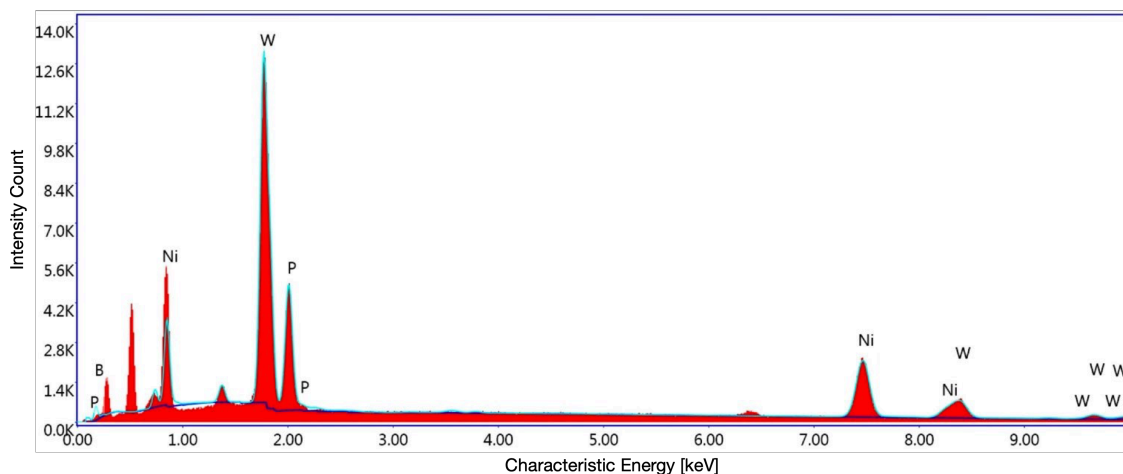


Figure 40: Sum spectrum of the mapping. Of the $W_2B_5P_x/NF$ sample before testing. Vertical axis represents the intensity count and horizontal axis in keV each element's characteristic energy.

foam with P deposited on it, and it shows that the P is lightly deposited on Ni foam. Figure 46 shows $W_2B_5P_x/NF$ before testing, and it shows that P has been deposited on the Ni foam in an almost uniform fashion. Figure 47 is close-up image the sample after testing, and it shows layering of material on the Ni foam.

4.7 Summary

Tungsten borides for the use of oxygen evolution reaction can have great improvement in its performance when properly prepared. As opposed to other attempts where chemicals and electroplating was used as the method to synthesize tungsten borides, the ball-milling, hot-pressing, and deposition on metal foam has been demonstrated to improve performance and show good performance at higher current densities than what was previously reported. With the addition of P to the samples, the performances greatly improve by decreasing the overpotential for even higher current densities. Table 18 shows the performances of the other metal boride OER samples that have been reported and how they compare to samples in this work. Table 19 shows the performances of some of the best OER samples that have been reported. When others report the performances of the samples, the current density is usually measured from one or two sides of the sample. In this work, five sides of sample have been measured. The reason for considering all fives sides is because all sides, which

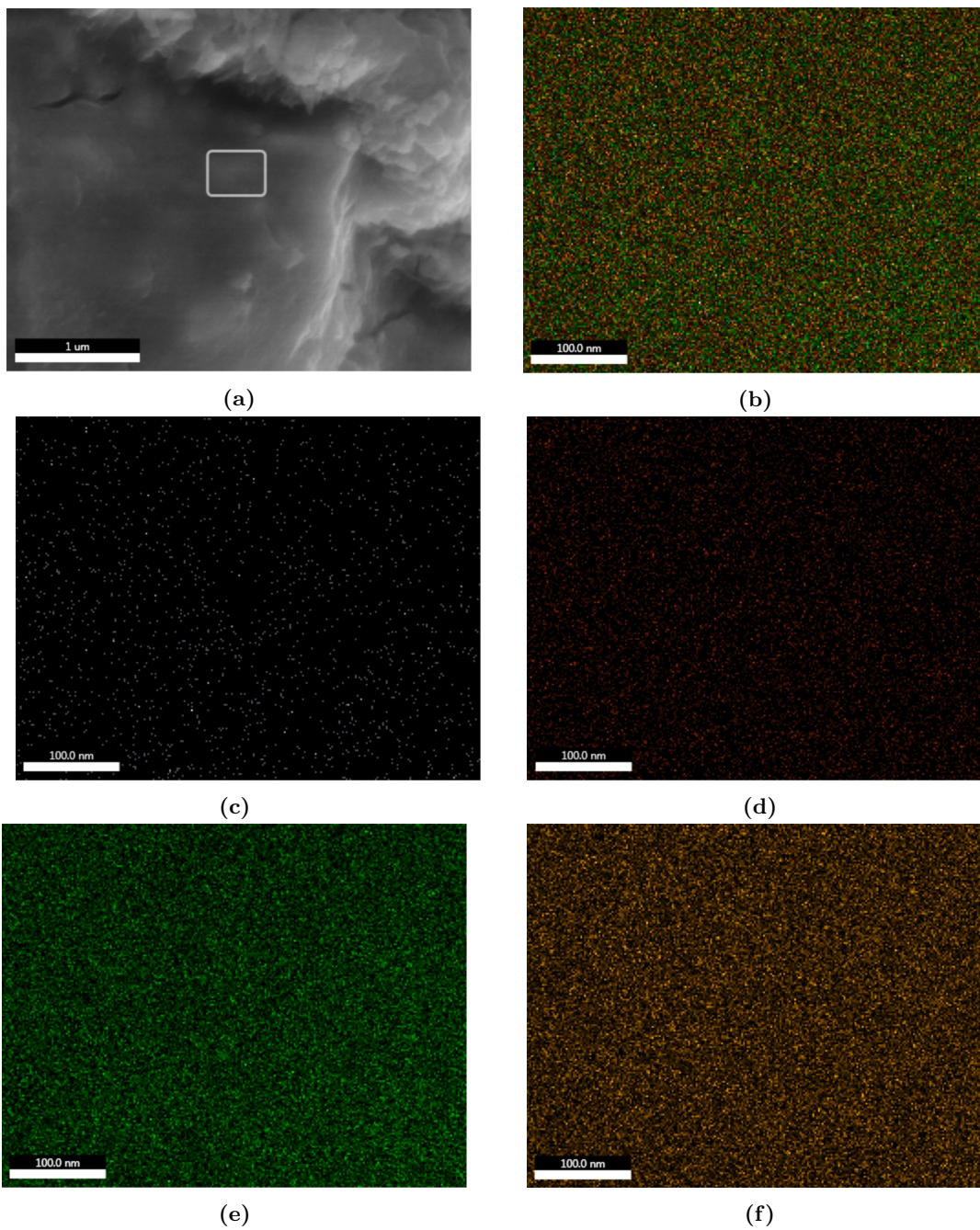


Figure 41: The (a) image is the area of the $W_2B_5P_x/NF$ sample after testing that was mapped. The (b) image is the mapping overlay of the elements. The (c) image is the B. The (d) image is the W. The (e) image is the P. The (f) image is the Ni.

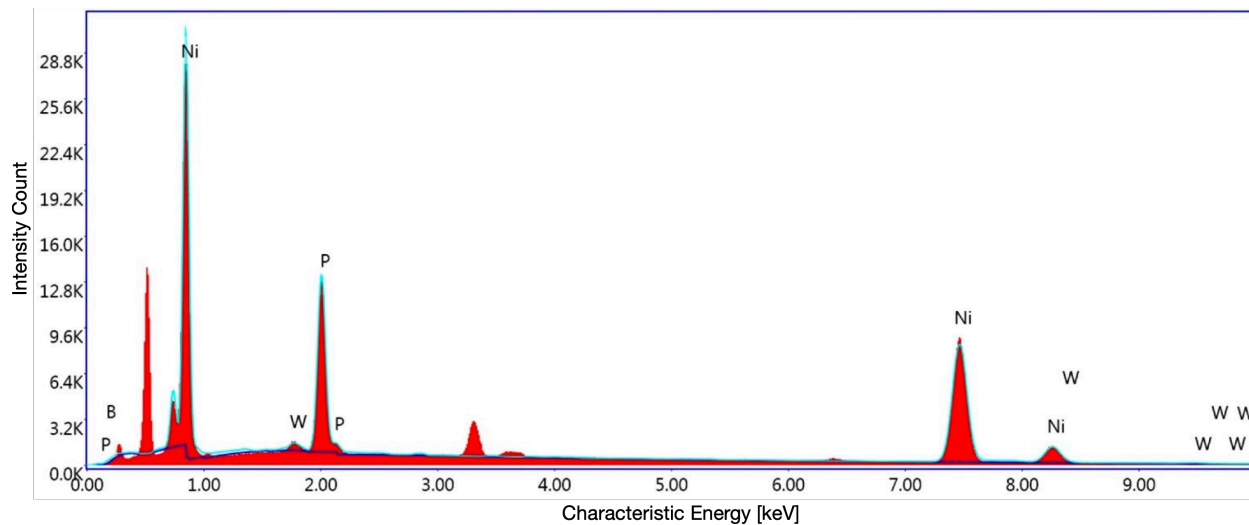
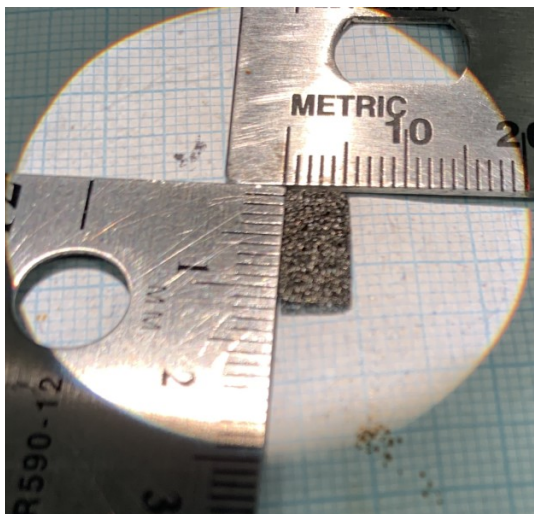
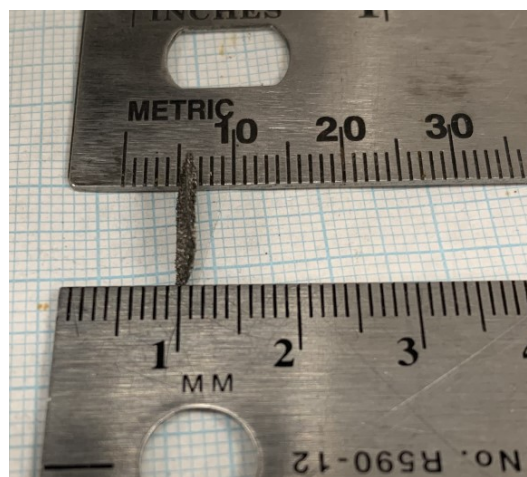


Figure 42: Sum spectrum of the mapping. Of the $W_2B_5P_x/NF$ sample after testing. Vertical axis represents the intensity count and horizontal axis in keV each element's characteristic energy.



(a)



(b)

Figure 43: Image (a) is of the length width of the Ni foam sample. Image (b) is of the gauge of the Ni foam sample.

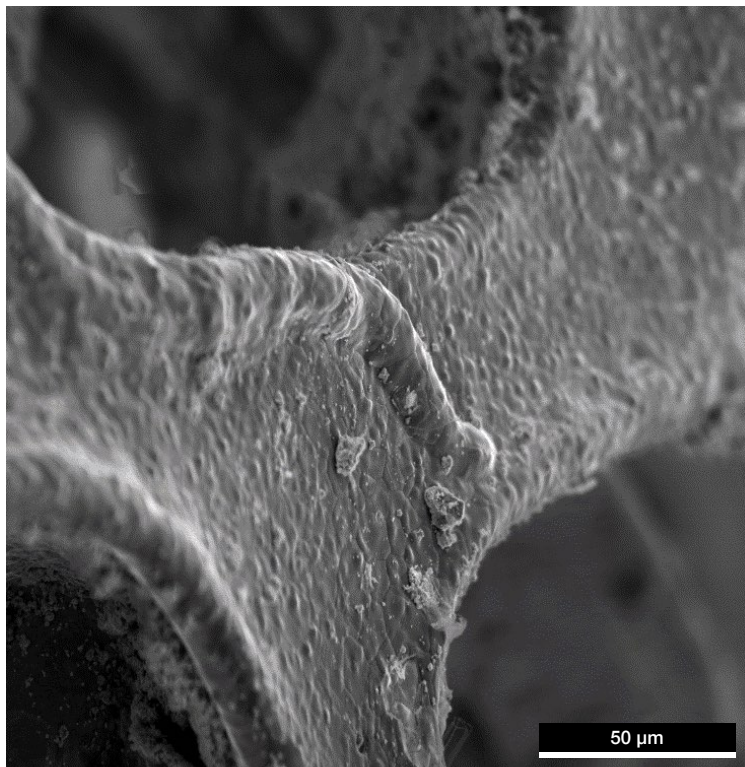


Figure 44: W₂B₅/NF before testing.

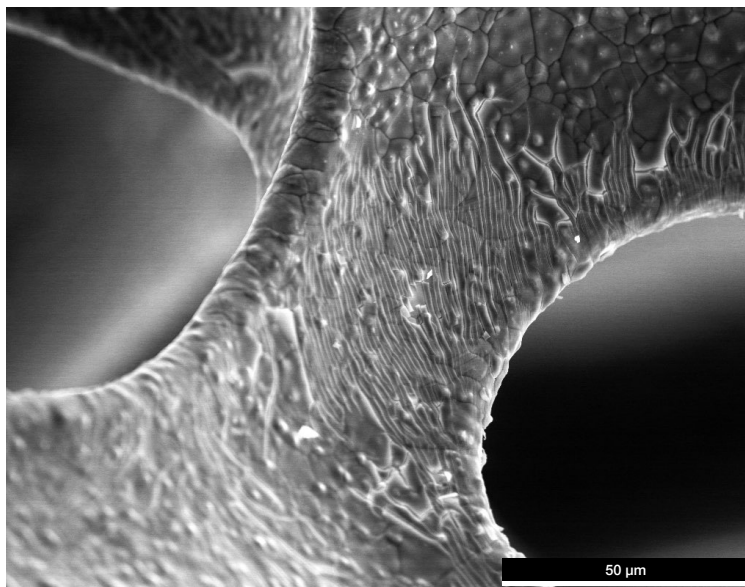


Figure 45: Ni foam before testing with P deposited on the surface.

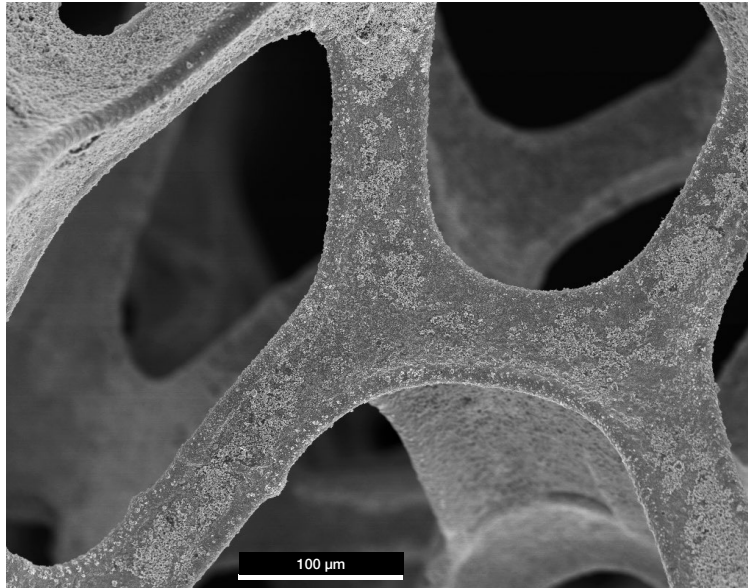


Figure 46: W₂B₅P_x/NF before testing.

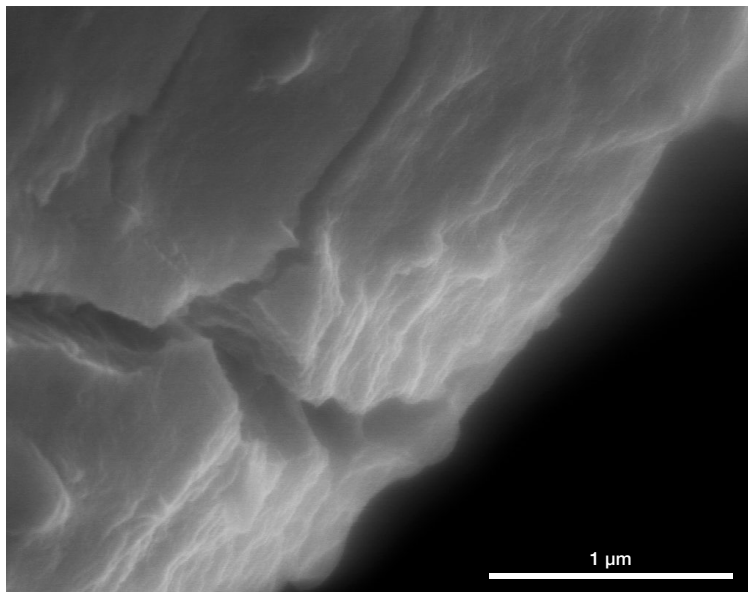


Figure 47: W₂B₅P_x/NF after testing.

includes the substrate, contributes to the reaction and therefore has to be considered.

The conclusion that could be drawn as to explain why some samples performed better than others can only be attributed to R_{ct} . Samples with lowest R_{ct} consistently performed the best out of any other samples and had the lowest overpotentials. Other measurements such as most active sites, highest C_{dl} , or highest C_p do not always reflect into a sample having lowest overpotential. The lowest R_{ct} translating into the lowest overpotential is a reflection of the theoretical assertion of the B electron transport properties. The electron transport efficiency is a reflection of lower R_{ct} . Therefore, for metal borides to work as a water-splitting electrocatalysts, one must decrease the charge transfer resistance.

Table 18: Comparison of $W_2B_{5.25}/NF$ and $W_2B_{5.25}P_x/NF$ with other metal borides in 1M KOH.

Sample	Support	Electrolyte	Overpotential	Reference
Co- B_x	Glass Carbon	1M KOH	$\eta_{10} = 290$	[141]
Co@Co- B_x	Ti Mesh	1M KOH	$\eta_{10} = 327$	[142]
Ni- B_x @Ni-B	Glass Carbon	1M KOH	$\eta_{10} = 364$	[143]
Co-Fe-B	Cu Sheet	1M KOH	$\eta_{10} = 298$	[141]
Fe-Co-Ni-B	Glass Carbon	1M KOH	$\eta_{10} = 274$	[144]
Ni-Bi@Ni ₃ B	Glass Carbon	1M KOH	$\eta_{10} = 302$	[143]
Ni-B@NiO	Cu Foil	1M KOH	$\eta_{10} = 296$	[145]
Ni _x -B	Glass Carbon	1M KOH	$\eta_{10} = 380$	[146]
Ni-Fe-B	Glass Carbon	1M KOH	$\eta_{10} = 251$	[147]
Fe ₃ Co ₇ B/CNT	Glass Carbon	1M KOH	$\eta_{10} = 265$	[148]
$W_2B_{5.25}/NF$	Ni Foam	1M KOH	$\eta_{10} = 280$	This Work
$W_2B_{5.25}P_x/NF$	Ni Foam	1M KOH	$\eta_{10} = 250$	This Work

Table 19: The performances of other OER electrocatalysts with reported low overpotentials.

Sample	Support	Electrolyte	Overpotential	Reference
NiFeS	Ni Foma	1M KOH	$\eta_{10} = 65$	[149]
MoO _x /Ni ₃ S ₂ ms	Ni Foam	1M KOH	$\eta_{10} = 136$	[150]
p Ni ₂ P-6	Ni Foam	1M KOH	$\eta_{10} = 142$	[151]
(Ni _{0.33} Fe _{0.67}) ₂ P NS	Ni Foam	1M KOH	$\eta_{10} = 150$	[152]
Cu@CoS _x	Ni Foam	1M KOH	$\eta_{10} = 160$	[153]
Ni(OH) ₂ NS	Ni Foam	1M KOH	$\eta_{10} = 170$	[154]
FeNiP NPl	Ni Foam	1M KOH	$\eta_{10} = 180$	[155]
p NiS _x	Ni Foam	1M KOH	$\eta_{10} = 49$	[156]
Cu-NiFe LDH	Ni Foam	1M KOH	$\eta_{10} = 199$	[157]
Ni ₂ P pu	Ni Foam	1M KOH	$\eta_{10} = 200$	[156]

5 OVERALL PERFORMANCE

5.1 Introduction

The overall performance test of water splitting is the two-electrode system. In the two-electrode system, the anode is the counter electrode, and there is no reversible hydrogen electrode (RHE). The system works by current originating at the cathode and flowing to the anode. It is at the anode where reaction starts. The oxidation of the four-electron oxygen evolution reaction (OER) starts at the positively-charge anode and flowing to the negatively-charged cathode, where the reduction two-electron hydrogen evolution reaction (HER) occurs.

5.2 Electrochemical Sample Testing and Results

For the linear sweep voltammetry (LSV) test, the $W_2B_{5.25}$ bulk sample will be the cathode and $W_2B_5P_x/NF$ will be anode. To measure the current density, both electrodes must have the same the geometric surface area. The geometric surface area is measured by measuring length, width, and gauge of each sample. The geometric surface areas must be the same for both samples because there is no RHE or counter electrode. The anode must stand in for the counter electrode. The readout from the LSV measurements are the combined output of both cathode and anode.

5.3 Summary

With iR compensation, the overall overpotential at 10 mA cm^{-2} is 370 mV and is 560 mV at 100 mA cm^{-2} as shown in Figure 48. Without iR compensation, the overall overpotential at 10 mA cm^{-2} is 420 mV as shown in Figure 49. The overpotentials appear to be higher for the overall overpotential than the V vs. RHE. The reason for this could be an increase in charge transfer resistance (R_{ct}). A solution to high overpotential would be to decrease the surface area exposure in the electrolyte. With a lower exposure of surface area, the current density would increase.

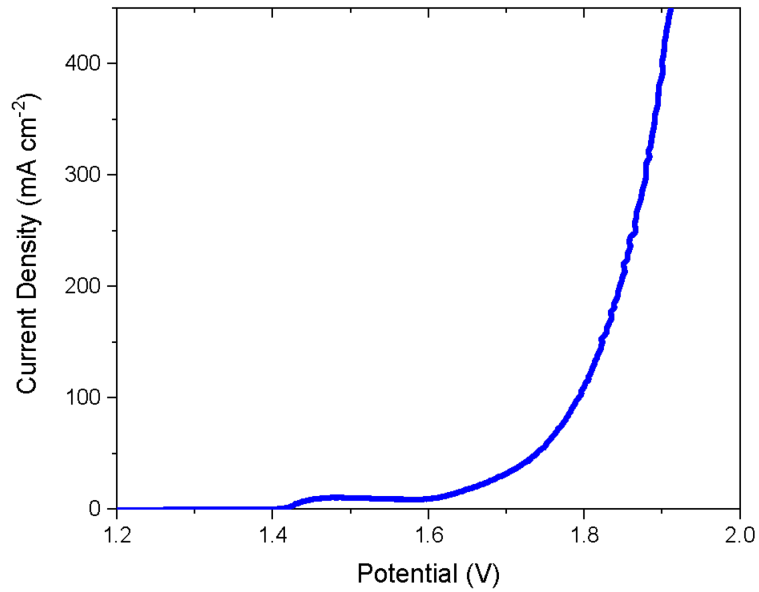


Figure 48: Overall water splitting performance with iR compensation

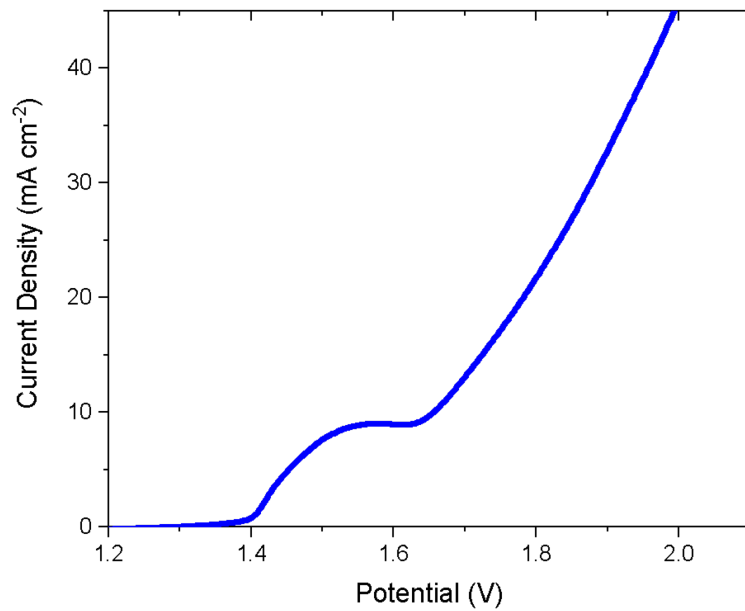


Figure 49: Overall water splitting performance without iR compensation

A Derivation for Impedance Curve Equations for Randles Circuit

Let the charge transfer resistance be equal to the resistance of the charge transfer (R_{ct}) such that:

$$Z_{\text{Resistor}} = R_{ct}. \quad (\text{A.1})$$

If we write R in terms of the double-layer capacitance (C_{dl}), then

$$Z_{\text{capacitor}} = \frac{1}{i\omega C_{dl}}. \quad (\text{A.2})$$

If we write the equivalent resistance of a network of resistors in parallel using the expressions above, we get that:

$$\frac{1}{Z_{eq}} = \frac{1}{R_{ct}} + \frac{1}{\frac{1}{i\omega C_{dl}}} = \frac{1}{R_{ct}} + \frac{i\omega C_{dl}}{1} = \frac{1 + iR_{ct}\omega C_{dl}}{R_{ct}}. \quad (\text{A.3})$$

Inverting the equivalent resistance we get

$$Z_{eq} = \frac{R_{ct}}{1 + i\omega R_{ct} C_{dl}}, \quad (\text{A.4})$$

and summation of Z is R_s and $Z_{eq} = R_{eq}$ which is

$$Z = R_s + R_{eq}, \quad (\text{A.5})$$

and can be rewritten as

$$Z = R_s + \frac{R_{ct}}{1 + i\omega R_{ct} C_{dl}}. \quad (\text{A.6})$$

Time is equivalent to

$$\tau = R_{ct} C_{dl} \quad (\text{A.7})$$

which can be inverted to acquire frequency

$$\omega = \frac{1}{R_{ct}C_{dl}} \quad (\text{A.8})$$

and substituted into A.6 and re-arranged to acquire

$$Z = R_s + \frac{R_{ct} - i\omega R_{ct}^2 C_{dl}}{1 + \omega^2 R_{ct}^2 C_{dl}^2}. \quad (\text{A.9})$$

A.9 can be separated into real and imaginary parts

$$Z = Z_{Im} + Z_{Re}, \quad (\text{A.11})$$

where the real part is

$$Z_{Re} = R_s + \frac{R_{ct}}{1 + \omega^2 R_{ct}^2 C_{dl}^2} \quad (\text{A.12})$$

and the imaginary part is

$$Z_{Im} = \frac{-i\omega R_{ct}^2 C_{dl}}{1 + \omega^2 R_{ct}^2 C_{dl}^2}. \quad (\text{A.13})$$

The radius of the Nyquist plots is

$$|Z| = \sqrt{Z_{Re}^2 + Z_{Im}^2} \quad (\text{A.14})$$

and the phase angle is

$$\varphi = \tan^{-1} \left(\frac{Z_{Im}}{Z_{Re}} \right). \quad (\text{A.15})$$

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