Improving The Efficiency Of Ammonia Electrolysis For Hydrogen Production

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ABSTRACT

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Improving the Efficiency of Ammonia Electrolysis for Hydrogen Production

Director of Dissertation: Gerardine G. Botte

Given the abundance of ammonia in domestic and industrial wastes, ammonia electrolysis is a promising technology for remediation and distributed power generation in a clean and safe manner. Efficiency has been identified as one of the key issues that require improvement in order for the technology to enter the market phase. Therefore, this research was performed with the aim of improving the efficiency of hydrogen production by finding alternative materials for the cathode and electrolyte.

1. In the presence of ammonia the activity for hydrogen evolution reaction (HER) followed the trend Rh>Pt>Ru>Ni. The addition of ammonia resulted in lower rates for HER for Pt, Ru, and Ni, which have been attributed to competition from the ammonia adsorption reaction.

2. The addition of ammonia offers insight into the role of metal-hydrogen underpotential deposition (M-H_{upd}) on HER kinetics. In addition to offering competition via ammonia adsorption it resulted in fewer and weaker M-H_{upd} bonds for all metals. This finding substantiates the theory that M-H_{upd} bonds favor HER on Pt electrocatalyst. However, for Rh results suggest that M-H_{upd} bond may hinder the HER. In addition, the presence of unpaired valence shell electrons is suggested to provide higher activity for HER in the presence of ammonia.
3. Bimetals Pt\(_x\)M\(_{1-x}\) (M = Ir, Ru, Rh, and Ni) offered lower overpotentials for HER compared to the unalloyed metals in the presence of ammonia. The activity of HER in the presence of ammonia follows the trend Pt-Ir>Pt-Rh>Pt-Ru>Pt-Ni. The higher activity of HER is attributed to the synergistic effect of the alloy, where ammonia adsorbs onto the more electropositive alloying metal leaving Pt available for H\(_{\text{upd}}\) formation and HER to take place. Additionally, this supports the theory that the presence of a higher number of unpaired electrons favors the HER in the presence of ammonia.

4. Potassium polyacrylate (PAA-K) was successfully used as a substitute for aqueous KOH for ammonia electrolysis. PAA-K allowed for a wider operating potential for the electrolytic cell while increasing the rate for HER at lower cell voltages. The conversion of ammonia improved from 16 % to 25 %, while the current efficiency for the consumption of ammonia increased from 92 ± 1 % to 97 ± 2 % by using PAA-K in lieu of KOH. The use of PAA-K also prevented the crossover of the hydrogen produced to the anode side, unlike aqueous KOH.
DEDICATION

For my beloved wife Uma.
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Among many things that I have gained during this course, is a life-time experience of learning, friendship, and professional experience. For this opportunity, I would like to thank God and my advisor Dr. Gerardine Botte. I would like to express my gratitude to her for providing me the independence to work on this dissertation, being an example, and continuing to inspire me to reach for higher grounds.

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<th>Meaning</th>
<th>Symbol</th>
<th>Meaning</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>Electrode area</td>
<td>R</td>
<td>Universal Gas Constant</td>
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<tr>
<td>b</td>
<td>Tafel slope</td>
<td>r₀</td>
<td>Rate of electron consumption</td>
</tr>
<tr>
<td>C&lt;sub&gt;a,i&lt;/sub&gt;, C&lt;sub&gt;a,f&lt;/sub&gt;</td>
<td>Concentration at anode (initial and final)</td>
<td>r₁</td>
<td>Rate of surface coverage</td>
</tr>
<tr>
<td>C&lt;sub&gt;dl&lt;/sub&gt;</td>
<td>Double layer capacitance</td>
<td>R&lt;sub&gt;f&lt;/sub&gt;</td>
<td>Faradaic resistance</td>
</tr>
<tr>
<td>C&lt;sub&gt;p&lt;/sub&gt;</td>
<td>Pseudo-capacitance</td>
<td>R&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Solution resistance</td>
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<td>Frequency dispersion in C&lt;sub&gt;dl&lt;/sub&gt;</td>
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<td>Time</td>
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<td>Frequency dispersion in C&lt;sub&gt;p&lt;/sub&gt;</td>
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<td>X</td>
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<tr>
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<td>Z&lt;sub&gt;f&lt;/sub&gt;</td>
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<td>i</td>
<td>Current density</td>
<td>β₁, β₂</td>
<td>Transfer Coefficients</td>
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<tr>
<td>i₀</td>
<td>Exchange current density</td>
<td>η</td>
<td>Overpotential</td>
</tr>
<tr>
<td>J</td>
<td>Diffusion flux</td>
<td>θ</td>
<td>Fractional Surface Coverage</td>
</tr>
<tr>
<td>k₁, k₋₁, k₂, k₃</td>
<td>Rate Constants (potential independent)</td>
<td>ρ</td>
<td>Density</td>
</tr>
<tr>
<td>N&lt;sub&gt;c,i&lt;/sub&gt;, N&lt;sub&gt;c,f&lt;/sub&gt;, N&lt;sub&gt;expt&lt;/sub&gt;, N&lt;sub&gt;theo&lt;/sub&gt;</td>
<td>No. of moles</td>
<td>ν₁, ν₂, ν₃</td>
<td>Rate of reaction</td>
</tr>
<tr>
<td>P&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Partial pressure for species i</td>
<td>ῦ</td>
<td>Angular velocity</td>
</tr>
<tr>
<td>q</td>
<td>Charge for monolayer surface coverage</td>
<td></td>
<td></td>
</tr>
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# ABBREVIATION LIST

<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>AEC</td>
<td>Ammonia Electrolytic Cell</td>
</tr>
<tr>
<td>AER</td>
<td>Ammonia Electrooxidation Reaction</td>
</tr>
<tr>
<td>APGE</td>
<td>Alkaline Polymer Gel Electrolyte</td>
</tr>
<tr>
<td>CFP</td>
<td>Carbon Fiber Paper</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant Phase Element</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>CSA</td>
<td>Chemical Specific Area</td>
</tr>
<tr>
<td>EASA</td>
<td>Electrochemical Active Surface Area</td>
</tr>
<tr>
<td>EDS / EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
</tr>
<tr>
<td>H_{opd}</td>
<td>Hydrogen Overpotential Deposition</td>
</tr>
<tr>
<td>H_{upd}</td>
<td>Hydrogen Underpotential Deposition</td>
</tr>
<tr>
<td>ICD</td>
<td>Inter Crystalline Distance</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear Sweep Voltammetry</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>PAA-K</td>
<td>Potassium salt of Poly Acrylic Acid</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Polymer Electrolyte Membrane Fuel Cell</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible Hydrogen Electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TS</td>
<td>Tafel Slope</td>
</tr>
<tr>
<td>VHT</td>
<td>Volmer-Tafel-Heyrovsky</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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</tbody>
</table>
1.1. Project Overview

Based on the reports from the Energy Information Administration, in 2011, an estimated 97 quadrillion BTU of energy was consumed in the United States, of which 40.04 quadrillion BTU was used to generate electricity and 80% came from fossil fuels such as coal, and natural gas (Appendix A). The exponential increase in the energy demand is leading to depletion of non-renewable sources, besides building-up greenhouse gases in the atmosphere, a principal cause of global warming. In addition, during the same year 7% of energy that was generated was lost during transmission and distribution, while the CO₂ levels in the atmosphere rose to 400 ppm, which is well above the advocated value of 350 ppm for a sustainable environment (Appendix B). Thus, a transformation from non-renewable energy to renewable energy is inevitable.

Hydrogen has been identified as a potential alternative energy carrier. The chemical energy stored in hydrogen can be converted into useful energy in a number of ways viz., electric energy by a fuel cell, mechanical energy by a hydrogen combustion engine, and heat energy by a hydrogen water heater. Some of the major factors preventing the commercialization of this hydrogen based energy technology are associated with the costs of production, storage and safe transportation of hydrogen.

Another major issue that lingers in the other end of the spectrum is the groundwater contamination by ammonia-nitrates from domestic and industrial wastes. The current energy demand for denitrification is estimated to be 1.013 kWh per million gallons of wastewater and expected to rise by 20% in the next 15 years due to the
increasing nitrogen content in wastes. Ammonia has a hydrogen density of 136 kg m\(^{-3}\), which is the highest among liquids. As a result, it is considered to be one of the safer ways to store and transport hydrogen. Ammonia Electrolysis is a novel technology to produce hydrogen, developed by Dr. Gerardine G Botte at Center for Electrochemical Engineering Research (CEER) at Ohio University. This technology facilitates safe, efficient, clean and inexpensive production of hydrogen. In addition, this technology offers the possibility of using the ammonia and urea from human, animal, agricultural and industrial wastes. In essence, ammonia electrolysis offers a technology to reduce nitrate contamination in ground water while cogenerating power when coupled with a fuel cell or a hydrogen combustion engine.

The theoretical power required to produce hydrogen using ammonia electrolysis is 1.55 Wh g\(^{-1}\) that will allow hydrogen production at 0.89 $ kg\(^{-1}\). The theoretical energy required to produce hydrogen by ammonia electrolysis is significantly lower than 33 Wh g\(^{-1}\), the theoretical energy required by water electrolysis. However, literature suggests a 14.54 Wh g\(^{-1}\) achieved with micro-sized electrodes [1]. This corresponds to an energy efficiency of 10.66 %, thereby leaving plenty of room for improvement.

The focus of this research will be the development of an efficient ammonia electrolytic cell system. More precisely, this research seeks to increase both the ammonia conversion rate and the overall efficiency of hydrogen production. Although, several efforts have been made to understand the cause of limitation of the reaction at the Pt anode catalyst, the exact reason is still evasive. Therefore, an attempt will be made to decipher the source for the limitation. Previous researchers, both at CEER [1-7] and
elsewhere [8-11], have focused on the search for a better anode electrocatalyst. In contrast, this research will focus on the improvement of the electrolyte and material for the cathode electrocatalyst. Emphases will be placed on understanding the effect of ammonia on the cathode and the alternative electrolyte on both anodic and cathodic reactions to facilitate a directed search for an improved material.

1.2. Statement of Objectives

Ammonia electrolysis comprises of ammonia electro-oxidation reaction at the anode and hydrogen evolution reaction (HER) at the cathode as shown in Equations 1-3.

Anode: \[ 2\text{NH}_3 + 6\text{OH}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O} + 6\text{e}^- \] \[ E^0 = -0.770 \text{ V vs SHE} \] (1)
Cathode: \[ 6\text{H}_2\text{O} + 6\text{e}^- \rightarrow 3\text{H}_2 + 6\text{OH}^- \] \[ E^0 = -0.828 \text{ V vs SHE} \] (2)
Overall: \[ 2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 \] \[ E^0 = 0.058 \text{ V} \] (3)

It has been observed that the ammonia electro-oxidation current on a Pt electrode drops after reaching a maximum at 0.7 V versus RHE [12-15]. The widely accepted Gerischer mechanism suggests that the limitation at the anode is due to the strong adsorption of nitrogen (N_{ads}) on Pt [13, 16-19]. However, Cooper and Botte speculate the hydroxyl (OH^-) ion electrosorption on Pt to be the main reason for the limiting behavior [20]. Recently, from our results it has been identified that the reaction does not require the OH^- ion to be adsorbed in contrast to the Gerischer mechanism thereby leaving some ambiguity in the mechanism of ammonia electro-oxidation on Pt. Moreover the cause for the limitation is still unknown. Understanding this mechanism would provide better
insights to the cause of this phenomenon and in turn help researchers in postulating solutions.

In order to improve the efficiency of the electrolytic cell it is crucial to operate it within limiting potential of the anode. Previous research has focused on identifying a better anode material. In contrast, this research will try to improve the hydrogen production efficiency thereby obviating the need to operate the electrolytic cell at voltages where the anode could reach its limiting potential. The electrocatalysts that have been developed for the cathodic HER are based on non-noble metals (Ni, Co, Fe) and are primarily designed for water electrolysis [21-28]. It has been observed that these electrocatalysts have a large overpotential, thereby making them unsuitable for use as cathodes for ammonia electrolysis. Hence it is implicit to investigate alternative electrodes for HER and the effect of ammonia on the HER for the catalysts.

Currently the supporting electrolyte used for ammonia electrolysis is aqueous potassium hydroxide (KOH) [1, 3-6]. The costs associated with the recirculation and recovery of KOH causes an increase in the operating cost of the ammonia electrolytic cell (AEC). The use of a solid polymer electrolyte embedded between the electrodes as the supporting electrolyte would eliminate the above-mentioned parasitic costs and also avoid any increase in the vapor pressure of ammonia, which would have been predominant otherwise (as reported in the vapor liquid equilibrium data for the ammonia-water-KOH system [29, 30]).

In retrospect, the specific goals for this research focused on the improvement of ammonia conversion rate and the power efficiency of the AEC:
1. Electrode synthesis via., electrodeposition and characterization of catalysts Pt, Ru, Rh, and Ni onto carbon fiber paper. Studying the effect of ammonia on HER for Pt, Rh, Ru, and Ni cathodes. (Chapter 4)

2. Synthesis and characterization of Pt-based bimetallic catalysts Pt-Ir, Pt-Ru, Pt-Rh, and Pt-Ni electrodeposited onto carbon fiber paper. Evaluating the activity of the metallic and bimetallic electrocatalysts towards HER in the presence of ammonia was investigated. (Chapter 5)

3. Investigating the effectiveness of (poly)acrylic acid hydrogel matrix as a substitute to aqueous potassium hydroxide electrolyte. (Chapter 6)

1.3. Significance of Research

1.3.1. Social Impact

The current atmospheric CO₂ reaching the historic 400 ppm mark is a reason significant enough for making paradigmatic shifts in the source of our energy. In 2009, the global CO₂ emissions were estimated to be 30.398 billion metric tons of carbon into the atmosphere. Despite a 7% drop in emissions from the previous year, the USA accounted for 17.8% (5.168 billion metric tons of CO₂) of world’s total emissions (Figure B3, Appendix B). The power generated by the United States in 2011, to meet the demands of the stationary sector in the energy market (which includes household, commercial and industrial sectors) was 70.2 quadrillion BTU of energy [31]. The carbon dioxide (CO₂) emitted by these power plants, not including industries, automobiles and other greenhouse gas generators, during this period was reported to be 3.6 billion metric
tons, which increased the CO₂ in the earth’s atmosphere by 1.71 ppm. On a lateral note, it is also important to know that, about 20% of the total energy that was consumed during this year came from foreign sources.

The current average electricity cost for residential units in the United States is 8.9 cents per kWh. The Department of Energy (DOE) goal for 2015 is to bring down the average power cost to 6 to 8 cents per kWh of electricity. The inspiration for this study is to meet this requirement, thereby paving the way to the new horizon of distributed power production. The successful commercialization of this technology would:

1. Facilitate the production of clean power, by lowering greenhouse gases emission.
2. Cut nitrate contamination of ground water from domestic and industrial wastes.
3. Decrease energy cost for remediating wastes, as a result of power co-generation.
4. Enable distributed power production, thereby avoiding transmission energy losses.
5. Reduce the cost of hydrogen production resulting in a lower power cost.
6. Increase energy security by reducing dependence on foreign oil.

1.3.2. Educational Impact

The results of this research will be published in peer-reviewed journals, making the data available to the global scientific community, and improve the knowledge base of ammonia electrolysis to allow further developments.
1. Chapter 4 discusses the effect of ammonia and H_{upd} on the kinetics of HER using Pt, Ru, Rh, and Ni electrodes. The research discussed in this chapter has been published in the Journal of Physical Chemistry C.

2. Chapter 5 discusses the activity of metallic and bimetallic catalysts for the HER in the presence of ammonia. This chapter has been submitted to the Journal of Electrochemical Society for consideration for publication.

3. Chapter 6 discusses the efficacy of a solid alkaline polymer gel electrolyte as a substitute to aqueous potassium hydroxide in an ammonia electrolytic cell. This research has been published in the Electrochimica Acta.

The knowledge gained from this research would potentially aid in providing direction to future research to improve the efficiency of ammonia electrolysis. In addition to improving the efficiency, this research will aid the construction of a compact cell for mobile applications.

1.4. References

CHAPTER 2: LITERATURE REVIEW

2.1. Need for Alternative Energies and the Role of Hydrogen

Renewable energy is the favored solution to strengthen national energy security and reduce the carbon footprint of the power industry. Some examples of renewable energies are solar energy, wind energy, hydroelectric power, and geothermal energy. Even though the aforementioned renewable energy technologies have existed for centuries, the ability to harness them on a need basis remains elusive [1, 2]. After a considerable amount of research, it has been established that hydrogen stands among the top contenders for clean alternative fuels. The chemical energy stored in hydrogen is converted to electricity using a fuel cell [1, 3, 4]. Currently, the technologies such as steam methane reforming and ammonia cracking that is predominantly used for hydrogen production, require very high temperatures and are energy inefficient. The major problems preventing the commercial use of hydrogen are its production, storage, and transportation [1, 5]. According to an economic analysis of hydrogen production by various technologies, steam methane reforming is the cheapest way of producing hydrogen amongst existing technologies [6].

2.2. Why Ammonia?

Ammonia is considered to be an ideal carrier for hydrogen based on the fact that it has a hydrogen density higher than most hydrocarbon fuels as shown in Figure 2-1. Ammonia is also readily available in fertilizer, dairy, and industrial waste [7-10].
Ammonia exists as a liquid in the form of ammonium hydroxide with a very low freezing point and a high boiling point (Appendix C).

It is non-explosive and can be easily transported. It has an inherently pungent odor, making it easy to detect in case of leaks. Ammonia can be stored in the form of tablets of ammine salts (e.g. Mg(NH₃)₆Cl). These tablets, shown in Figure 2-1 (B), exhibit very high density of ammonia (615 kg m⁻³) and hydrogen (114 kg m⁻³) with a very low relative volatality hence facilitate the transport of ammonia [11].

![Figure 2-1](image.jpg)

**Figure 2-1.** (A) Comparison of the hydrogen densities and heat of formation for different fuels[12]. (B) Ammonia complex salt tablets which offer high hydrogen density [11].

Traditionally, the hydrogen was produced from ammonia using cracking at high temperatures. This process was deemed not to be economically feasible by the U.S. Department of Energy (DOE). On the contrary, ammonia electrolysis occurs at room temperatures and found to be suitable for on-demand production of 100% pure hydrogen, when ammonia is obtained from wastes or purchased for under 150 $ ton⁻¹.
2.3. Introduction to Ammonia Electrolysis

Ammonia electrolysis is a method by which ammonia is electrochemically oxidized on a suitable electrocatalyst to nitrogen and hydrogen. The technology to primarily generate hydrogen using this process was invented and patented at Ohio University[13]. Based on thermodynamics, the energy required to produce hydrogen by ammonia electrolysis is 97% lower than that required by electrolyzing water [14]. From the research done at CEER, it was found that at a pH of 14 it takes 14.54 Wh to produce 1g of hydrogen at a current efficiency of 100% [15, 16]. In relation to the kinetics, it was found that ammonia electrolysis occurs at a faster rate in highly alkaline media than when compared to neutral and acidic media [17, 18].

2.4. Applications for Ammonia Electrolysis

2.4.1. Power Production:

AEC when coupled with a fuel cell produces electricity. Therefore this technology could be used for producing power. At an ammonia cost of 360 $ ton⁻¹, the cost of hydrogen produced using ammonia electrolysis is 2.02 $ kg⁻¹, which is well within the DOE goal of 2-3 $ kg⁻¹ [19]. The ultimate goal of the research will be to produce hydrogen that will lead to the production of electricity at 6 to 8 cents kWh⁻¹ to meet the DOE goal for 2015. This technology can be incorporated in a dairy farm, the fertilizer and leather industries, which has high ammonia content in their wastes, thereby offsetting the cost of ammonia. These industries can benefit from this technology in terms of remediating the wastes and producing power. By using a battery unit other renewable
energy to operate the AEC, this system has the potential to be completely grid independent. Additionally, this technology has the potential to produce hydrogen, which can be used to power residential units, industries, automobiles, and hand-held devices.

2.4.2. Ammonia Sensors:

Another major application for ammonia electrolysis will be the development of an ammonia sensor. Ammonia sensors have a market in:

1. Personnel protection
2. Emergency equipment shutdown control
3. Machinery room ventilation control
4. Safety relief monitoring

Ammonia was traditionally measured by the Kjeldahl method, which is time consuming thereby making timely detection of ammonia leaks impossible. On the other hand, commercially available ammonia sensors can be classified into electrochemical sensors[20-22], solid state sensors[23-25], and optical sensors[26, 27] based on the operating principle. In relation to the requirements for different applications, none of these sensors is able to satisfy all the requirements for an ammonia sensor. For example, the solid state sensor has a longer life and low detection limit, however it has a slow response time and low selectivity for ammonia [28]. The commercially available electrochemical sensors have a range (0-500 ppm) and deteriorate within a short span of time (1-3 years) [20, 22, 29]. It is believed that the increase in knowledge of the mechanism of ammonia electro-oxidation will lead to the development of better
electrocatalysts thereby leading to the development of ammonia sensors with larger detection range, high sensitivity and longer life. Though the advantages of this technology are numerous, this is an upcoming technology that calls for more research in this field.

2.5. Scope for Research

Optimizing the anode, cathode, and electrolyte is essential to achieving a reliable source for sustainable power generation. The anode catalyst for ammonia electro-oxidation has been studied earlier [30], yet further research has to be dedicated to the improvement of this technology in order for it to be comparable to the existing technologies from every aspect, including ease of usability. Power consumption for the production of hydrogen has to be reduced, which can be achieved by

1. Understanding the mechanism for anodic ammonia electro-oxidation and cathodic reduction of water in the presence of ammonia.

<table>
<thead>
<tr>
<th>Principle</th>
<th>Lower detection limit</th>
<th>Response time</th>
<th>Temperature range</th>
<th>Remarks</th>
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<tbody>
<tr>
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<td>1 ppm</td>
<td>~5 min</td>
<td>400 °C</td>
<td>Low selectivity drift</td>
</tr>
<tr>
<td>Catalytic metal</td>
<td>1 ppm</td>
<td>~1 min</td>
<td>Up to 600 °C</td>
<td>Low selectivity</td>
</tr>
<tr>
<td>Palladium</td>
<td>1 ppm</td>
<td>~3 min</td>
<td>Up to 150 °C (regeneration)</td>
<td>Irreversible reactions</td>
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<tr>
<td>Conducting polymer</td>
<td>1 ppm</td>
<td>~5 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyamide</td>
<td>1 ppm</td>
<td>~5 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optical gas sensors</td>
<td>50 μM (90 nM)</td>
<td>~1 min</td>
<td>37 °C</td>
<td>For ammonia in water</td>
</tr>
<tr>
<td>Nessler</td>
<td>1 pt</td>
<td>~5 min</td>
<td></td>
<td>Expensive setup</td>
</tr>
<tr>
<td>Coulometry</td>
<td>1 ppm</td>
<td>~5 min</td>
<td></td>
<td>Large and expensive</td>
</tr>
<tr>
<td>Absorption spectroscopy</td>
<td>1 ppb</td>
<td>~5 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-selective detectors</td>
<td>100 ppt</td>
<td>~20 min</td>
<td>0–40 °C</td>
<td>Fluidic system</td>
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<tr>
<td>pH-transitions and EC detectors</td>
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</tbody>
</table>
2. Optimizing the materials used as electrocatalysts for both reactions and the electrolyte.

3. Engineering the electrolytic cell right from the electrode structure to the cell stack assembly.

2.6. Ammonia Electro-oxidation Reaction

2.6.1. Ammonia Electro-oxidation Mechanism on Pt

The mechanism for electrochemical oxidation of ammonia on platinum was first reported by Oswin and Salomon [31], it was and later modified by Gerischer and Mauerer [32]. The mechanism assumes the following steps:

\[
\begin{align*}
\text{NH}_3(\text{aq}) & \rightarrow \text{NH}_3,\text{ads} & (1) \\
\text{NH}_3,\text{ads} + \text{OH}^- & \rightarrow \text{NH}_2,\text{ads} + \text{H}_2\text{O} + e^- & (2) \\
\text{NH}_2,\text{ads} + \text{OH}^- & \rightarrow \text{NH}_{\text{ads}} + \text{H}_2\text{O} + e^- & (3) \\
\text{NH}_{x,\text{ads}} + \text{NH}_{y,\text{ads}} & \rightarrow \text{N}_2\text{H}_{x+y,\text{ads}} & (4) \\
\text{N}_2\text{H}_{x+y,\text{ads}} + (x+y)\text{OH}^- & \rightarrow \text{N}_2 + (x+y)\text{H}_2\text{O} +(x+y)e^- & (5) \\
\text{NH}_{\text{ads}} + \text{OH}^- & \rightarrow \text{N}_{\text{ads}} + \text{H}_2\text{O} + e^- & (6)
\end{align*}
\]

Where, \(x = 1 \text{ or } 2\), \(y = 1 \text{ or } 2\).

Though this mechanism gives a general idea of certain steps involved in the ammonia electro-oxidation, it is not complete. The ammonia oxidation in polycrystalline platinum starts at 0.45 V versus RHE and reaches a maximum at 0.7 V versus RHE as shown in Figure 2-2. According to Gerischer [32], step 6 is the most favorable path, where adsorbed nitrogen atom (\(N_{\text{ads}}\)) is formed, and is responsible for the drop in the
cyclic voltammetric currents after 0.6 V versus RHE. This N$_{\text{ads}}$ acts as a poison due to the fact that it is strongly bonded to the electrode surface until it gets released as NO$_x$ at potentials higher than 0.8 V versus RHE; this has been verified by the differential electrochemical mass spectroscopy (DEMS) study [33, 34]. It has also been proven that the electro-oxidation of ammonia in Pt is better on the (100) plane [35-37]. This is attributed the (100) plane favoring the formation of nitrogen at 0.33V according to step 4 and the formation of N$_{\text{ads}}$ in this plane is less favorable. Most studies conform to the above mentioned theory[33, 35].

**Figure 2-2.** Cyclic voltammogram of polycrystalline Pt in 0.1 M NaOH with (-) and without (--) the presence of 0.001 M NH$_3$[35]

Endo *et al.*, observed an uncharacteristic decrease in the peak current with increased rotation rates using a rotating disk electrode (RDE) for the electrochemical oxidation of ammonia on Pt as shown in Figure 2-3. This was attributed to the oxidizable intermediate species leaving the electrode rather than the N$_{\text{ads}}$ poisoning of the Pt
electrode evident from the drop in current during potentiostatic experiments at potentials early as -0.4 V versus Ag/AgCl electrode for rotating electrodes [38]. It will be interesting to see if this still holds for the Pt-Ir type electrodes, where the kinetics of ammonia electro-oxidation is reported to be better. A surface enhanced Raman spectroscopic study by Vidal-Iglesias et al., proves the presence of an azide anion during the electro-oxidation of ammonia, supporting the Gerischer mechanism which involves the reaction between hydrazine and ammonia leading to the formation of an azide ion [39]. Recently, Raman spectroscopic study has confirmed a second alternative mechanism proposed by Botte[40], where OH\(^-\) adsorption on the anode acts as a poison to ammonia electro-oxidation [41].

Mechanistic studies on ammonia electrolysis assume a simple Langmuir type ammonia adsorption on Pt electrode. However, it is hard to accept that is the case, especially since the adsorption of hydroxyl ions on the Pt is of a Frumkin type [42] and there could be interaction between the adsorbed hydroxyl ions and the ammonium ions.

*Figure 2-3.* Linear sweep voltammograms of Pt disk electrode in 0.1 M NH\(_3\) + 1 M KOH solution at various electrode rotation rates at 25°C and a scan rate of 5 mVs\(^{-1}\) [38]
From cyclic voltammograms for ammonia on Pt electrodeposited on Ni (Pt/Ni) electrodes, it can be observed that the electro-oxidation peak current increases as a function of the square root of the scan, which means that ammonia electrolysis is a mass transfer controlled reaction [43].

2.6.2. Choice of Electrocatalyst for Anode

The anode is where the electro-oxidation of ammonia occurs as shown below:

\[ 2\text{NH}_3 + 6\text{OH}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O} + 6e^- \quad E^0 = -0.770 \text{ V vs SHE} \quad (7) \]

The different types of catalysts that have been used for studying ammonia electrolysis are Pt black [44], Pt single crystal[33, 35], polycrystalline Pt[38, 41, 45], Rh, Ru, Pd, [46] Ni, [47] Ir, [48] Pt-bimetals (such as Pt-Ir, Pt-Ru, Pt-Rh, Pt-Pd, Pt-Ni, Pt-Cu catalysts) [46, 49, 50], and Pt electrodeposited on Ni[43].

Several studies, including those done by previous researchers at CEER confirm that Pt-Ir catalysts are better for the electro-oxidation of ammonia [46, 49, 50]. Recently, Moran et al., showed from XRD that the structure of the Pt-Ir electrode transformed after being used for ammonia electro-oxidation, however no further information has been provided to explain the causes for the transformation [51]. They have also not acknowledged or explained the occurrence of newer peaks after ammonia electro-oxidation as seen in Figure 2-4. It has been reported that the oxidation current reaches a peak value at potentials between 0.7 and 0.8 V versus RHE on Pt-Ir and the peak current for this electrode is smaller than that was observed on Pt alone [46, 49, 51]. This lower current value is attributed to Ir not being a good electrocatalyst for ammonia oxidation.
Nevertheless, it increases the potential range for operating the electrolytic cell. This is because $N_{\text{ads}}$ preferentially adsorbs on Ir, leaving some Pt sites open for ammonia oxidation [46, 49].

It has been found that the Pt-Ir electrode degrades over time, similar to those observed with the Pt electrode, when operated at potentials above 0.6 V versus RHE [49]. In addition, reversing the polarity of a cell, the anode can be recovered back to its original performance. Due to the existence of plenty of literature in this area this will not be a subject of research for this dissertation.

![XRD spectra for 60min Pt–Ir electrodeposit alloy on Au foil (a) before and (b) after using the catalysts for ammonia oxidation [51]](image)

**Figure 2-4.** XRD spectra for 60min Pt–Ir electrodeposit alloy on Au foil (a) before and (b) after using the catalysts for ammonia oxidation [51]

2.6.3. Choice of Electrocatalyst for Cathode

The cathodic reaction is the hydrogen evolution reaction (HER) in alkaline medium as shown below:

$$6\text{H}_2\text{O} + 6\text{e}^- \rightarrow 3\text{H}_2 + 6\text{OH}^- \quad E^0 = -0.828 \text{ V vs SHE} \quad (8)$$
The important criteria for selecting a material for the cathode will be the Tafel slope and the exchange current density. A low Tafel slope with a low overpotential and a high exchange current density would mean the catalyst is active for the particular reaction. At a current density of 230 mA cm\(^{-2}\) a overpotential value of 100 mV or greater for the HER is high according to industrial standards [52].

HER follows the Volmer-Heyrovsky-Tafel mechanism, according to which the low Tafel slopes would indicate that the desorption of the discharged proton is the rate determining step, and this can cause the hydrogen to diffuse into the catalyst causing hydrogen embrittlement. Tilak et al., evaluated a wide range of catalysts from noble metals (Pt, Ir, Ru, and Rh), non-noble metals (Fe, Ni, Co), doped catalyst such as as Pt doped Fe, semiconductors (Si, P, B, Bi, ZrO\(_2\) ) doped Ni, to alloys (Ni-Ir, Ni-Ru, Ni-W, Ni-Co), activated catalysts (Surface roughened Ni, Ni foam, Raney Ni, Ni-Sn, and Ni-Al deposits respectively). The low Tafel slope and low overpotential could be attributed to the high surface area. In fact the increase in surface area by a factor of six decreases the overpotential approximately 80-100 mV, while simultaneously increasing the exchange current density [52].

The reduction of water in alkaline media has been studied extensively. It has also been reported that alloying W or Mo to Ni or Co reduces the overpotential for the HER. It was also found that Co-Mo had a better activity and stability for the alkaline water electrolysis reaction [52].

Sheela et al. found that the effect of alloying Zn is to increase the surface area of Ni thereby enhancing the HER significantly[53]. A study showed that HER on Ni-15Mo
was considerably increased due to the synergistic effects that occurred when the electron density of states was in the d-orbitals which was modified when Ni was doped with Mo\[54\]. A theoretical study to determine the hydrogen evolution on various noble metals by Norksov \textit{et al.}, showed that Pt was the best catalyst based on a comparison of exchange current densities\[55\].

Table 2-2.

\textit{Tafel parameters for different materials for HER in alkaline medium}[52].

\begin{center}
\begin{tabular}{cccc}
\hline
 & \text{Low $\eta$ region} & \text{High $\eta$ region} & \text{Tafel slope (mV)$^\ast$} \\
\hline
\text{Exchange current density (mA/cm}$^2$) & \text{Low $\eta$ region} & \text{High $\eta$ region} & \text{Low $\eta$ region} & \text{High $\eta$ region} \\
Pt & 0.022 & 0.80 & 65 & 170 \\
Ir & 0.006 & 0-25 & 0-002 & 70 & 220 & 110 \\
Rh & 0-08 & 1-3 & 70 & 170 \\
Ru & 0-05 & 1-8 & 0-00001 (?) & 50 & 155 & 45 (?) \\
Fe & 0-014 & 0-24 & 100 & 170 \\
Co & 0-032 & 0-038 & 0-00001 & 120 & 135 & 40 \\
Ni & 0-009 & 0-003 & 130 & 100 \\
Ti & 0-02 & 0-80 & 120 & 240 \\
C & 0-0001 & 7 (?) & 120 & 700 (?) \\
W & 0-02 & 0-54 & 120 & 200 \\
Sn & – & 0-00002 & – & 140 \\
Re & 0-002 & 1-0 & 50 & 160 \\
Mo & 0-0013 & 0-01 & 96 & 120 \\
TiC & 1-2 & 0-35 & 0-0003 & 120 & 200 & 130 \\
WC & 0-015 & 0-13 & 100 & 160 \\
\hline
\end{tabular}
\end{center}

$^\ast$ Values obtained by extrapolation from the linear regions at low and high overpotentials ($\eta$).

Ni based electrodes are preferred to noble metal electrocatalysts due to their relative low-cost. However Ni based electrocatalysts and its alloys have a higher overpotential for HER [52]. But since the anode for ammonia oxidation has a surface poisoning effect at higher potentials (-0.1 V versus Hg/HgO) it would be safe for the electrolyzer to be operated at potentials below this value.
Even though Equation 8 is the same reaction observed at the cathode in alkaline water electrolysis and is widely studied, the effect of ammonia on the kinetics of the reaction is an area that is unexplored. Moreover it is essential to devote our attention in developing a cathode material most suited for ammonia electrolysis, which would lead to a higher hydrogen production rate before the anode reaches the potential of catalyst deactivation.

2.6.4. Choice of Electrolyte

The choice of an electrolyte is crucial to the performance of an electrochemical cell as it contains the reacting species. In addition, the electrolyte defines the pH, conductivity, and ionic mobility in the cell. It is prevalent in electrochemistry to add a secondary electrolyte to enhance the mobility of the reacting species. The supporting electrolyte is usually comprised of ions that have a high mobility and are non-reactive in the operating potential. The electrolyte in an alkaline ammonia electrolytic cell is ammonium hydroxide and aqueous KOH. The KOH in the electrolyte acts as a source for the OH\(^-\) ions for the anodic reaction. Consequently, the OH\(^-\) ions also provide the highest mobility amongst anions, therefore eliminating the need for a supporting electrolyte.

2.6.4.1. Aqueous Electrolyte

Electro-oxidation of ammonia is highly pH dependent. The increase in pH increases the rate of ammonia electro-oxidation. The rate of ammonia electro-oxidation is highest at KOH concentration of 5 M where the pH is greater than 14 [17, 18, 56]. This
has been attributed to the fact that ammonia electrolysis in alkaline medium is a direct electrochemical oxidation and occurs at a rate faster than both acidic and neutral mediums [17].

For the continuous remediation of wastewater, the supporting electrolyte needs to be added continuously into the inlet stream of the system. Therefore it is also required to separate the KOH from the remediated stream before it can be discharged. Moreover, from the vapor liquid equilibrium data for the ammonia-KOH-water system, the vapor pressure of ammonia increases along with the KOH concentration resulting from the common-ion effect. It is also noted that the OH− that is consumed at the anode is generated from the cathode. Therefore it would be beneficial to have a conducting matrix between the two electrodes that can rapidly transport the hydroxyl ions from the cathode to the anode.

2.6.4.2. Alkaline Polymer Gel Electrolytes (APGE)

Alkaline polymer gel electrolytes (APGE) are used in the alkaline battery industry as they exhibit conductivities comparable to the aqueous electrolyte and stable [57-59]. Using an APGE as the supporting electrolyte will:

1. Remove any parasitic power losses associated with pumping the viscous KOH.
2. Facilitate the ammonia to stay in the solution phase.
3. Avoid any KOH recovery costs associated with the ammonia removal from the wastewater as shown in Fig 2-5.
4. Make the system more compact, making the technology adaptable to portable applications.

APGE’s are widely used in electrochemical sensors, Ni-Metal Hydride[58, 60, 61], Ni-H₂, Ni-Cd[62], Ni-Zn[57, 63], Zn-Air batteries[64], electrochemical capacitors, solid state sensors, and other alkaline batteries. Polyvinyl alcohol (PVA)[65], polyethylene oxide (PEO)[59, 61, 62], polyacrylic acid (PAA)[66], Potassium salt of poly acrylate (PAA-K)[58], and polyepichlorhydrin(PECH) [64, 67] are some of the common polymers used in the synthesis of APGE (either alone or in combination with another polymer). It would be interesting to see how the APGE affects the performance of the ammonia electrolytic cell.

![Flow diagram for alkaline ammonia electrolyzer without and with APGE.](image)

**Figure 2-5.** Flow diagram for alkaline ammonia electrolyzer without and with APGE.

2.7. References


CHAPTER 3: EXPERIMENTAL BACKGROUND

3.1. Electrochemical Methods

3.1.1. Electrochemical Cell Setup

All electrochemical experiments were performed with a potentiostat (Solartron 1287) coupled with a frequency response analyzer (Solartron 1252A) with an electrochemical interface or a Aribin BT-2000 battery cycler.

3.1.1.1. Three-Electrode Setup

The three-electrode setup consists of a working electrode, i.e., the electrode to be evaluated, reference electrode to facilitate control of the potential for the working electrode, and the auxiliary electrode to sustain the balance of electrons for the reaction at the working electrode. mercury-mercuric oxide (Hg/HgO) electrode saturated with KOH (20% by weight), purchased from Koslow Scientific, was used as the reference electrode for measurements in alkaline solution, whereas an silver-silver chloride (Ag/AgCl) electrode with saturated KCl, purchased from Fisher Scientific, was used in acidic solutions. A glass-body luggin capillary was used to house the reference electrode in order to reduce the solution resistance and avoid contamination of the solution.

3.1.1.2. Two-Electrode Setup

A two-electrode cell setup consists of a working electrode and a counter electrode. It is usually used to evaluate the performance of the complete end product,
usually an electrolyzer. The potential for a two-electrode setup is reported with respect to the counter electrode and is termed as ‘cell voltage’.

3.1.2. Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV)

CV and LSV studies were performed in a 3-electrode cell. Each cycle for a CV experiment was carried out by scanning the potential of the working electrode from an initial value to a final value and back to the initial value. On the other hand, each cycle of the LSV experiment was carried out by a potential scan in the forward direction alone. The scan rate was chosen such as to maintain the reaction under kinetic-control by allowing enough time for the diffusion of fresh reacting species to the electrode surface. The cycles were repeated until a sustained periodic state was achieved. The results for the CV tests are presented with i-E curves, while the results for the LSV tests are presented using traditional Tafel plots (overpotential-log I plots).

3.1.3. Electrochemical Impedance Spectroscopy (EIS)

EIS studies were carried out in a 3-electrode cell. The EIS experiments were performed by applying a AC amplitude of 10 mA with a frequency range between 10 kHz and 0.1 Hz superimposed over a DC potential of interest. The electrodes were polarized at the DC potential for 15 min prior to the EIS measurements.
3.1.4. Constant Potential Studies

Constant potential studies were carried out in a 3-electrode cell. A constant potential was applied between the working electrode and the reference electrode for a specified time, while the current was continuously monitored.

3.1.5. Galvanostatic Experiments

Galvanostatic experiments were carried out in a 2-electrode cell. A constant current was applied between the working and counter electrodes in steps of 10 mA increasing progressively, while the voltage was continuously monitored. The duration for each step was three minutes.

3.2. Electrode Synthesis

The electrocatalysts used in this study were synthesized by electrodeposition onto two untreated Toray TGP-H-30 CFP, purchased from Electrochem Inc., of size 2 cm x 2 cm sandwiched on either side of an 18-mesh titanium gauze substrate of purity 99.9% (Alfa Aesar) as mentioned by Boggs and Botte previously [1]. The substrate was then degreased with acetone, washed with de-ionized water, dried thoroughly in an oven at 80°C and weighed using a microbalance with an accuracy of 0.1 mg, prior to and after the electrodeposition. The electrodepositions were conducted at constant potentials that were chosen based on metal ion reduction peaks in the CV as described in Appendix D. The electrodeposition was conducted in a 250 ml Pyrex-glass beaker on a stirring hot plate with an in-built thermocouple and a glass-ceramic surface from Corning®. The contents
of the beaker was stirred at 100 rpm using a magnetic stirrer bar to maintain uniform temperature and minimize mass transfer limitations; the temperature was maintained using the thermocouple in-built with the hotplate. A 5 cm x 5 cm Pt foil of thickness 0.01 cm and purity 99.999% (ESPI Metals) and an Ag/AgCl electrode with saturated KCl were used as the counter electrode and reference electrode, respectively.

3.3. Physicochemical Characterization:

The CFP electrodes were physically characterized using SEM, EDX, and XRD. Ammonia measurements were done using an ammonia ion selective electrode (ISE), while the gases produced during the reaction were analyzed using a gas chromatograph.

3.3.1. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX)

The surface morphological and elemental compositions of the electrodes were studied using SEM and EDX performed on a JEOL JSM 6390 scanning electron microscope coupled with a Genesis Apex EDS system available at the Institute for Corrosion and Multiphase Technology (ICMT) at Ohio University. The sample size was maintained at 1 cm x 1 cm. The SEM images were taken at different magnifications, while the EDX was performed on the whole sample.

3.3.2. X-Ray Diffraction (XRD) Studies

The signature crystallographic orientations of the synthesized electrodes were studied using a Rigaku Ultima IV X-ray diffractometer available at CEER. The
diffraction spectrum were collected by using Cu Kα (1.54 Å) radiation generated at 40 kV and 30 mA, at a goniometer rotation rate of 0.5 ° min⁻¹.

3.3.3. X-Ray Photoelectron Spectroscopy (XPS) Studies

XPS spectra for the catalysts were collected using a Monochromatic Al-Kα X-rays (hv = 1486.6 eV), which was used as the source from Kratos XSAM 800 instrument with VISION2 control. The instrument was calibrated prior to obtaining the XPS spectrum for the samples.

3.3.4. Ammonia and pH measurements

The ammonia concentration and pH were measured using a high performance ammonia ISE (No. 9512HPBNWP), and a pH electrode (No. 9172BNWP) respectively, in conjunction with an ISE/pH/mV/ORP meter (Model 710Aplus), which was obtained from Orion Research. The ISE and pH electrodes were calibrated with standard solutions prior to its use. The detection limit of the ISE was 0.01 ppm NH₃.

3.3.5. Gas Chromatography (GC)

The gases that were collected during the electrolysis experiments were analyzed by a SRI8610 gas chromatograph (GC) equipped with two columns (molecular sieve 13X and HayeSep D) and a thermal conductivity detector. Argon was used as the carrier gas with a flowrate of 25 ml min⁻¹. The GC was calibrated prior to use, first by injecting 10 ml calibration samples prepared by mixing samples from pure hydrogen (5.0UH)
methane (PDI 05925), pure carbon dioxide (PDI 05924), 6% by volume of carbon dioxide (PDI 05931), 1000 ppmv of nitrogen dioxide (PDI 05932), and 2000 ppmv of nitrogen oxide (PDI 05966) from Praxair. Following this the calibration was verified using Scotty 14 calibration gas mixtures Cat. No. 501697 with the composition in weight: 4% Hydrogen, 5% carbon dioxide (CO₂), 5% carbon monoxide (CO), 4.01% methane (CH₄), 5% nitrogen, 5.01% oxygen, and balance helium. The injector temperature was kept at 130°C and the oven temperature was maintained at 50°C for a stabilizing period of three minutes. The oven temperature was then set to increase at a rate of 5° min⁻¹ until it reached 150°C.

3.4. Electrochemical Characterization

The electrodes were primarily evaluated using CV, LSV, EIS, and constant potential techniques.

3.4.1. Pretreatment

All the electrodes were pretreated prior to the electrochemical measurement. Choice of a pretreatment procedure is dependent upon the nature of the electrocatalyst and the substrate, and it is crucial to obtaining reproducible results. The pretreatment was done in two stages: first by performing a CV in 1 M KOH solution at 50 mV s⁻¹ in the region where there is no oxide formation, until a sustained periodic state was achieved, so that any impurity that might hinder the electrochemical measurement in the potential range would be removed. Secondly, the electrode was subjected to a potential of -1.42 V
versus Hg/HgO saturated with KOH in 1 M KOH for 1 hour in order to remove any surface oxides that might have formed on the electrode, during the previous step or while drying [2]. Steps 1 and 2 were repeated until a reproducible surface was obtained.

3.4.2. Electrochemical Active Surface Area (EASA) Measurements

The EASA for a material is usually measured by evaluating the ratio of the charge required to form a monolayer of adsorbed hydrogen, or carbon monoxide, or copper, to the theoretical charge required to form the same monolayer on a unit surface area of that electrode [3]. It is also evaluated by measuring the double layer charge of a material. The choice of the technique to measure the EASA of a material is particularly important to its validity. Care should be taken when choosing a method to measure the EASA, so that it is not obscured by secondary parallel reactions thereby leading to the erroneous reporting of the EASA. For example, the oxygen adsorption on Ru interferes with the hydrogen adsorption rendering the EASA measurements for Ru, with hydrogen adsorption, erroneous [3]. The EASA for Pt and Rh were evaluated by measuring the hydrogen adsorption charge in 0.5 M sulfuric acid,[3-6] while the EASA for Ni was evaluated by the charge required to produce $\alpha$-Ni(OH)$_2$ in 1 M KOH [7].

3.4.2.1 Hydrogen Adsorption Voltammetry

The 0.5 M sulfuric acid solution was deaerated by bubbling argon gas (99.999% purity) from Praxair for 15 minutes prior to the measurements. A CV was performed with a 25 cm$^2$ Pt foil, Ag/AgCl saturated with KCl reference electrode and a potential scan rate
of 50 mVs$^{-1}$. Figure 3-1 (A) through (B) show the steady state voltammograms for Pt and Rh, electrodes respectively, in 0.5 M H$_2$SO$_4$ and 1 M KOH, respectively. The area under the hydrogen adsorption peaks corresponds to the charge for a monolayer hydrogen adsorption.

![Figure 3-1](image.png)

**Figure 3-1.** EASA measurements by Hydrogen Adsorption Voltammetry for (A) Pt and (B) Rh electrodes using CV in a solution of 1 M KOH and a 5 cm x 5 cm Pt foil counter electrode at a potential scan rate of 50 mV s$^{-1}$ at STP. The scan range for the Rh electrode (Figure 3-1B) was chosen such that the surface oxide formation and subsequent growth of the oxide layer is prevented.

### 3.4.2.2 Carbon Monoxide (CO) Stripping Voltammetry

CO stripping voltammetry was used to measure the EASA for Ru and to verify the EASA for Pt obtained via hydrogen adsorption.[8, 9] The CO stripping voltammetry was carried out under a fume hood. Carbon monoxide gas of purity 99.9% from Praxair was used. The electrode was held at a constant potential of 25 mV versus RHE in the respective test solution (1 M KOH for Pt and 0.5 M H$_2$SO$_4$ for Ru) saturated with carbon monoxide. The solution was then purged with argon gas for 15 minutes, while continuing
to hold the electrode at the same potential. Thereafter, CV tests were carried out on the working electrode in the CO electro-oxidation region.

**Figure 3-2.** EASA measurements by CO Stripping Voltammetry for (A) Pt and (B) Ru electrodes using CV in a solution of 0.5 M H₂SO₄ and a 5 cm x 5 cm Pt foil counter electrode at a potential scan rate of 50 mV s⁻¹ at STP.

The CVs for EASA measurement were carried out with a 5 cm x 5 cm Pt foil counter electrode at a scan rate of 50 mV s⁻¹. The sustained periodic state in the voltammograms was obtained after 5 cycles. Cyclic voltammograms for evaluating the EASA shown in Figures 3-2 (A) and 3-2 (B) represent the CO stripping voltammograms for platinum and ruthenium in 0.5 M H₂SO₄. The (-) solid line represents the first positive-going sweep and the (- -) dashed line represents the first negative going sweep and the subsequent positive sweep.

The EASA of Ni, like Rh, is convoluted by the formation of different phases of hydroxides and oxy-hydroxides. Of those, the α-phase hydroxide is known to be
reversible and occurs at potentials as low as 0.25 V versus RHE. However, the $\alpha$-Ni(OH)$_2$ transforms into a more irreversible $\beta$-Ni(OH)$_2$ at more positive potentials. In a recent study, Grdeñ et al., gives a thorough evaluation of the EASA of Ni, by using X-ray photoelectron spectroscopy and impedance spectroscopy to quantify any contribution to the EASA from hydroxides. However, from Figure 3-3, it can be observed that Ni is present in its metallic form and therefore EASA can be evaluated based on the charge required for the formation of a monolayer of reversible Ni(OH)$_2$ from Ni.

**Figure 3-3.** EASA measurements for Ni electrode in a solution of 1 M KOH and a 5 cm x 5 cm Pt foil counter electrode at a potential scan rate of 50 mV s$^{-1}$ at STP.

3.5. References

CHAPTER 4: EFFECT OF AMMONIA AND HUPD ON THE KINETICS OF HER ON PT, RU, RH, AND NI ELECTRODES

(Part of the contents of this chapter has published by the Journal of Physical Chemistry C [81]. Ramasamy Palaniappan (R.P.) and Gerardine G. Botte (G.G.B.) developed the idea and designed the experiments. R.P. performed the experiments and data analyses. R.P. and G.G.B. discussed the results and co-wrote the paper.)

4.1. Introduction

The history of ammonia electrolysis dates back to 1836 and possibly beyond that [1]. Recent developments in electrocatalysts for ammonia electro-oxidation have led to the recognition of ammonia as a safe and clean hydrogen carrier for distributed power generation [2-7]. It facilitates a robust and economical method to produce hydrogen as opposed to the traditional high temperature cracking of ammonia and high-energy consuming water electrolysis processes. The reactions for an ammonia electrolytic cell consist of ammonia electro-oxidation at the anode and alkaline water reduction at the cathode as shown in Equations 1-3 (vide infra) [8]. Pt and Pt-Ir alloys have been identified as the most suitable electrocatalysts for the oxidation of ammonia [9-12]. The anodic electro-oxidation of ammonia has been identified as the limiting reaction for this process, as it reaches a maximum at 0.6 to 0.8 V versus reversible hydrogen electrode (RHE) on polycrystalline Pt [12-14]. On the other hand, the cathodic hydrogen evolution reaction (HER), shown in Equation 2, is known for its facile kinetics.
In order to realize higher efficiencies it is required to operate the electrolytic cell at voltages such that the potential at the anode is maintained below its limiting potential. It is desired that cathode electrocatalysts facilitate high hydrogen production efficiencies at such voltages. Previous studies have reported the operation of an ammonia electrolyzer stack in a divided cell mode, where the anolyte containing ammonia and ammonia-free catholyte are fed in separate compartments [15, 16]. However, during the electrolysis of ammonia, traces of ammonia can diffuse into the cathodic compartment at the rate of $6.33 \times 10^{-8}$ mol cm$^{-2}$ s$^{-1}$ [17]. It has also been noticed that the pH of the anode compartment drops while that at the cathode compartment is found to increase during a single pass of the electrolyte in an ammonia electrolyzer [16].

Operating the electrolytic cell in a continuous stirred tank type mode would help alleviate the problems associated with the divided-cell electrolyzer, which implies that the concentration of ammonia at the cathode is the same as that at the anode. Therefore, it is critical that the presence of ammonia does not provide any detrimental effect on the stability of the catalyst and its activity towards HER. An understanding of HER kinetics on the electrocatalyst is vital to comprehend the effect of ammonia on the HER for that material. HER has been a subject of interest for over two centuries, since the invention of water electrolysis. Ever since Horiuti published on the matter, [18, 19] numerous researchers have independently studied the reaction and have made significant

\[
\begin{align*}
\text{Anode:} & \quad 2\text{NH}_3 + 6\text{OH}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O} + 6\text{e}^- \quad E^0 = -0.770 \text{ V vs SHE} \\
\text{Cathode:} & \quad 6\text{H}_2\text{O} + 6\text{e}^- \rightarrow 3\text{H}_2 + 6\text{OH}^- \quad E^0 = -0.828 \text{ V vs SHE} \\
\text{Overall:} & \quad 2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 \quad E^0 = 0.058 \text{ V}
\end{align*}
\]
contributions to the mechanism of HER [20-25]. HER has played an important role in the development of electrochemical principles, including the famous Butler-Volmer equation in 1924 [26].

A wide range of materials has been tested for their efficacy as electrocatalysts for the HER in alkaline media, of which the group IV metals in the periodic table (Fe, Co, Ni, Cu) and their alloys have received predominant attention [27-41]. They are preferred to noble metal based cathodes for the HER due to their relative low-cost. Nevertheless, they have drawbacks owing to their ease of deactivation, high overpotentials, and low activity towards HER [42, 43]. A wide variety of noble metals (including Pt, Ir, Rh, Ru, Pd) and their alloys, [27, 44-48], oxides[25, 49] and perovskites have been evaluated for activity towards HER. Studies range from theoretical modeling, such as quasi steady state calculations,[50] density functional theory studies,[24] and volcano plot (exchange current density for hydrogen evolution versus enthalpy of formation of M-H bond) simulations,[21] to experiments utilizing cyclic voltammetry (CV), linear sweep voltammetry (LSV), [27, 51] constant potential and electrochemical impedance spectroscopy (EIS) [52, 53]. In addition, it has been reported that the HER is sensitive to the electrocatalyst crystal structures [54, 55].

\[
\text{Volmer: } M + H_2O + e^- \rightleftharpoons MH + OH^- \quad (4) \\
\text{Heyrovsky: } MH + H_2O + e^- \rightleftharpoons M + H_2 + OH^- \quad (5) \\
\text{Tafel: } 2MH \rightleftharpoons 2M + H_2 \quad (6)
\]
The HER proceeds through Volmer-Heyrovsky-Tafel (VHT) mechanism in both acidic and alkaline environments [26, 27, 53]. The mechanism in the alkaline medium is shown in Equations 4-6. The Heyrovsky (or electrochemical desorption) step and the Tafel (or chemical recombination) step are parallel and competing reactions. It is important to know which of these steps will be rate determining as it determines the stability of the electrode. The extent of the reaction proceeding through one of the two steps should be directly related to the resistance of the other (i.e., the reaction will proceed via the step with a lower resistance or a higher rate constant), which can be evaluated by potential decay and EIS.

EIS is one of the standard techniques to estimate the impedance of various components of an electrochemical reaction and therefore rate constants for the steps involved in the mechanism [52, 53, 56-58]. Armstrong and Henderson derived the equivalent circuits for a two-step electrochemical reaction with one intermediate in the absence of diffusion control by evaluating the impedance from their corresponding rate equations [59]. Harrington and Conway extended this procedure to derive the impedance equations for the three-step HER and subsequently verified the validity of the equations using complex plane plots obtained from EIS experiments using Pt electrodes in 0.5 M sodium hydroxide solution [52, 60].

So far, the effect of ammonia on HER has not been reported. This can be better understood by evaluating the kinetic parameters such as Tafel slope (TS), exchange current density ($i_0$), and rate constant, in the presence and absence of ammonia. Based on an extensive theoretical study, Greeley et al., concluded that Pt, Ir, Rh, Ru, Pd, Ni, and
Co displayed high activities for HER [24]. In addition, Pt, Rh, Ru, and Ni continued to show high activities for HER, when alloyed with wide range of transition materials [52, 60].

Within this context, the objective of this chapter is to determine the effect of ammonia on the alkaline HER kinetics on Pt, Ru, Rh, and Ni electrocatalysts using voltammetric, AC impedance and current transient techniques [24]. It has been shown that potassium hydroxide (KOH) solution exhibits maximum ammonia electro-oxidation rate at a concentration of 5 M, therefore it was chosen for our studies. Carbon fiber paper (CFP) substrates were used for electrodeposition of the catalysts as they demonstrated a better performance for the electrolysis in alkaline medium [4, 9]. In order to address the main objective the following tasks were performed:

1. Pt, Rh, Ru, and Ni electrodes were prepared by electrodeposition onto CFP substrates. The electrodes were then characterized using scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, and X-ray diffraction (XRD) while the electrochemical active surface area (EASA) was determined using CV.

2. The kinetic parameters of the electrodes for HER in aqueous 5 M KOH were determined in the presence and absence of ammonia using LSV and EIS techniques.

3. The effects of ammonia on long-term stability of the electrocatalysts were evaluated using constant potential experiments.
4.2. Materials and Methods

All of the chemicals used in this study were of analytical grade and were obtained from Alfa Aesar. All the experiments were repeated in order to check for reproducibility and the errors reported in the chapter were calculated through error propagation, taking into account the instrumental error and standard deviations in the measurements. All electrochemical experiments were performed with a potentiostat (Solartron 1287) coupled with a frequency response analyzer (Solartron 1252A) with an electrochemical interface. Hg/HgO saturated with KOH (20% by weight), purchased from Koslow Scientific, was used as the reference electrode for measurements in alkaline solution, whereas an Ag/AgCl electrode saturated with KCl, purchased from Fisher Scientific, was used in acidic solutions. A glass-body luggin capillary was used to house the reference electrode in order to reduce the solution resistance and avoid contamination of the solution.

4.2.1. Electrode Preparation and Physical Characterization

The electrocatalysts used in this study were prepared by electrodeposition onto two untreated Toray TGP-H-30 CFP, purchased from Electrochem Inc., of size 2 cm x 2 cm sandwiched on either side of an 18-mesh titanium gauze substrate of purity 99.9% (Alfa Aesar) as reported by Boggs and Botte [9]. The substrate was then degreased with acetone and rinsed with de-ionized water, dried in an oven at 80°C and weighed using a microbalance with an accuracy of 0.1 mg, prior to and after the electrodeposition.
The electrodepositions were conducted at constant potentials that were chosen based on metal ion reduction peaks in the CV as described in Appendix D. The conditions for Pt, Rh, Ru, and Ni electrodeposition are detailed in Table 4-1. The electrodeposition experiments were conducted in a 250 ml Pyrex glass beaker on a stirring hot plate with a built-in thermocouple and a glass-ceramic surface from Corning. The constant potentials used for electrodeposition are also provided in Table 4-1.

**Table 4-1.**

Electroplating solution composition, operating conditions, and results for constant potential electrodeposition of Pt, Rh, Ru, and Ni on untreated carbon fiber paper (Toray TGP-H-30) substrate. Electrodeposition was carried out for all catalysts until a loading of 5 mg was achieved, except iridium for which there was no appreciable mass gain after 2 hours.

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrodeposition Solution Composition</th>
<th>Temp (°C)</th>
<th>E (V) vs Ag/AgCl</th>
<th>Average Current Density (mA cm(^{-2}))</th>
<th>Total Deposition Time (s)</th>
<th>Loading (± 0.1 mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>H(_2)PtCl(_6) - 3 g l(^{-1})</td>
<td>78</td>
<td>-0.100</td>
<td>-4.328</td>
<td>1000</td>
<td>5.1</td>
</tr>
<tr>
<td>Rh</td>
<td>RhCl(_3) - 3 g l(^{-1})</td>
<td>78</td>
<td>0.01</td>
<td>-1.879</td>
<td>2500</td>
<td>5.5</td>
</tr>
<tr>
<td>Ru</td>
<td>RuCl(_3) - 3 g l(^{-1})</td>
<td>78</td>
<td>-0.200</td>
<td>-3.472</td>
<td>4000</td>
<td>5.8</td>
</tr>
<tr>
<td>Ni</td>
<td>NiSO(_4).6H(_2)O - 280 g l(^{-1}); NiCl(_2).6H(_2)O - 40 g l(^{-1})</td>
<td>40</td>
<td>-0.800</td>
<td>-7.537</td>
<td>240</td>
<td>5.3</td>
</tr>
</tbody>
</table>

The contents of the beaker were stirred at 100 rpm using a magnetic stirrer bar to maintain uniform temperature and minimize mass transfer limitations; the temperature was maintained using the thermocouple built-in with the hotplate. A 5 cm x 5 cm Pt foil of thickness 0.01cm and purity 99.999% (ESPI Metals) and an Ag/AgCl electrode
saturated with KCl were used as the auxiliary and reference electrodes, respectively. The electrodepositions were carried out until a loading of 1.25 mg cm\(^{-2}\) was obtained. The CFP on one side of the sandwich was cut for physical characterization of the electrode, which was used for surface morphology by SEM and elemental analysis by EDX studies using a JEOL JSM 6390 scanning electron microscope. The signature crystallographic orientation of the synthesized electrodes were studied using XRD on a Rigaku Ultima IV using Cu K\(\alpha\) (1.54 Å) radiation generated with 40 kV and 30 mA, at a goniometer rotation rate of 0.5° min\(^{-1}\).

4.2.2. Pretreatment and EASA Measurements

All the electrodes were pretreated prior to the electrochemical measurement. Choice of a pretreatment procedure is dependent upon the nature of the electrocatalyst and the substrate and is crucial to obtaining reproducible results. The pretreatment was performed in two stages: first by performing a CV in 1 M KOH solution at 50 mV s\(^{-1}\) in the region where there is no oxide formation, until a sustained periodic state for the voltammogram was achieved, so that any impurity that might hinder the electrochemical measurement in the potential range would be removed. Second, the electrode was subjected to a potential of -1.42 V versus Hg/HgO in 1 M KOH for 1 hour in order to remove any surface oxides that might have formed on the electrode, during the previous step or while drying [35]. Steps 1 and 2 were repeated until a reproducible surface was obtained.
The electrodes were then subjected to EASA measurements followed by the CV, LSV, and EIS studies. The EASA for Pt and Rh were evaluated by measuring the hydrogen adsorption charge in 0.5 M sulfuric acid,[61-64] while the EASA for Ni was evaluated by the charge required to produce $\alpha$-Ni(OH)$_2$ in 1 M KOH using CV [65]. The solution was deaerated by bubbling argon gas (99.999% purity, from Praxair) at 15 ml min$^{-1}$ for 15 minutes prior to the measurements.

Carbon monoxide (CO) stripping voltammetry was used to measure the EASA for Ru and to verify the EASA for Pt obtained $via$ hydrogen adsorption [66, 67] [68]. The CO stripping voltammetry was carried out under a fume hood. The test solution (1 M KOH for Pt and 0.5 M H$_2$SO$_4$ for Ru) was saturated with carbon monoxide, of purity 99.9% from Praxair, which is evident from the open circuit voltage reaching steady state. The electrode was held at a constant potential of 25 mV versus RHE in the respective test solution. The solution was then purged with argon gas for 15 minutes, while continuing to hold the electrode at the same potential. Thereafter, CV tests were carried out on the working electrode in the CO electro-oxidation region. The CV for EASA measurement was carried out with a 5 cm x 5 cm Pt foil auxiliary electrode at a scan rate of 50 mV s$^{-1}$. The sustained periodic state for the voltammograms was obtained after 5 cycles.

4.2.3. Electrochemical Characterization

The CV, LSV, EIS, and constant potential experiments were carried out with a 3-electrode setup in 5 M KOH solution in the presence and absence of 1 M ammonia. A 5 cm x 5 cm Ni gauze (100 mesh woven from 0.1 mm diameter wire, Alfa Aesar) was used
as the counter electrode for each experiment. The Ni gauze was sandblasted using a micro sand blaster (Swam Blaster, Crystal Mark Inc.,) with alumina (size 27.5 µm, purchased from Crystal Mark Inc.,) for two minutes, then degreased with acetone and rinsed with de-ionized water.

The CV tests were carried out by scanning the potential from -1.1 V to 0.1 V versus Hg/HgO and back at 10 mV s⁻¹. While the LSV experiments were carried out by scanning the potential between -0.9 V to -1.3 V versus Hg/HgO at 1 mV s⁻¹. The low scan rate of 1 mV s⁻¹ was sufficient to maintain the reaction under kinetic-control by allowing enough time for the diffusion of fresh reacting species to the electrode surface. Sustained periodic results were obtained for both CV and LSV after the 5th scan.

The EIS experiments were performed by applying an AC amplitude of 10 mA with a frequency range between 10 kHz and 0.1 Hz superimposed over a DC potential -1.1 V versus Hg/HgO in the HER region. The electrodes were polarized at the DC potential for 15 minutes prior to the EIS measurements.

Constant potential experiments were carried out in a solution of 5 M KOH in the presence and absence of ammonia at a potential of -1.1 V versus Hg/HgO for three hours.

4.3. Results and Discussion

4.3.1. Electrodeposition and Physical Characterization

Pt, Rh, Ru, and Ni were successfully deposited on the CFP electrodes and verified by an increase in the electrode mass as well as by SEM and EDX studies. The results for the electrodeposition (average current and catalyst loading) are reported along with the
electrodeposition solutions and conditions in Table 4-1. SEM and EDX results for the electrodes after electrodeposition are reported in Figure 4-1. The SEM images for Pt, Rh, and Ni show globule type deposition with the size of each globule in the range 10 nm to 100 nm and pertaining to carbon fibers in the first two layers, consistent with the literature. On the other hand, the SEM image for Ru shows a layer type deposition. The EDX images show that the electrodes are predominantly comprised of respective metal along with carbon from the substrate and trace amounts of oxygen that occurred as a result of exposure to atmosphere. The slightly higher oxygen content on the nickel electrode could be attributed to the existence of hydroxides.

**Figure 4-1.** EDX for metals plotted in intensity (cps) versus binding energy (keV) Pt, Rh, Ru, and Ni are labeled A1, B1, C1, and D1 respectively. The SEM images of the corresponding metals at 2500x are A2, B2, C2, and D2. It can be observed that the plating occurs in a globule-type fashion occurring uniformly along the lengths of the carbon fibers for all but Ru, where the deposition occurred in a more layered structure.
The EASA for the catalysts were evaluated as mentioned in the Chapter 3 (Section 4.3.4.2). Table 4-2 provides the results of the EASA, the specific area of the catalysts and the method adopted to evaluate the EASA. The EASA for Pt obtained using CO stripping voltammetry agreed to that obtained using the hydrogen adsorption method, providing credence to the technique used. It can be observed that Ru displayed the highest EASA and roughness, consistent with the SEM images, which indicate a rough layer type deposition that is equally prevalent in the gaps between the carbon fibers. The high EASA for Ru and Rh is attributed to the smaller particle size of the deposits. The results reported in this study, unless mentioned otherwise, have been normalized with respect to the EASA.

Table 4-2.
Electrochemical active surface area for Pt, Rh, Ru, and Ni electrodeposited on carbon fiber paper. Errors reported were calculated through error propagation using instrumental errors for current and voltage. Ru had the highest surface area among the electrodes prepared.

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Charge (± 7 µC)</th>
<th>Specific Charge (µC cm⁻²)</th>
<th>Surface Area (±1.01 cm²)</th>
<th>Roughness Factor (± 0.04)</th>
<th>Specific Area x10⁻³ (± 0.02 cm² g⁻¹ catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>CO Stripping</td>
<td>68643</td>
<td>420</td>
<td>181.60</td>
<td>45.40</td>
<td>35.61</td>
</tr>
<tr>
<td>Pt</td>
<td>H_ads</td>
<td>37262</td>
<td>210</td>
<td>177.44</td>
<td>44.36</td>
<td>34.79</td>
</tr>
<tr>
<td>Rh</td>
<td>H_ads</td>
<td>92959</td>
<td>221</td>
<td>420.63</td>
<td>105.16</td>
<td>76.48</td>
</tr>
<tr>
<td>Ru</td>
<td>CO Stripping</td>
<td>289529</td>
<td>420</td>
<td>689.35</td>
<td>172.34</td>
<td>118.85</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni--&gt;Ni²⁺</td>
<td>116834</td>
<td>514</td>
<td>227.30</td>
<td>56.83</td>
<td>47.35</td>
</tr>
</tbody>
</table>
4.3.2. Voltammetry Studies

Figure 4-2 illustrates the Tafel plots for the catalysts under investigation in 5 M KOH in the presence and absence of 1 M ammonia. It can be observed from Figure 4-2 that the noble metals exhibit two different Tafel slopes (TS) in the region below and above -200 mV. However, for Ni, two different TS were measured in regions below and above -240 mV. This is in agreement to that observed by Vilekar et al., based on quasi-steady state theory [50].

Figure 4-2. Tafel plots for steady state linear sweep voltammograms for Pt, Rh, Ru, and Ni in 5 M KOH in the presence and absence of 1 M ammonia. Voltammograms without ammonia are shown by dashed lines (--) while solid lines (-) represent the presence of ammonia. Inset to figure represents the data in the region of interest -110 mV to -250 mV for enhanced clarity. Current densities ($i_{\text{real}}$) were evaluated based on the electrochemical active surface area. Voltammograms were carried out at a potential scan rate of 1 mVs$^{-1}$.

The TS in the low overpotential (< 200 mV) region has been attributed to the reaction proceeding through Volmer-Tafel pathway, while the TS at high overpotential (>
200 mV) is due to Volmer-Heyrovsky path.[50] The Tafel constants were estimated by fitting the LSV data to the Tafel equation after correcting for the IR drop using linear regression with a 95% confidence level.

The HER kinetics at the low overpotential region is of particular interest to ammonia electrolysis as one tries to achieve maximum hydrogen production at low cell voltages and prevent the anode of the electrolytic cell from reaching its limiting potential. In addition, it was observed that at high overpotentials the difficulty for hydrogen to escape the wet surface of the untreated CFP electrode was enhanced. Consequently, it is also observed that the high TS that accompanies the high $i_0$ at high overpotentials, implying that the HER currents in this region is masked by diffusion. Therefore, only the Tafel parameters (TS and $i_0$) calculated at the lower overpotential region (between -118 mV and -200 mV) will be used in this study. The Tafel constants along with the overpotentials at current density of 0.25 mA cm$^{-2}$ (corresponding to a hydrogen evolution rate of 1.73 l h$^{-1}$ for an electrode with EASA 1 m$^2$) are reported in Table 4-3. The overpotential at 0.25 mA cm$^{-2}$, without ammonia, follows the order Pt<Ru<Rh<Ni, whereas the exchange current densities followed the trend Pt>Rh>Ru>Ni in this region.

In the absence of ammonia, Pt displayed the least overpotential and highest $i_0$ amongst the catalysts studied, confirming the highest activity of Pt for HER as seen from the volcano plots. The TS obtained for the catalysts in 5 M KOH in the absence of ammonia in the low overpotential region increased in the order Ni<Ru<Pt<Rh. The TS for the noble metal catalysts follow the trend observed by Fournier et al., for the same catalysts embedded in a porous LaPO$_4$ matrix in 1 M KOH [69].
Table 4-3.

Tafel parameters obtained from linear sweep voltammetric studies for Pt, Rh, Ru, and Ni electrodes in 5 M KOH in the presence and absence of ammonia. The Tafel slope and exchange current density were calculated for cathodic HER at the low overpotential region. The exchange current density and the overpotentials at 0.25 mA cm$^{-2}$ were evaluated based on the electrochemical active surface area (EASA) of the catalyst.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ammonia Concentration (M)</th>
<th>Tafel Slope (±3 mV / decade$^{-1}$)</th>
<th>Exchange Current Density (±0.002 mA cm$^{-2}$)</th>
<th>Overpotential, $\eta$, $i_{\text{esa}}$=0.25 mA cm$^{-2}$ (± 1 mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>0</td>
<td>-157</td>
<td>0.043</td>
<td>-125</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-171</td>
<td>0.031</td>
<td>-152</td>
</tr>
<tr>
<td>Rh</td>
<td>0</td>
<td>-220</td>
<td>0.040</td>
<td>-162</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-219</td>
<td>0.069</td>
<td>-125</td>
</tr>
<tr>
<td>Ru</td>
<td>0</td>
<td>-140</td>
<td>0.021</td>
<td>-147</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-222</td>
<td>0.047</td>
<td>-159</td>
</tr>
<tr>
<td>Ni</td>
<td>0</td>
<td>-95</td>
<td>0.0005</td>
<td>-255</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-108</td>
<td>0.001</td>
<td>-260</td>
</tr>
</tbody>
</table>

Lower TS indicate higher hydrogen evolution rate for an increase in overpotential. Although Ni has the lowest TS, it also has the highest overpotential at a current density of 0.25 mA cm$^{-2}$ as well as an $i_0$ at least 100 times lower than the other catalysts. The higher overpotentials exhibited by Ni electrodes could be due to the existence of hydroxides even at potentials as low as -1.0 V versus Hg/HgO confirmed by Silverman in the revised EMF-pH diagrams for the Nickel-Water system [70]. The existence of hydroxides results in a high activity for the electrochemical dissociation of water. However, it also exhibits a considerably low activity for the desorption steps, resulting in the formation of hydrides thereby leading to the deactivation of Ni.
It can also be observed from Figure 4-2 that, in the presence of ammonia, the overpotential-log i behavior for the catalysts continue to exhibit a low TS in the low overpotential region and a high TS in the high overpotential region. This behavior is similar to that without ammonia, implying that the VHT mechanism still applies to the HER in the presence of 1 M ammonia. It can be noticed that the overpotentials for Pt (Figure 4-2 A), Ru (Figure 4-2 B), and Ni (Figure 4-2 D) are higher due to a partial surface deactivation reaction in the presence of ammonia [69].

**Figure 4-3.** Cyclic voltammograms for (A) Pt, (B) Rh, (C) Ru, and (D) Ni in 5 M KOH with the presence and absence of 1 M ammonia. (-) Solid lines indicates presence of ammonia while the (- -) dashed lines indicate the absence of it. The voltammograms shown above are representative of the steady state cycle achieved at the 5th cycle and at a potential scan rate of 10 mVs$^{-1}$. It can be seen that in the presence of ammonia all the Hupd peak is more pronounced and occurs at a slightly more negative potential for all the catalysts.
However, the overpotentials observed for HER on Rh with 1 M ammonia are lower than that observed without ammonia, this could be attributed to another reaction contributing to the HER currents or surface activation thereby increasing the HER on Rh. From Table 4-3 it can be noted that the overpotentials for HER at 0.25 mA cm\(^{-2}\) in 5 M KOH with 1 M ammonia follows the trend: Rh<Pt<Ru<Ni.

The cyclic voltammograms for Pt, Rh, Ru, and Ni in 5 M KOH with 1 M ammonia and ammonia-free solutions in the region preceding the HER, shown in Figures 4-3A through 4-3D, provide a deeper insight to the surface process. It is known that catalyst utilization and the kinetics for HER are dependent upon the surface coverage of the overpotential deposited hydrogen (H\(_{\text{upd}}\)) which is weakly bonded to the catalyst surface and is considered to be the actual intermediate for the HER.[23, 52, 53] \(E_0\) of \(H_{\text{upd}}\) is in turn dependent upon the potential for the hydrogen underpotential deposition (H\(_{\text{upd}}\)), i.e., the hydrogen that is adsorbed at potentials lower than equilibrium potential (\(E^0\)) as shown in Equation 7. It is agreed upon that the H\(_{\text{upd}}\) is strongly bound to the catalyst surface [23, 52].

\[
M + H_2O + e^- \rightleftharpoons MH_{\text{upd}} + OH^- \quad E < E^0
\]  

where, \(E^0 = 0\) V versus SHE. The potential of occurrence for the H\(_{\text{upd}}\) is indicative of the strength of the metal-H\(_{\text{upd}}\) bond, i.e., the more positive it is, relative to the HER, the stronger the metal-H\(_{\text{upd}}\) bond will be [23, 71, 72]. However, the role of the H\(_{\text{upd}}\) on HER is a controversial subject, with opposing views: Markovic et al.[23] reported that the strong H\(_{\text{upd}}\) hinders the HER, while Conway et al. claims that the presence of H\(_{\text{upd}}\)
enhances the rate of HER [20, 71, 72]. Coincidentally, by evaluating the shift in the $H_{\text{upd}}$ peaks that arises due to the addition of ammonia and relating the shifts in potential for $H_{\text{upd}}$ formation to the changes in HER kinetics provides important information to understand the role of $H_{\text{upd}}$.

In the absence of ammonia, the CV for Pt (Figure 4-3A) shows three reversible peaks A01, A02, and A03 associated with $H_{\text{upd}}$ in the Pt (111), Pt (100) planes, and the reduction of the surface oxide or $\text{OH}^-$ ion desorption for Pt, respectively [23, 73]. However, the CV for Rh and Ru, in the absence of ammonia were similar [45, 67]. The cathodic peaks B01, B02 (Figure 4-3B) for Rh and peaks C01, C02 (Figure 4-3C) for Ru can be attributed to the $H_{\text{upd}}$ and the reduction of the metal-oxide that was formed during the forward scan, thereby implying that the overpotential for $H_{\text{upd}}$ follows the trend Pt$>$Rh$>$Ru. On the other hand, the CV for Ni indicates a small plateau type feature at D01, attributed to the reduction of the Ni(OH)$_2$ [74, 75]. However, the absence of a distinct reduction peak indicates the transformation of Ni(OH)$_2$ from the reversible $\alpha$-phase to an irreversible $\beta$-phase. The presence of oxides for Ni at such low potentials can be verified by the Pourbaix diagram and obviates the existence of $H_{\text{upd}}$ [70].

The voltammograms in the presence of ammonia display three distinctive features: (1) the absence of the metal-oxide reduction, (2) the significantly larger cathodic currents in the $H_{\text{upd}}$ region between -0.4 V to -0.9 V, and (3) the presence of an additional reduction peak. The absence of the metal oxide desorption peak indicates the removal of oxides by taking part in the ammonia electro-oxidation reaction or its masking by the significantly larger ammonia electro-oxidation currents.
For Pt, the potential scan in the positive direction shows a peak A14 corresponding to the adsorption of ammonia and another at -0.25 V corresponding to the onset of ammonia electro-oxidation. Upon evaluating the charges under the reversible peak A11-A11’, after accounting for the double layer and desorption of ammonia, this agrees with the charge required for H\text{upd} in the absence of ammonia, implying that the peak A11 is due to H\text{upd}. The additional reduction peaks A12 and A13 can be attributed to the reduction of the intermediates of ammonia oxidation and ammonia desorption as verified by stripping studies by Vooys et al. [12] and differential electrochemical mass spectroscopy studies by Wasmus et al. [76].

In the presence of ammonia, Rh and Ru did not exhibit any distinct ammonia electro-oxidation peaks during the potential scan in the positive direction. This has been attributed to surface blockage by intermediates from chemical or a minor electrochemical oxidation of ammonia along with the OH\textsuperscript{-} ions that were adsorbed at considerably lower potentials [12]. This can be verified by the presence of an additional reduction peaks B12 and C12 for Rh and Ru respectively. The additional reduction peaks B12 and C12 and larger H\text{upd} peaks B11 and C11, could be attributed to either the ammonia desorption or a shift in the surface-oxide reduction peak in the negative direction or both. In addition, the presence of ammonia indicates no metal-oxide reduction peaks for Rh and Ru.

In addition, it could be observed that the H\text{upd} peaks for Pt A01 and A02 appear to have slightly shifted by 120 mV to 180 mV in the negative direction, implying a weak Pt-H\text{upd} bond. The shift in the H\text{upd} to a more negative potential could be a result of adsorbed ammonia or intermediates for ammonia electro-oxidation. Similarly, the presence of
ammonia causes the H\textsubscript{upd} peaks B01 for Rh and C01 for Ru, to be shifted in the negative direction by 40 mV and 30 mV, respectively, implying that the metal-H\textsubscript{upd} bond is weak. The extent of the shift appears to be caused by the sensitivity of electrocatalyst surface to ammonia.

The CV for Ni Figure 4-3D in the presence of ammonia indicates peak D11 corresponding to the reduction of Ni(OH)\textsubscript{2} to Ni [74, 77]. This suggests a reversible nature of the hydroxide and could in turn imply that the presence of ammonia prevents the conversion of the hydroxide from the reversible $\alpha$ phase to its irreversible $\beta$ phase. The figure also shows that the ammonia adsorption or electro-oxidation peaks are absent, since they do not occur until considerably higher potentials through a direct electron transfer reaction with the NiOOH catalyst [74].

Upon adding ammonia and by correlating the shift in the H\textsubscript{upd} with the change in the overpotential of the catalyst, the role of H\textsubscript{upd} on the HER could be understood. The addition of ammonia results in weaker metal-H\textsubscript{upd} bonds for Pt, Rh, and Ru. The weaker metal-H\textsubscript{upd} bond (Figures 4-3A and 4-3C) is accompanied by a decrease in the HER activity on Pt and Ru in the presence of ammonia, thereby implying that the activity for HER is higher on a surface with H\textsubscript{upd} than on the bare metal [20, 71, 72]. This hypothesis can also be confirmed from the shift in H\textsubscript{upd} (i.e., an H\textsubscript{upd} of -140 mV results in an overpotential decrease of 27 mV for Pt, whereas a H\textsubscript{upd} shift of -40 mV results in an overpotential decrease of 11 mV). This validates the hypothesis by Conway et al that the activity of HER is thermodynamically more favorable on the surface with the stronger H\textsubscript{upd}, rather than on the bare metal itself [72]. However for Rh, the increase in activity
towards HER accompanies the weaker metal-H\textsubscript{upd} bonds, indicating that the activity of HER is higher on the bare Rh surface, as suggested by Markovic \textit{et al} [23].

4.3.3. EIS Measurements

The EIS technique can be used to identify the rate constants for each step in the reaction mechanism. Figure 4-4 shows the various equivalent circuit models that were evaluated to describe the HER [56, 57, 69]. The procedure for estimating the best equivalent circuit for the impedance data is explained in the Appendix E.

4.3.3.1. Estimation of Equivalent Circuit and Circuit Parameters for HER

A list of equivalent circuit models that were evaluated for HER are described in Figures 4-4A through 4-4E. The Armstrong-Henderson model [59] (Figure 4-4A) describes a typical case for HER, the model is usually used in a scenario where the Nyquist plots indicate the presence of two time constants.

The constant phase element (CPE) model (Figure 4-4B) is an extension to the Randles circuit and a simplified version of the Armstrong-Henderson model, where the impedance of the parallel Rp-Cp branch is eliminated due to the considerably low pseudocapacitance. The CPE model is designed to fit systems with one time constant and frequency dispersion [78]. Additionally, in the derived circuits (Figure 4-4C through 4-4E), a CPE element replaced the capacitor in the Armstrong-Henderson model, were evaluated. The procedure adopted for optimal equivalent circuit fitting is described in Appendix E (Figure E1) to this dissertation.
The EIS results for Pt, Rh, Ru, and Ni are presented in Figures 4-5A through 4-5D, in the form of Nyquist (or) Cole-Cole (or) complex-plane plots along with its equivalent circuit fit and the fit obtained from the rate constants derived for the VHT mechanism (Section 4.3.4).

As a rule of thumb, the high frequency intercept in the Nyquist plot represents the solution resistance, while the diameter of the semicircle represents the Faradaic resistance. Harrington and Driessche [79] give an excellent description on how to decipher an impedance spectra and the significance of the equivalent circuit elements for specific cases. The Nyquist plots indicate the presence of only one time constant and no Warburg-type feature at the lower frequency range, indicating that the HER is charge transfer controlled. Nevertheless, due to its practical significance to HER, the Armstrong-Henderson model was evaluated to fit the impedance spectra.

Figures 4-5A to 4-5C show that the CPE model offered the best possible fit for HER on the noble metals. The CPE accounts for the capacitance dispersion with frequency as a result of the inhomogeneity of the electrode surface.[56, 69, 78] While Figure 4-5D shows that the Armstrong-Henderson model offered the best fit for the Ni electrodes conforming to that found in the literature.[56, 59] The derived circuits did not offer any significant improvement in the fit when compared with the CPE model, suggesting a faster recombination reaction. The total impedance for all the models in Figure 4-4 obeys the equation:

\[ Z_T = R_s + (Z_f^{-1} + Z_{CPE}^{-1})^{-1} \] (8)

\[ Z_f = R_{ct} + 1/(j\omega C_p + (1/R_p)) \] (9)
Figure 4-4. Equivalent circuit models evaluated for the representation of HER impedance spectra at \( E = -1.161 \text{ V vs Hg/HgO} \). Figures A through E depict: Armstrong-Henderson model (A-H), Modified Randles circuit (CPE model), A-H model with capacitance dispersion at a high frequency, A-H model with capacitance dispersion at low frequency, and A-H model with capacitance dispersion at low and high frequency domains, respectively [59].

where \( Z_f \) and \( Z_{CPE} \) are given by Equations 9 and 10

\[
Z_{CPE} = 1/\left[ T (j\omega)^\phi \right] \quad \text{(10a)}
\]

\[
T = C_{dl}^{\phi} \left[ R_s^{-1} + R_{ct}^{-1} \right]^{(1-\phi)} \quad \text{(10b)}
\]

where, \( R_s \) – solution resistance, \( R_{ct} \) - charge transfer resistance, \( R_p \) – polarization resistance, \( C_p \) – pseudocapacitance, and \( \omega \) – angular frequency. \( C_{dl} \) is the double layer capacitance and \( \phi \) is the angle that describes the extent of frequency dispersion of the double layer capacitance.
Figure 4-5. Nyquist (or) complex-plane plot for the experimental impedance spectra for HER obtained with electrocatalysts: Pt (A), Rh (B), Ru (C), and Ni (D) at \( E = -1.102 \text{ V vs Hg/HgO} \) \( (\eta = -166 \text{ mV}) \) in the presence and absence of ammonia. In addition, the spectra for equivalent circuit models (described in Figure 4-4) that best fit the experimental values are shown along with the spectra obtained by using the rate constants evaluated for the VHT mechanism. The experimental data for HER in the absence and presence of ammonia are represented by clear (red) and filled (blue) square markers, respectively.

Upon fitting equivalent circuit to the impedance data, as mentioned in Appendix E, suggests that the pseudocapacitance term is negligible for the noble metals and obeys the CPE model. Thereby implying that the H adsorption formed as a result of the Volmer step quickly recombined to form hydrogen molecule, in turn suggesting that the water dissociation step is the slow step. However for Ni, the pseudocapacitance offers
significant impedance towards the HER, thereby following the Armstrong Henderson model.

The values for the circuit elements for the equivalent circuit fit for the impedance spectra at -166 mV, along with the goodness of fit (chi-squared and sum squared values) are reported in Table 4-4. The maximum average error for the fit, estimated from the sum squared values for 45 data points, for the noble metal is 0.016 Ω obtained using the CPE model, whereas the average error for Ni is 0.043 Ω obtained using the Armstrong-Henderson model. The results for other models exhibited higher errors and therefore were not reported.

From Table 4-4, it could be observed that there is no significant difference in the solution resistance, whereas the double layer capacitance per unit area decreased in the order Rh>Pt>Ru>Ni in the absence and presence of ammonia. In addition, it is noticed that the double layer capacitance (C_{dl}) is greater than the expected 20 mF cm^{-2}, for all the noble metals. The higher C_{dl} values is specific to the alkaline medium and specifically to the coadsorption of the OH^{-} anion in the double layer region [23]. On the other hand, the Faradaic resistance per unit area increased in the order Pt<Ru<Rh<Ni, thereby concurs with the LSV results. The addition of ammonia did not result in any change in the trend for the double layer capacitance per unit area.

Meanwhile the Faradaic resistance (R_f) increased for Pt, Ru, and Ni, altering the trend in R_f to Rh<Pt<Ru<Ni. The results are consistent with the LSV studies, confirming their validity. The higher activity on Rh can be attributed to (1) the weakening of the surface hindering Rh-H_{upd} bonds [23], or (2) the high tendency to adsorb OH^{-} ions and
therefore its reduced activity for H$_{\text{upd}}$ formation [45] or (3) its selectivity of reducing nitrates and its intermediates, or a combination of the three. Further study is required to explain the higher activity for Rh towards HER in the presence of ammonia. Evaluating the variation in the H$_{\text{upd}}$ surface coverage and rate constants for the Volmer, Heyrovsky, and Tafel steps in the presence of ammonia could offer a deeper understanding to the effect of ammonia on the HER.

Table 4-4.

Circuit parameters for the equivalent circuit fit to the impedance spectra for the HER on Pt, Rh, Ru, and Ni in the presence and absence of ammonia at an overpotential of -166 mV. The CPE model offered the best fit the impedance data for Pt, Rh, and Ru. However the Armstrong-Henderson model offered the best fit for the impedance data for the Ni electrode. It can be observed that Pt offered the least Faradaic resistance in the absence of ammonia, while Rh offered the least resistance in the presence of ammonia.
4.3.3.2. NH$_3$ Effect on Kinetic Rate Constants for HER and H$_{\text{opd}}$ Surface Coverage

Upon assuming Langmuirian adsorption, and neglecting the backward reactions for the Heyrovsky and Tafel steps, the final expression for the rate equations for reactions in equations Volmer, Heyrovsky, and Tafel steps are given below:

\[
\begin{align*}
\upsilon_1 &= k_1(1-\theta)\exp(-\beta_1 f \eta) - k_{-1} \theta \exp((1-\beta_1) f \eta) = \tilde{k}_1(1-\theta) - \tilde{k}_{-1}\theta \\
\upsilon_2 &= k_2 \theta \exp(-\beta_2 f \eta) = \tilde{k}_2 \theta \\
\upsilon_3 &= k_3 \theta^2 
\end{align*}
\]  

(11a) (11b) (11c)

where $k_1$, $k_{-1}$, $k_2$, and $k_3$ are the potential independent rate constants; $\eta$ is the overpotential; $\theta$ is the fractional surface coverage of H$_{\text{opd}}$ species; $\beta_1$ and $\beta_2$ are the transfer coefficients.

\[
\begin{align*}
r_0 &= i / F = (\upsilon_1 + \upsilon_2) \\
r_1 &= (q / F)(d\theta / dt) = (\upsilon_1 - \upsilon_2 - 2\upsilon_3)
\end{align*}
\]

(12a) (12b)

where $r_0$ is the rate of electron consumption; $r_1$ is the rate of surface coverage and $q$ is the charge required for the formation of a monolayer of H$_{\text{opd}}$. The expression for fractional surface coverage at a steady state can be obtained by solving the quadratic equation, from Equation 11b, for $\theta$

\[
\theta = -\left[\left(\tilde{k}_1 + \tilde{k}_{-1} + \tilde{k}_2\right) + \sqrt{\left(\tilde{k}_1 + \tilde{k}_{-1} + \tilde{k}_2\right)^2 + 8\tilde{k}_1\tilde{k}_3}\right] / 4\tilde{k}_3
\]

(13)

Upon linearizing Equations 12a and 12b; applying the phasors to introduce the AC component and eliminating $\theta$, one obtains
\[ Y_f = 1/Z_f = A + B / (j\omega + C) \]  \hspace{1cm} (14)

where, \( A = -F(\partial r_0 / \partial \eta)_{\theta} \)  \hspace{1cm} (14a)
\( B = -(F^2 / q)(\partial r_0 / \partial \eta)_{\theta}(\partial r_1 / \partial \eta)_{\theta} \)  \hspace{1cm} (14b)
\( C = -(F / q)(\partial r_1 / \partial \eta)_{\theta} \)  \hspace{1cm} (14c)

The expressions for the equivalent circuit elements from the EIS experiments in relation to the HER can be obtained by comparing Equations 14 with 9,[52]

\[ R_{ct} = 1 / A \]  \hspace{1cm} (15a)
\[ R_p = -1 / ((A^2 C / B) + A) \]  \hspace{1cm} (15b)
\[ C_p = -A^2 / B \]  \hspace{1cm} (15c)

The HER kinetics is usually described by 4 independent kinetic parameters (k1, k-1, k2, k-2) and the fractional surface coverage \( \theta \) as described in Equations 11a-11c and Equation 13 respectively. \( \beta_1 \), and \( \beta_2 \) was assumed to be 0.5. However, EIS experiments yield only 3 values for \( R_{ct} \), \( R_p \), and \( C_p \) for Equations 15a-15c. The value for \( i_0 \) obtained from LSV studies was used in the expression for the average rate constant described in Equation 16. The solutions to the rate constants were obtained by maintaining \( \theta \) constant.

\[ k_{av} = 1 / (k_1^{-1} + k_2^{-1}) = i_0 / 2F = \exp(-\beta f \eta) / (k_1^{-1} + k_2^{-1}) \]  \hspace{1cm} (16)

The potential independent rate constants for the reactions 4-6 were estimated, by fitting the circuit elements from impedance measurements to Equations 15a-15c, derived from the impedance equation for the VHT mechanism. The Levenberg-Marquardt algorithm was used for the non-linear fitting with a tolerance level of 1x10^{-14}. The estimated rate constants were then used in the impedance Equation 14 to re-evaluate the impedance spectra in the interested frequency range. The surface coverage was varied
until the rate constants were able to closely predict the impedance spectra. These potential independent rate constants and surface coverage are reported in Table 4-5.

Table 4-5.

Rate constants and surface coverage were estimated for the catalysts in the presence and absence of ammonia at an overpotential of -166 mV. Rate constants and surface coverage were derived for the catalysts using the equivalent circuit parameters shown in Table 4-4 by Levenberg-Marquardt algorithm for the Volmer-Heyrovsky-Tafel mechanism. The addition of ammonia leads to a decrease in the rate constant for the slowest step, $k_1$ for Pt and Ru, and $k_2$ for Ni. However, for Rh, the addition of ammonia results in an increase in the rate constant for the Volmer step ($k_1$).

<table>
<thead>
<tr>
<th>Material</th>
<th>Ammonia Concentration (M)</th>
<th>Rate Constant (mol cm$^{-2}$ s$^{-1}$)</th>
<th>Surface Coverage ($\mu$C cm$^{-2}$)</th>
<th>Fractional Coverage $\theta$ (monolayers)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_1$ ($x10^{-10}$)</td>
<td>$k_1$ ($x10^{-6}$)</td>
<td>$k_2$ ($x10^{-8}$)</td>
</tr>
<tr>
<td>Pt</td>
<td>0</td>
<td>3.22</td>
<td>2.47</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2.26</td>
<td>2.10</td>
<td>0.35</td>
</tr>
<tr>
<td>Rh</td>
<td>0</td>
<td>2.64</td>
<td>0.98</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2.76</td>
<td>0.50</td>
<td>1.16</td>
</tr>
<tr>
<td>Ru</td>
<td>0</td>
<td>2.77</td>
<td>0.24</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2.02</td>
<td>0.19</td>
<td>1.13</td>
</tr>
<tr>
<td>Ni</td>
<td>0</td>
<td>30.67</td>
<td>3.73</td>
<td>0.0002</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>32.74</td>
<td>3.28</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

From Table 4-5, at an overpotential of -166 mV, the trends in the average rate constants ($k_{av}$) in the absence and presence of 1 M ammonia agreed with the results obtained using the LSV studies. In addition, for all the noble metals the rate constant for the Volmer or the water dissociation step ($k_1$) is lower than that of the desorption steps. However, the rate constant for the water dissociation step ($k_1$) for the Ni electrode is higher than that of the desorption steps, as expected, thereby causing a low surface...
coverage for the noble metal electrodes, and a higher surface coverage for Ni as mentioned in Table 4-5. Amongst desorption steps, the rate constant for the non-electrochemical Tafel step was higher than the electrochemical Heyrovsky step for all the catalysts at -166 mV. In addition, Pt presents the highest rate constant for the slow Volmer step, explaining its superior activity.

The addition of ammonia results in a decrease in the average rate constant \( (k_{av}) \) for HER, which is observed for Pt, Ru, and Ni. Moreover, the presence of ammonia results in the reduction of the rate constant \( k_1 \) for the slow Volmer step for Pt and Ru, accompanied by a drop in the rate constant for the desorption steps thereby resulting in a lower \( H_{opd} \) surface coverage. This is evident for Pt and Ru, which in turn cause a decline in the average rate constant and activity for HER. On the other hand an increase in \( k_1 \) was observed for Rh, which explains the rise in the \( H_{opd} \) surface coverage and therefore the increase in the average rate constant and activity for HER. For Ni, although an increase in \( k_1 \) and \( H_{opd} \) surface coverage is observed with the addition of ammonia, this results in a reduction in the rate of the slow rate-determining Tafel step. This decrease in the rate constant of the rate determining Tafel step explains the \( H_{opd} \) higher surface coverage and lower activity towards HER for Ni.

4.3.4. Constant Potential Studies

Figure 4-6 shows the current density–time plots at a potential of -1.1 V versus Hg/HgO for the CFP based Pt, Rh, Ru, and Ni electrocatalysts in 5 M KOH, in the presence and absence of ammonia. A high surface area Ni gauze was used as the
auxiliary electrode in place of a Pt foil counter to avoid the depletion of ammonia through electro-oxidation. The current densities shown were evaluated based on the EASA. All four catalysts present sufficient stability at the applied potential in the presence and absence of ammonia.

From Figure 4-6, Ni has the lowest cathodic current density irrespective of the presence of ammonia. In addition, it is also observed that Pt continued to display the highest current density in the absence of ammonia despite losing 0.38 mA cm⁻² after three hours, confirming the LSV and EIS studies. Although, the addition of ammonia resulted in a minimum current loss of 0.1 mA cm⁻² for Pt and Ru, the catalysts appear to be stable. On the contrary, an increase in the current density with time is observed for Rh. This performance is very similar to the performance of a deactivated Rh electrode in 1 M KOH [80]. Wrona et al., attribute this deactivation to traces of unknown metal impurities on the electrode. However, the deactivation of the Rh electrode could be attributed to the formation of a Hupd layer on Rh, which acts as a barrier to HER. In addition, the higher HER current in the presence of ammonia could be attributed to the weaker Rh-Hupd bond formation, evident from CV measurements (as seen in Figure 4-3C), which tends to easily break off from the surface thereby creating fresh active sites for HER. The rather slow reactivation could be due to the constant competition from Hupd formation at -0.127 V, specific only to HER sites, resulting in a delay in reaching the steady state. The studies confirm highest activity towards HER on Rh in the presence of ammonia as expected from the LSV and EIS results.
Figure 4-6. Current density-time plot for constant potential studies for Pt, Rh, Ru, and Ni in 5 M KOH in the presence and absence of ammonia at -1.1 V vs Hg/HgO for a period of 3 hours. It can be observed that the addition of ammonia resulted in lower reduction current densities for all materials except Rh. Rh also displayed the most stable and highest activity towards HER in the presence of ammonia.

4.4. Conclusion

A study of the effect of ammonia on the HER on Pt, Rh, Ru, and Ni electrodes was performed. The following conclusions were made based on the results obtained:

1. The LSV, EIS, and chronoamperometric results for HER in ammonia free alkaline solutions were similar to that reported in the review on HER. The activity of the catalysts for HER followed the order Pt>Ru>Rh>Ni.

2. The presence of ammonia results in a slight loss in the HER activity for Pt, Ru, and Ni. However Rh displayed a higher activity towards HER in the presence of ammonia, resulting in the trend in activity Rh>Pt>Ru>Ni.

3. EIS results confirm that the noble metal catalysts have a slow water dissociation step and a fast recombination step, while the vice versa was observed for Ni. The
addition of ammonia resulted in a decrease in the average rate constant of the slow step for Pt, Ru, and Ni. However, the opposite behavior was observed for Rh.

4. EIS results also indicate that the presence of ammonia causes a decrease in the rate constant $k_1$ of rate-determining Volmer step for Pt and Ru and $k_3$ for Ni thereby explaining the decrease in their activity towards HER. Whereas, the addition of ammonia results in the increase in $k_1$ substantiating the increase in H$_{upd}$ surface coverage and in turn the HER activity on Rh.

5. The addition of ammonia resulted in the weakening of the metal H$_{upd}$ bond accompanied by a decrease in the activity of the catalysts towards HER for Pt and Ru. Thereby supporting the hypothesis that HER is more active on the surface with hydrogen than the surface containing bare metal. However the opposite was observed for Rh, suggesting that HER on Rh is higher on the surface with H$_{upd}$.

Figure 4-7. Graphic depicting how the presence of ammonia reduces the H$_{upd}$ formation on Pt, Ru, Rh, and Ni electrocatalysts during the hydrogen evolution reaction.
In conclusion, Rh offers the highest activity towards HER in the presence of ammonia, amongst the catalysts evaluated. Further studies need to be performed to evaluate the effect of ammonia on the activity of HER for bimetallic alloys. Figure 4-7 represents the formation of H_{upd} layer on a metallic cathode in the presence and absence of ammonia.

4.5. References

CHAPTER 5: HER KINETICS ON ELECTRODEPOSITED PLATINUM$_{X}$-M$_{1-X}$ (M = IR, RU, RH, AND NI) CATALYSTS FOR AMMONIA ELECTROLYSIS

(Part of the contents of this chapter has been submitted to the Journal of Electrochemical Society for publication. Ramasamy Palaniappan (R.P.) and Gerardine G. Botte (G.G.B.) developed the idea and designed the experiments. R.P. performed the experiments and data analyses. David C. Ingram (D.C.I.) did the XPS experiments for this chapter. R.P. and G.G.B. discussed the results. R.P. and G.G.B. co-wrote the paper.)

5.1. Introduction

Electrochemical power sources such as batteries and fuel cells present as the frontrunners in the search for alternative energy. The limitations of fuel cell technology are source, storage, and transportation of the hydrogen [1-3]. The high hydrogen density and non-explosive nature makes ammonia a suitable hydrogen carrier. Ammonia electrolysis facilitates a safe, robust and economical method to produce hydrogen from ammonia on demand [4-15]. In addition, ammonia electrolysis can be used for remediating ammonia rich wastes from municipal waste water treatment plants [12, 16], dairy farms [17, 18], and other industries [19], thereby offering a solution to prevent groundwater contamination from ammonia and its derivatives including nitrates [12, 19-23].

The reactions for an ammonia electrolytic cell comprise of ammonia electro-oxidation at the anode and alkaline water reduction at the cathode as shown in Equations 1-3. Most of the previous work in this area has been devoted to the development of electrocatalysts for the anode, since ammonia oxidation has been identified as the
limiting reaction [6, 14, 20, 24-38]. Nevertheless, the choice of a suitable cathode electrocatalyst could allow higher hydrogen production rates, while operating the electrolyzer at voltages low enough to keep the anodic reaction under its limiting rate, which is key to achieving higher efficiencies.

Although, the cathodic reaction is identical to that in the alkaline water electrolysis, the effect of ammonia present in the electrolyte mix is a subject that has received little attention. This is a crucial issue as it has been recently shown that ammonia from the anodic compartment diffuses with ease into the catholyte [39]. Additionally, the consumption of OH\(^{-}\) ions at the anode leads to a decrease in the anolyte pH, while the generation of OH\(^{-}\) ions at the cathode leads to the increase in the catholyte pH during a single pass through a continuous electrolyzer [40]. Therefore, identifying a cathode, where the hydrogen evolution reaction (HER) is unhindered by the presence of ammonia is critical and would annul or reduce the problems associated with ammonia diffusion. Furthermore, such a cathode would enable the operation of the ammonia electrolytic cell in a stirred-tank mode, thereby circumventing the problems associated with the filter-press type electrolyzer.

Savadogo gives a comprehensive introduction to the theory behind HER, along with the importance of synergistic effect on the activity of composite electrocatalysts on HER [41]. A wide range of materials has been tested for their efficacy as electrocatalysts

\[
\text{Anode: } 2\text{NH}_3 + 6\text{OH}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O} + 6\text{e}^- \quad E^0 = -0.770 \text{ V vs SHE} \\
\text{Cathode: } 6\text{H}_2\text{O} + 6\text{e}^- \rightarrow 3\text{H}_2 + 6\text{OH}^- \quad E^0 = -0.828 \text{ V vs SHE} \\
\text{Overall: } 2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 \quad E^0 = 0.058 \text{ V}
\]
for the HER in alkaline media [42-50]. The Ni group metals in the periodic table and their alloys have received predominant attention, due to the relative low costs [47, 51-62]. Nevertheless, they are also recognized for their ease of deactivation, high overpotentials, and low activity toward HER. A variety of noble metals (including Pt [45, 63], Ir [46], Rh [49], and Pd [48]) and their alloys, oxides [64, 65] and perovskites [66] have been evaluated for their activity for HER. Volcano plots (exchange current density versus metal-hydrogen bond strength) [63, 67, 68], quasi steady state calculations [69], density functional theory (DFT) studies [70], voltammetry [42, 45-49, 60, 71] and impedance spectroscopy experiments [44, 50, 51, 54, 58, 72-76] have been used to determine the activity of several electrocatalysts for the HER. From the volcano plots it can be observed that Pt has the highest catalytic activity among transition metals [67, 68]. It has also been reported that the HER is sensitive to the electrocatalyst crystal structures [77, 78]. DFT calculations performed by Greeley et al. show that, amongst 700 binary alloys evaluated: Rh, Ru, Ir, Ni, Co, and Bi offered excellent catalytic activity for HER when alloyed with Pt [70]. However, in the presence of ammonia the trend in HER electrocatalytic activity follows Rh>Pt>Ru>Ni [79].

Within this context, the objective of this study is to determine the effect of ammonia on the alkaline HER kinetics on metals Pt, Ir, Ru, Rh, Ni and bimetallic alloys of Pt with Ru, Rh, Ir and Ni. Electrodeposition was chosen as the route for synthesis as it offers greater stability and durability to the electrodes as opposed to those synthesized from chemical reduction [80]. The electrocatalysts were deposited onto polyacrylonitrile based carbon fiber papers (CFP), due to their high catalytic activity and stability in
ammonia solutions [14, 39]. In addition to affecting the economics of electrolysis, the catalyst loading (Metal / [Metal + Carbon]) weight percentage plays a major role in bimetal electrodeposition and subsequently influences the electrochemical kinetics [81, 82]. Therefore, the effect of catalyst loading on the nature and composition of the bimetallic deposits and subsequently the HER kinetics was investigated as a part of this chapter. In order to address the objectives the following tasks were performed:

1. Metallic (Pt, Rh, Ru, Ir and Ni) and bimetallic (Pt-Ir, Pt-Ru, Pt-Rh, and Pt-Ni) electrodes were synthesized by electrodeposition onto CFP substrates.
2. The morphology and chemical composition of the electrodes’ surface were characterized using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).
3. Bulk compositions of the alloys were determined by elemental analysis using energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD).
4. The electrochemical active surface area (EASA) was determined by estimating the hydrogen adsorption charge or CO stripping charge. The catalyst utilization was estimated by evaluating the chemical specific area (CSA) using XRD data.
5. The kinetics of HER in ammonia solution (1 M ammonia + 5 M KOH) was evaluated at the synthesized electrodes and compared with one another using cyclic voltammetry (CV) and linear sweep voltammetry (LSV). Additionally, the effect of the Pt content in the alloy, catalyst loading, Pt-Pt bond length, and intercrystallite distance on the activity of the electrocatalysts for HER was also investigated.
5.2. Materials and Methods

All of the chemicals used in this study were of analytical grade and were obtained from Alfa Aesar. All the experiments were repeated in order to check for reproducibility and the uncertainties reported in the paper were calculated through error propagation, taking into account the instrumental error and standard deviations in the measurements. All electrochemical experiments were performed with a potentiostat (Solartron 1287) with an electrochemical interface. Hg/HgO saturated with KOH (20% by weight), purchased from Koslow Scientific, was used as the reference electrode for measurements in alkaline solution, whereas an Ag/AgCl electrode saturated with KCl, purchased from Fisher Scientific, was used in acidic solutions. A glass-body luggin capillary was used to house the reference electrodes in order to reduce the solution resistance and avoid contamination of the solution. All comparisons were statistically justified using t-tests with a 95% confidence limit.

5.2.1. Electrodeposition

The electrocatalysts used in this study were synthesized by potentiostatic electrodeposition onto two 2 cm x 2 cm, untreated Toray TGP-H-30 CFP substrate, purchased from Electrochem Inc. The procedure to prepare the substrate has been described previously by Boggs and Botte [14]. The amount of catalyst deposited was determined gravimetrically using a microbalance with 0.1 mg accuracy. The conditions for metal (Pt, Ru, Rh, Ir, and Ni) and bimetal (Pt-Ir, Pt-Ru, Pt-Rh, and Pt-Ni) electrodeposition are detailed in Tables 5-1 and 5-2. The electrodeposition was conducted
in a 250 ml Pyrex-glass beaker on a stirring hot plate with an in-built thermocouple and a glass-ceramic surface from Corning® which was used to control the temperature for the electroplating bath. The contents of the beaker were stirred at 100 rpm using a magnetic stirrer bar to maintain uniform temperature and minimize mass transfer limitations. A 5 cm x 5 cm Pt foil of thickness 0.01 cm and purity 99.999% (ESPI Metals) was used as the counter electrode except for the deposition of Ni for which a 5 cm x 5 cm Ni foil of thickness 0.01 cm and purity 99.99% (Alfa Aesar) was used as the counter electrode.

Table 5-1.

Electrodeposition conditions for metals (Pt, Ru, Rh, Ir and Ni). Pt foil was used as the auxiliary electrode at 78° C for all metals except Ni, for which a Ni foil auxiliary electrode was used at 45° C

<table>
<thead>
<tr>
<th>Material</th>
<th>Plating Bath Composition</th>
<th>Reaction</th>
<th>E^0 (V) vs SHE</th>
<th>Potential (V) vs Ag/AgCl</th>
<th>Deposition Charge (± 0.1 C)</th>
<th>Loading (± 0.1 mg cm^-2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>15.4mM H₂PtCl₆</td>
<td>Pt⁴⁺ + 2e⁻ → Pt²⁺</td>
<td>0.680 0.755</td>
<td>-0.10</td>
<td>34.6</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt²⁺ + 2e⁻ → Pt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>29.2mM RhCl₃</td>
<td>Rh³⁺ + 3e⁻ → Rh</td>
<td>0.758</td>
<td>-0.20</td>
<td>111.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Ru</td>
<td>29.6 mM RuCl₃</td>
<td>Ru³⁺ + e⁻ → Ru²⁺</td>
<td>0.249 0.431</td>
<td>0.01</td>
<td>37.6</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ru²⁺ + 2e⁻ → Ru</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>15.6 mM IrCl₃</td>
<td>Ir³⁺ + 3e⁻ → Ir</td>
<td>1.156</td>
<td>-0.25</td>
<td>60.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Ni</td>
<td>1.1 M NiSO₄ 0.2 M NiCl₂</td>
<td>Ni²⁺ + 2e⁻ → Ni</td>
<td>0.257 -0.80</td>
<td>14.5</td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>


Table 5–2.

Electrodeposition conditions for bimetals. Pt foil was used as the auxiliary electrode for all bimetals. Electrodeposition was carried out at 78° C for Pt-Ir, Pt-Ru, and Pt-Rh, whereas the deposition of Pt-Ni electrodes was carried out at 25° C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Plating Bath Composition</th>
<th>Potential (V) vs Ag/AgCl</th>
<th>Electrode label</th>
<th>Deposition Charge (± 0.1 C)</th>
<th>Loading (± 0.1 mg cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ir</td>
<td>7.8 mM IrCl₃ 7.7 mM H₂PtCl₆</td>
<td>-0.127</td>
<td>A1</td>
<td>12.4</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A2</td>
<td>35.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Pt-Ru</td>
<td>14.8 mM RuCl₃ 7.7 mM H₂PtCl₆</td>
<td>-0.120</td>
<td>B1</td>
<td>63.1</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B2</td>
<td>52.1</td>
<td>2.0</td>
</tr>
<tr>
<td>Pt-Rh</td>
<td>14.6 mM RhCl₃ 7.7 mM H₂PtCl₆</td>
<td>-0.100</td>
<td>C1</td>
<td>13.3</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C2</td>
<td>63.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Pt-Ni</td>
<td>25 mM NiCl₂ 7.7 mM H₂PtCl₆</td>
<td>-0.500</td>
<td>D1</td>
<td>4.7</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D2</td>
<td>8.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>

5.2.2. Physicochemical Characterization

Surface morphological characteristics of the deposits were studied using a JEOL JSM 6390 scanning electron microscope. XPS spectra for the catalysts were collected using a Kratos XSAM 800 instrument with VISION2 control and a stainless steel sample holder. A monochromatic Al-Kα X-rays (hv =1486.6 eV) was used as the source. The instrument was calibrated using Au 4f, C 1s, Ag 3d, and Cu 2p peaks obtained from calibration samples, prior to obtaining the XPS spectra for the samples.
Elemental analysis was performed by measuring the characteristic X-rays emitted from the samples using a Genesis Apex EDS system coupled with the SEM. Crystallographic pattern of the electrodes was determined by XRD using a monochromatic Cu-Kα radiation (λ=1.54 Å) generated by a Rigaku Ultima-IV diffractometer operating at 40 kV and 30 mA at a scan frequency of 0.5 ° min⁻¹.

5.2.3. Electrochemical Characterization

The electrodes were subject to pretreatment and EASA measurements prior to all electrochemical measurements. The procedure for pretreatment and estimating the EASA for the electrodes has been detailed previously [79]. The CV and LSV measurements for the HER were carried-out in a 5 M KOH solution with 1 M ammonia. A 5 cm x 5 cm Ni gauze (100 mesh woven from 0.1 mm diameter wire, Alfa Aesar) was used as the counter electrode to avoid electrolyzing ammonia at the anode thereby maintaining the concentration of ammonia. The Ni gauze was sand blasted using a micro sand blaster (Swam Blaster, Crystal Mark Inc.,) with 27.5 µm Alumina (purchased from Crystal Mark Inc.,), then degreased with acetone and washed with de-ionized water prior to each experiment.

The CV tests were carried out by scanning the electrode potential from -1.1 V to 0.1 V versus Hg/HgO and back at 10 mV s⁻¹. While the LSV experiments were carried out by scanning the electrode potential between -0.9 V and -1.3 V versus Hg/HgO at 1 mV s⁻¹. The low scan rate of 1 mV s⁻¹ was sufficient to maintain the reaction under kinetic-control by allowing enough time for the diffusion of fresh reacting species to the
electrode surface. Sustained periodic results were obtained for both CV and LSV after the 5th scan.

5.3. Results and Discussion

The results for the metallic and bimetallic electrodeposition experiments are reported in Tables 5-1 and 5-2, respectively. In order to investigate the effect of catalyst loading on the physical morphology, the composition of the catalyst and its activity toward HER, electrodeposition for bimetals was carried out for 0.6 mg cm\(^{-2}\) (low) and 1.9 mg cm\(^{-2}\) (high) loadings with a variation of +/- 0.1 mg cm\(^{-2}\). The electrodeposition was confirmed by an increase in the mass for all materials except Ir. Besides, varying the Ir electrodeposition potential to more negative values did not result in any appreciable mass gain. Therefore IrCl\(_3\) was deemed to be an unsuitable salt for Ir electrodeposition.

5.3.1. Physicochemical Characterization

5.3.1.1. Surface Characterization (SEM and XPS)

The SEM images depicting the surface morphology of the metallic and bimetallic catalysts electrodeposited on CFP are shown in Figure 5-1. The SEM images show globule type deposition for both metallic and bimetallic electrocatalysts. The size of each globular particle is in the 100 nm range. As the catalyst loading increases the globule type deposits combine to exhibit a cluster type surface morphology. However, the SEM image for Ru deposits occurred in the form of a layer, while Pt-Ni displayed a rather dispersed deposit.
Figure 5-1. A-D represents SEM images of metals Pt, Rh, Ru, and Ni, while Figures A1 through D1 represents the SEM images for bimetals Pt-Ir, Pt-Rh, Pt-Ru, and Pt-Ni at a loading of ~0.6 mg cm\(^{-2}\) and Figures A2 through D2 represents the SEM images for bimetals Pt-Ir, Pt-Rh, Pt-Ru, and Pt-Ni at a loading of ~1.9 mg cm\(^{-2}\). The deposits are in the form of globules, which form clusters at higher loadings.

The electrode composition for Pt-Ir, Pt-Ru, and Pt-Rh electrodes were determined using XPS. Figures 5-2A through 5-2E show the XPS spectrum for Pt 4f and Ir 4f, Pt 4d, Ru 4d, Pt 4f, and Rh 3p photoelectron spin doublet peaks, respectively. The curves are labeled to distinguish the low (1) and high loadings (2) according to the nomenclature used in Table 5-2. On the other hand, the XPS measurements for Pt-Ni electrodes were not performed since the electrode composition obtained from EDX spectra (5.3.1.2) gives a fair estimation of the surface composition of the Pt-Ni electrode. As shown in Figure 5-2A, no shift in the peak electron binding energies, with respect to that of Pt 4f and Ir 4f
for pure Pt and Ir listed in the NIST database, was observed for the Pt-Ir alloy at both low and high catalyst loadings. Similarly from Figures 5-2D and 5-2E no shift in the Pt 4f and Rh 3p electron binding energies was observed for Pt-Rh alloy, implying the chemical state of the metals at the surface remained unchanged upon increasing the catalyst loading. On the contrary, an increase in the loading for the Pt-Ru resulted in a shift in the Pt 4d and Ru 4d electron binding energies by 2 eV (as shown in Figure 5-2B and 5-2C), indicating that part of the Pt-Ru surface was present in its oxidized state. Since the oxides present in electrodes will be in its reduced state when used at HER potentials, they were included in computing the surface composition for the bimetals.

The surface composition of the electrode, from XPS, was determined by evaluating the area \((\text{Area}_i)\) under the photoelectron peak after removing effects from the background electrons. The composition of each element in the bimetal is given by the ratio of the resulting area for an element normalized for its relative sensitivity factor (RSF) to the sum of the areas of all metals in the alloy normalized for their respective RSF. Prior to obtaining the area, the curve was smoothed using a Savitzky-Golay algorithm. The surface metal concentration is then obtained using the formula:

\[
X_{Pt} = \frac{\text{Area}_{Pt}/\text{RSF}_{Pt}}{\sum \left( \frac{\text{Area}_i/\text{RSF}_i}{1} \right)}
\]  

\[
X_2 = 1 - X_{Pt}
\]

where, \(X_{Pt}\) and \(X_2\) are the surface atomic fraction of Pt and the alloying material present with Pt, respectively. The results obtained are tabulated in Table 5-3. Upon increasing the catalyst loading, no significant difference in the surface composition of Pt-Ir and Pt-Rh was observed. On the contrary, the increase in catalyst loading for Pt-Ru resulted in an
increase in the Ru content. This increase in Ru content could be attributed to the ease of oxide formation.

*Figure 5-2.* XPS spectra for bimetallic catalysts electrodeposited on CFP. (A) Pt and Ir 4f lines from Pt-Ir electrodes. (B) Pt 4d lines from Pt-Ru electrode. (C) Ru 3p lines from Pt-Ru electrodes. (D) Pt 4f lines from Pt-Rh electrode. (E) Rh 3p lines from Pt-Rh electrode. The spectral lines A1 and A2 represent Pt-Ir with low and high catalyst loadings, respectively. Likewise spectral lines B1 and B2, C1 and C2 represent low and high loadings for Pt-Ru, and Pt-Rh, respectively. The Pt and Ru XPS peaks for the Pt-Ru electrocatalyst exhibits a 2 eV shift in the binding energies at higher loading, implying the increase in Ru content in the alloy increases the tendency of the catalyst to get oxidized.
Table 5-3.

Bulk and surface composition of electrodeposited bimetals. Bulk compositions estimated using XRD and EDX for all bimetals except Pt-Ru are within reasonable agreement. The surface composition of Pt-Ni alloys are not included in the table, since they are the same as the bulk composition obtained from EDX spectra.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Label</th>
<th>Catalyst Loading (% wt)</th>
<th>Nominal Composition (% At)</th>
<th>Bulk Alloy Composition $X_{Pt}:X_{2}$ (% At)</th>
<th>Surface Alloy Composition from XPS (± 3% At)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ir</td>
<td>A1</td>
<td>12</td>
<td>50:50</td>
<td>62:38</td>
<td>60:40</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>30</td>
<td></td>
<td>68:32</td>
<td>61:39</td>
</tr>
<tr>
<td>Pt-Ru</td>
<td>B1</td>
<td>14</td>
<td>35:65</td>
<td>51:49</td>
<td>49:51</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>31</td>
<td></td>
<td>47:53</td>
<td>34:66</td>
</tr>
<tr>
<td>Pt-Rh</td>
<td>C1</td>
<td>14</td>
<td>35:65</td>
<td>49:51</td>
<td>22:78</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>29</td>
<td></td>
<td>38:62</td>
<td>24:76</td>
</tr>
<tr>
<td>Pt-Ni</td>
<td>D1</td>
<td>14</td>
<td>53:47</td>
<td>89:11</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>29</td>
<td></td>
<td>93:7</td>
<td>--</td>
</tr>
</tbody>
</table>

5.3.1.2. Bulk Composition (XRD and EDX)

The bulk composition of the bimetals electrodeposited on CFP was evaluated and compared to the composition at the surface. Bulk compositions of the alloys synthesized in this study were obtained from EDX and XRD. Figures 5-3A and 5-3B represent the diffractograms from metals and bimetal electrodes, respectively. The diffractogram peaks for metals and bimetallic electrocatalysts are mapped according to the respective crystallographic planes. The additional peaks were due to the background (carbon substrate and sample holder). As expected, XRD peaks for Pt, Rh, Ni displayed diffraction from planes of a face centered cubic (fcc) crystal lattice, whereas the peaks for Ru represent reflections from the planes of a hexagonal close packed (hcp) lattice. From Figure 5-3B, it can be observed that the diffractograms of the bimetals all show just one
set of peaks with their peak positions shifted to higher $2\theta$ values compared to Pt, implying alloy formation. The XRD results for the bimetals correspond to the fcc lattice where the peak maximum shifted to higher $2\theta$ values when compared to Pt and therefore indicates an increase in the lower d values (inter planar distance) and smaller lattice constants. This suggests the alloy formation by substitution of the alloying element into lattice of Pt.

Bulk compositions from XRD were obtained by using the shifts in $2\theta$ values for the peak maximum in Vegard’s law [83, 84]. It has to be noted that the law is applicable to pure unsupported alloys. Moreover, for supported alloys, it was shown that the Vegard’s law tends to underestimate the amount of Pt in a Pt-Ru alloy dispersed in a carbon support [83]. Therefore it is modified, as shown in Equation 5a, to include the effect of catalyst-support interaction, assuming that the effect of carbon paper support on the alloying material is the same as that for Pt.

$$A_{\text{alloy}} = A_{\text{Pt/c}} - [(A_{\text{Pt}} - A_2) X_2] \quad (5a)$$

$$X_{\text{Pt}} = 1 - X_2 \quad (5b)$$

where, $A_{\text{alloy}}$ is the lattice parameter of the bimetal alloy obtained from XRD data using crystallographic principles; $A_{\text{Pt/c}}$ is the lattice parameter for Pt on a carbon support obtained from XRD data; $A_{\text{Pt}}$ is the lattice parameter for pure Pt ($A_{\text{Pt}} = 3.9231 \text{ Å}$); $A_2$ is the lattice parameter of the alloying species $A_2$ ($A_{\text{Ir}} = 3.8394 \text{ Å}$, $A_{\text{Rh}} = 3.8031 \text{ Å}$; $A_{\text{Ru}} = 3.8013 \text{ Å}$; $A_{\text{Ni}} = 3.5239 \text{ Å}$); and $X_2$ is the bulk atomic fraction of the alloying element in the bimetal.
Figure 5-3. XRD spectra for (A) metals and (B) bimetals. The legends for bimetals are detailed in Table 5-2 (Letters A, B, C, and D refer to Pt-Ir, Pt-Ru, Pt-Rh, and Pt-Ni, respectively. While, numbers 1 and 2 in the legend refer to low and high catalyst loadings, respectively). The XRD spectra for all metals but Ru show the pattern for fcc lattice. Therefore Ru is plotted in the negative Y-axis to emphasize that the lattice (hcp) for Ru is different from the other catalysts. BG refers to the background XRD spectra obtained for the CFP substrate.
The composition of Pt-Ru electrocatalysts was evaluated by assuming fcc lattice for the alloy. The bulk atomic composition of alloys obtained from XRD and EDX are shown in Table 5-3. The bulk composition of the deposit mainly depends on the plating solution (pH, composition, type of metal salts) and deposition parameters (potential, temperature). As expected, the majority of the deposit for Pt-Ru and Pt-Rh alloys came from the more electropositive metal and the major component in the plating bath solution, i.e., Ru and Rh, respectively. The higher Pt content for Pt-Ni alloys can be attributed to the higher pH which results in the hydrogen adsorption ($H_{ads}$) on Ni, which facilitates the chemical reduction of Pt$^{4+}$ preferentially on Ni. Despite Ir being more noble than Pt, the Pt-Ir deposits exhibit an Ir content lower than Pt. This low Ir content in Pt-Ir alloys could be attributed to the complexity involved with Ir deposition and has been recognized by several researchers. Nevertheless, the reason for the sluggish deposition of Ir remains far-fetched. Based on experience in Pt-Ir electrodeposition, the low Ir deposition rate is attributed to the high density of Ir, which could enhance the difficulty to adhere to the CFP substrate upon reduction.

A reasonable agreement is observed for the compositions estimated using XRD and EDX techniques for all alloys except for Pt-Ru. The composition obtained for Pt-Ru from Vegard’s law overestimates the Ru content in the alloy [83]. This discrepancy could be attributed to the high Ru content in the alloy close to the threshold value of 62%, where the alloy is formed in the hcp crystal lattice resulting in a skewed 2θ values and broader peaks as observed in Figure 5-3B. A similar mismatch in the Pt-Ru composition
obtained from XRD and EDX data has been reported previously which has been attributed to the partial hcp lattice occurring at high Ru concentrations [83].

A comparison of the XPS and EDX measurements (Table 5-3) observed the null hypothesis due to the higher variability within a data set for all bimetals except for Pt-Rh. This implies that there is no significant difference in the composition at the surface from the bulk composition. However, the Pt-Rh data indicates a surface rich with Rh, implying a sequential or preferential deposition of Rh on Pt. Alternatively a surface segregation of Rh is possible. As for Pt-Ni, it has been previously reported that the bulk composition of Pt-Ni obtained from EDX results concurs to the surface composition obtained from XPS spectra for Pt-Ni electrodeposited, from the bath solution containing Pt/Ni ratio of 1/3 [85].

5.3.1.3. Particle Size and Specific Area of Catalyst

The particle size is usually estimated using Scherrer equation as shown in Equation 6.

\[ D_p = \frac{0.9 \lambda}{(\beta_{\text{size}} \cos \theta)} \]  

where, \( D_p \) is the average crystallite size (Å); \( \lambda \) is the wavelength of the Cu-K\( \alpha \) radiation from the source (1.5814 Å); \( \theta \) is the Bragg angle or the angle of maximum reflection intensity, in degrees; and \( \beta_{\text{size}} \) refers to the peak broadening (in 2\( \theta \) degrees) due to particle size effects. However, the peak broadening obtained from XRD experiments (\( \beta_{\text{expt}} \)) is convoluted by peak broadening due to particle strain (\( \beta_{\text{strain}} \)), instrumental profile (\( \beta_{\text{inst}} \)) and particle size. From Figure 5-3A and 5-3B, it can be observed that all the XRD peak
profiles for the metals are predominantly of the Lorentzian type, while the bimetals exhibit a mixed Lorentzian and Gaussian type profile. Deconvolution of the peak broadening was done using the Williamson-Hall (W-H) method, using a linear function as in Equation 7a for the Lorentzian type [86] and using the approximation proposed by Halder and Wagner shown in Equation 7b for the mixed type [87], respectively

\[
B_{\text{expt}} - B_{\text{inst}} = B_{\text{strain}} - B_{\text{size}}
\]  

(7a)

\[
\frac{B_{\text{size}}}{(B_{\text{expt}} - B_{\text{inst}})} = 1 - \left(\frac{B_{\text{strain}}}{(B_{\text{expt}} - B_{\text{inst}})}\right)^2
\]  

(7b)

where, \( B_{\text{strain}} = 4 \xi_{\text{strain}} \tan \theta \), in turn where \( \xi_{\text{strain}} \) is the modulus of elasticity. Upon substituting Equation 6 in Equation 7, equations for Williamson-Hall (W-H) plots for the two peak profiles were obtained and are shown in Equations 8a and 8b.

\[
( B_{\text{expt}} - B_{\text{inst}} ) \cos \theta = (4 \xi_{\text{strain}}) \sin \theta + 0.9 \lambda / D_p
\]

(8a)

\[
\frac{( B_{\text{expt}} - B_{\text{inst}} )}{\tan^2 \theta} = (0.9 \lambda / D_p) \left( B_{\text{expt}} - B_{\text{inst}} \right) / (\sin \theta \tan \theta) + 16e^2
\]

(8b)

The average crystallite size was obtained from the intercept of the \(( B_{\text{meas}} - B_{\text{inst}} ) \cos \theta \) versus \(\sin \theta\) plot and slope of \(( B_{\text{meas}} - B_{\text{inst}} )^2 / \tan^2 \theta \) versus \(( B_{\text{meas}} - B_{\text{inst}} ) / (\sin \theta \tan \theta)\) plot for the peaks (111) and (200). The CSA of the catalyst in m² g⁻¹ was then evaluated using Equations 9a and 9b.

\[
\text{CSA} = \frac{60000}{(\rho_{\text{alloy}} \times D_p)}
\]

(9a)

\[
\rho_{\text{alloy}} = Y_{\text{Pt}} \rho_{\text{Pt}} + Y_2 \rho_2
\]

(9b)

where, \( \rho_{\text{Pt}}, \rho_2, \) and \( \rho_{\text{alloy}} \) refers to the density in g cm⁻³ for Pt, alloying specie, and alloy. \( Y_{\text{Pt}} \) and \( Y_2 \) refer to the atomic mass fraction of Pt and alloying specie calculated from EDX data.
Tables 5-4 and 5-5 show the catalyst loading, particle size, CSA, EASA, and catalyst utilization for the metallic and bimetallic catalysts synthesized for this study. In addition, the ‘crystallite size’ evaluated from XRD data is in accordance to the ‘particle size’ observed from the SEM images and will be addressed as such in this study. From Table 5-5, it can be observed that the bimetallic alloy deposits exhibit a lower particle size and a higher CSA than their respective individual electrocatalysts, except for the Pt-Ni alloys. This can be attributed to the ease of nucleation and deposition of noble metals and lower pH, which in-turn facilitates the HER on the noble metal at the deposition potential. Hence any further deposition and $H_{ads}$ formation which in-turn favors reduction of the alloying material preferentially takes place on the carbon surface [38]. However, the larger deposits for Pt-Ni could be attributed to the presence of Ni deposits and higher pH. These results in a high overpotential for HER on Ni electrode, thereby leaving the Ni deposits covered with $H_{ads}$. This $H_{ads}$ on Ni acts as a reducing agent for the metal ion, thereby causing further deposition specifically on top of Ni, thereby resulting in a larger particle size.

5.3.2. Electrochemical Characterization

5.3.2.1. EASA and Catalyst Utilization

For a complete comparison of electrocatalytic activity between different catalysts, it is essential to normalize the current to the EASA. The choice of the technique used for estimating EASA is dependent upon the material of interest. Other researchers have described in detail the methodology, application, and limitations for various techniques to determine for EASA [88, 89]. EASA for the electrodes, in this study, were evaluated by
calculating the ratio of experimental charge ($Q_{\text{expt}}$) to the theoretical charge ($Q_{\text{theo}}$) required for the adsorption of a monolayer of hydrogen or hydroxide or from the charge required to strip a monolayer of CO. EASA and catalyst utilization were calculated using Equations 10a and 10b.

$$M \times \text{EASA} = \frac{Q_{\text{expt}}}{Q_{\text{theo}}} = \frac{Q_{\text{expt}}}{\sum (X_i q_i)} \quad (10a)$$

$$\text{Utilization} = \frac{\text{EASA}}{\text{CSA}} \quad (10b)$$

where, EASA is the electrochemical active surface area ($m^2 \cdot g^{-1}$); $M$ is the weight of the catalyst deposited in g, $X_i$ is the mole fraction of species $i$ present in the alloy surface taken from EDX data, $q_i$ is the theoretical charge required for a unit area of species $i$.

From Table 5-4, the EASA for metals follows the trend Rh>Ru>Ni>Pt. The higher EASA for Rh and Ru can be attributed to the smaller particle size of the Rh and Ru deposits. In addition, the EASA is lower than the CSA obtained from XRD measurements thereby resulting in catalyst utilization lower than 100%. This suggests that parts of the catalyst are electrochemically inactive due to masking, either by a fresh electrocatalyst layer or by other impurities such as oxides. From Table 5-5, The EASA for bimetals at low catalyst loadings follows the trend Pt-Rh>Pt-Ru>Pt-Ir>Pt-Ni and it increases with the catalyst loading. Furthermore, this increase in EASA is accompanied by a decrease in the catalyst utilization for Pt-Ir and Pt-Ru electrocatalysts, while no significant difference in the utilization was observed for Pt-Rh and Pt-Ni electrocatalysts. Thereby, suggesting that the EASA varies non-linearly with the loading. An elaborate surface response design of experiments is required to ascertain the relationship between the EASA and deposition parameters for bimetals and is beyond the scope of this study.
Table 5-4.

Physical properties (particle size and specific area) of metals electrodeposited on CFP. The higher surface area for Ru and Rh is due to their smaller particle size.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Catalyst Loading per Unit Area (± 1.1 mg cm⁻²)</th>
<th>Weight (± 2 %)</th>
<th>Average Particle Size (Å)</th>
<th>CSA (± 0.98 m² g⁻¹)</th>
<th>EASA (± 0.27 m² g⁻¹)</th>
<th>Utilization (± 2.4 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>1.91</td>
<td>30.3</td>
<td>478 ± 6</td>
<td>5.85</td>
<td>4.64</td>
<td>79.3</td>
</tr>
<tr>
<td>Ru</td>
<td>2.06</td>
<td>31.9</td>
<td>267 ± 3</td>
<td>18.27</td>
<td>10.20</td>
<td>55.8</td>
</tr>
<tr>
<td>Rh</td>
<td>2.18</td>
<td>33.1</td>
<td>178 ± 3</td>
<td>27.18</td>
<td>15.85</td>
<td>58.3</td>
</tr>
<tr>
<td>Ni</td>
<td>2.00</td>
<td>31.2</td>
<td>338 ± 5</td>
<td>19.92</td>
<td>5.70</td>
<td>28.6</td>
</tr>
</tbody>
</table>

Table 5-5.

Physical properties (particle size, alloy density and specific area) of bimetals electrodeposited on CFP. All bimetallic catalysts except Pt-Ni exhibit smaller particle size than their unalloyed constituents. The increase in particle size for Pt-Ni is attributed to the presence of $H_{ads}$ on Ni deposits, which acts as a reducing agent leading to further deposition on existing deposits.

<table>
<thead>
<tr>
<th>Electrode (label)</th>
<th>Catalyst Loading per Unit Area (± 1.1 mg cm⁻²)</th>
<th>% Weight (± 0.1)</th>
<th>Average Particle Size (Å)</th>
<th>$\rho_{alloy}$ (± 0.4 g cm⁻³)</th>
<th>CSA (± 1.34 m² g⁻¹)</th>
<th>EASA (± 0.22 m² g⁻¹)</th>
<th>Utilization (± 3.8 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ir (A1)</td>
<td>0.6</td>
<td>12.2</td>
<td>289 ± 8</td>
<td>21.8</td>
<td>9.54</td>
<td>5.40</td>
<td>56.6</td>
</tr>
<tr>
<td></td>
<td>(A2)</td>
<td>1.9</td>
<td>29.6</td>
<td>99 ± 2</td>
<td>21.7</td>
<td>27.88</td>
<td>6.80</td>
</tr>
<tr>
<td>Pt-Ru (B1)</td>
<td>0.7</td>
<td>14.1</td>
<td>272 ± 7</td>
<td>17.5</td>
<td>12.64</td>
<td>5.72</td>
<td>45.3</td>
</tr>
<tr>
<td></td>
<td>(B2)</td>
<td>2.0</td>
<td>30.8</td>
<td>100 ± 3</td>
<td>17.1</td>
<td>35.15</td>
<td>6.21</td>
</tr>
<tr>
<td>Pt-Rh (C1)</td>
<td>0.7</td>
<td>13.7</td>
<td>94 ± 1</td>
<td>18.0</td>
<td>38.12</td>
<td>12.21</td>
<td>32.0</td>
</tr>
<tr>
<td></td>
<td>(C2)</td>
<td>1.8</td>
<td>29.0</td>
<td>80 ± 2</td>
<td>16.8</td>
<td>41.55</td>
<td>13.36</td>
</tr>
<tr>
<td>Pt-Ni (D1)</td>
<td>0.8</td>
<td>14.3</td>
<td>631 ± 19</td>
<td>21.0</td>
<td>4.54</td>
<td>2.41</td>
<td>53.2</td>
</tr>
<tr>
<td></td>
<td>(D2)</td>
<td>1.6</td>
<td>29.0</td>
<td>347 ± 14</td>
<td>21.2</td>
<td>8.16</td>
<td>4.34</td>
</tr>
</tbody>
</table>
5.3.2.2. Voltammetry Study of HER with 1 M Ammonia

Figure 5-4, depicts a comparison of the Tafel plots, overpotential ($\eta$) versus log $i$, for metallic electrocatalysts with bimetallic electrocatalysts in alkaline solution with ammonia (5 M KOH + 1 M ammonia). The Tafel plots were constructed using the results from LSV experiments. HER follows the Tafel approximation in the high overpotential region where the charge-transfer dominates the reaction rate. The kinetic parameters for the reaction can be obtained from Tafel approximation as shown in Equation 11.

$$i = i_0 \exp \left( \frac{\alpha nF\eta}{RT} \right)$$  \hspace{1cm} (11)

where $i_0$ is the exchange current density (mA cm$^{-2}$) which is evaluated from the y intercept (Volts), $\alpha$ is the transfer coefficient, $n$ is the number of electrons, $F$ is the Faraday’s constant (96485 coulombs), $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$).

Figure 5-4. Tafel plots for HER on metallic and bimetallic electrodes in 5 M KOH and 1 M ammonia. The bimetallic electrocatalysts exhibit higher current densities when compared to their constituent unalloyed metallic electrodes. The higher activity of the bimetallic electrocatalysts is attributed to the synergistic effect of the alloys.
The Tafel parameters, Tafel slope and $i_0$, obtained from Equation 11 are dependent upon the region in which the approximation is applied and has been an object of misrepresentation. The Tafel approximation is applied over a region where the current from the reverse direction is less than 1% of the current from the forward direction for the reaction of interest and arrive at a threshold overpotential of at least 118 mV [90]. However, for fast reactions such as the HER, such high overpotentials could infringe into the mass transport controlled or mixed-kinetic controlled region [90]. A useful rule of thumb is that the overpotential region from which the Tafel parameters (TS, $i_0$, and $\eta$) are estimated should not be significantly lower than half the Tafel slope in that region. The Tafel parameters were evaluated at the low overpotential region, which is the desired range for operating the ammonia electrolytic cell such that the cell voltage is below the limiting value and sufficiently large enough to avoid interference from mass transport or secondary faradaic reactions that could directly contribute to the current [91].

5.3.2.2.1. Evaluation of Pt, Ru, Rh, and Ni as Ammonia Electrolysis Cathodes

Tables 5-6 details the Tafel parameters for HER on metallic electrocatalysts evaluated using Equation 11. From Table 5-6, Pt has the highest activity for HER in the absence of ammonia, and provides the lowest overpotential at -0.25 mA cm$^{-2}$. The overpotential for the HER follows the trend Pt<Ru<Rh<Ni as reported in the literature [42].
Table 5-6.

Tafel Parameters for HER on metallic electrodes in alkaline medium in the presence and absence of ammonia. The HER overpotential for Pt, Ru, and Ni increased with the presence of 1 M ammonia, whereas the overpotential for Rh decreased with the presence of 1 M ammonia.

<table>
<thead>
<tr>
<th>Electrolyst</th>
<th>Without Ammonia</th>
<th>With Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slope (±3 mV decade(^{-1}))</td>
<td>(i_0) (±0.002 mA cm(^{-2}))</td>
</tr>
<tr>
<td>Pt</td>
<td>-157</td>
<td>0.043</td>
</tr>
<tr>
<td>Ru</td>
<td>-140</td>
<td>0.021</td>
</tr>
<tr>
<td>Rh</td>
<td>-220</td>
<td>0.040</td>
</tr>
<tr>
<td>Ni</td>
<td>-95</td>
<td>0.001</td>
</tr>
</tbody>
</table>

However, in the presence of 1 M ammonia, the overpotential increases for all catalysts except Rh and follows the trend Rh<Pt~Ru<Ni. The increase in the overpotentials for HER could be attributed to the affinity of the catalysts toward the ammonia adsorption as shown in Equation 12.

\[
\text{M} + \text{NH}_3 \rightleftharpoons \text{M} - \text{NH}_3 \quad \text{E} = \text{E}_{\text{ads}} \quad (12)
\]

Ammonia exists in the molecular form with a lone pair of electrons, in alkaline medium. In order for the metal-ammonia bond formation to occur, the lone pair of electrons must be transferred to the electrocatalyst [92]. It has been reported that the activity of HER of a particular catalyst is higher on the surface with the hydrogen underpotential deposition \(H_{\text{upd}}\) for Pt, Ru, and Ni [42, 68, 79]. Ammonia adsorption takes place in the hydrogen underpotential deposition (\(H_{\text{upd}}\)) potential region [93]. Thereby resulting in the weaker M-\(H_{\text{upd}}\) bond strength, which is evident from the shift in the \(H_{\text{upd}}\)
potential in the negative direction [79]. The magnitude of reduction in the M-H$_{\text{upd}}$ bond strength is directly related to the binding energy (B.E) of ammonia on that particular metal, i.e., the stronger the B.E of ammonia on the metal, the weaker the M-H$_{\text{upd}}$ bond strength gets. The B.E of ammonia on Ru (0001), Ir (111), Pt (111), Rh (111), and Ni (111) with surface coverage of 0.25 is reported to be -1.0 eV [94, 95], -0.84 eV [96], -0.78 eV [15, 27, 32, 97], -0.73 eV [98], and -0.74 eV [99], respectively. Therefore the decrease in activity observed for Pt, Ru, and Ni in the presence of ammonia can be attributed to the decrease in the M-H$_{\text{upd}}$ bond strength.

On the contrary, Rh exhibits an increase in the HER activity in the presence of ammonia. The increase in HER activity on Rh, despite the decrease in the M-H$_{\text{upd}}$ bond strength has been attributed to the barrier effect of H$_{\text{upd}}$ on HER as proposed by Markovic et al. [79, 100]. Another interesting observation that can be made is that Ni, Ru, and Pt have an even number of valence shell electrons, which tends to attain a stable electronic structure upon adsorbing ammonia, thereby enhancing the difficulty of formation of an M-H bond [101]. However, Rh has three unpaired electrons and after adsorbing a molecule of ammonia will still have one available to participate in the H$_{\text{upd}}$.

5.3.2.2.2. Evaluation of PtxM$_{1-x}$ as Ammonia Electrolysis Cathodes

From Figure 5-4, it can be observed that all the bimetallic electrocatalysts exhibit a higher current density and lower overpotentials when compared with their respective unalloyed electrocatalysts. The increase in activity for the bimetals can be attributed to the synergistic effect of the constituent metals. Figures 5-5A through 5-5D compare the
CV of bimetallic catalysts Pt-Ir, Pt-Ru, Pt-Rh, and Pt-Ni with their respective unalloyed electrocatalysts in 5 M KOH in the presence of 1 M ammonia.

The HER currents for all bimetals in the presence of ammonia are higher than their respective constituent unalloyed metals. This increase in the activity for HER with bimetals could be due to the ammonia specifically adsorbing on the more electropositive alloying element, leaving the Pt surface active for HER. Moreover, this increase in HER
currents is accompanied by higher hydrogen $H_{\text{upd}}$ peak current on the Pt-Ir, Pt-Ru, and Pt-Rh electrodes, implying that activity of the catalyst for the HER is higher on the catalyst with $H_{\text{upd}}$. According to Ezaki et al., when alloying with a more electropositive metal, the alloying metal tends to donate electrons to the base metal. Thereby, a slight negative charge is created on the base metal, which in-turn increases the HER activity of the base metal [102]. Therefore, Ni, Rh, Ru, and Ir, all being electropositive to Pt, tend to exhibit a positive charge after donating electrons to Pt. Since the ammonia adsorption is an anodic reaction it prefers the Ni, Rh, Ru, and Ir sites in the alloy, leaving the Pt sites available for the cathodic hydrogen underpotential deposition ($H_{\text{upd}}$).

Table 5-7 shows the Tafel parameters and overpotentials at a current of -0.25 mA cm$^{-2}$ for HER using bimetals in 5 M KOH with the presence and absence of 1 M ammonia. In the absence of ammonia, the overpotentials for the bimetals follows the trend Pt-Ni<Pt-Rh~Pt-Ir~Pt-Ru. The Pt-Ni alloy displayed an overpotential that is 90 mV lower than that observed for the unalloyed Pt. This difference in overpotential is comparable to the 110 mV obtained for surface modified Pt electrode with Ni(OH)$_2$ clusters solution of 0.1 M KOH by Subbaram et al. [65]. The high activity of Pt-Ni for HER has been attributed to the higher activity of Pt for the adsorption and recombination reaction (Tafel step) and higher activity of Ni, which exists in its oxide state at the operating pH and potentials, for the electrochemical water decomposition reaction (Heyrovsky and Volmer step).

Upon introducing 1 M ammonia, the trend in overpotentials at -0.25 mA cm$^{-2}$ changed to Pt-Ir~Pt-Rh~Pt-Ru~Pt-Ni for electrodes with 15 % catalyst loading.
Furthermore, the alloy electrodes continued to display overpotentials lower than their corresponding unalloyed catalysts even in the presence of 1 M ammonia.

**Table 5-7**

*Tafel Parameters for HER on bimetallic electrodes in alkaline medium in the presence and absence of ammonia. For all electrocatalysts the increase in loading results in an increase in overpotential both in the presence and absence of ammonia, this is attributed to the big cluster type deposits, which in-turn causes a poor triple phase boundary.*

<table>
<thead>
<tr>
<th>Electrocatlyst</th>
<th>Label</th>
<th>Without Ammonia</th>
<th>With 1 M Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Slope (±3 mV decade⁻¹)</td>
<td>i₀ (±0.002 mA cm⁻²)</td>
</tr>
<tr>
<td>Pt-Ir</td>
<td>A1</td>
<td>-93</td>
<td>0.149</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>-172</td>
<td>0.075</td>
</tr>
<tr>
<td>Pt-Ru</td>
<td>B1</td>
<td>-91</td>
<td>0.108</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>-177</td>
<td>0.077</td>
</tr>
<tr>
<td>Pt-Rh</td>
<td>C1</td>
<td>-107</td>
<td>0.138</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>-160</td>
<td>0.096</td>
</tr>
<tr>
<td>Pt-Ni</td>
<td>D1</td>
<td>-82</td>
<td>0.140</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>-135</td>
<td>0.064</td>
</tr>
</tbody>
</table>

An increase in overpotentials is observed for Pt-Ni and Pt-Ru with the addition of 1 M ammonia. On the contrary, no significant difference in overpotential is noticed for Pt-Ir and Pt-Rh electrodes in the presence of ammonia. Although, the surface of the Pt-Rh bimetal is rich in Rh, no significant decrease in overpotential is observed as expected from the behavior of the Rh electrocatalyst. As mentioned previously, this behavior can be attributed to the behavior of the bimetal wherein the more electropositive Rh donates electrons to the less electropositive Pt in the alloy, thereby creating a positive charge on Rh, which then facilitates the adsorption of ammonia on Rh thereby masking its surface...
While Ru and Ni are more electropositive than Pt, their surfaces are masked by their hydroxides at potentials as low as -0.1 V and -0.3 V versus RHE at pH 14 [103, 104]. This in-turn causes ammonia adsorption to compete with H$_{\text{upd}}$ for sites on Pt instead of the alloying material. This causes the potential for H$_{\text{upd}}$ to be shifted in the negative direction, which in turn results in weak Pt-H$_{\text{upd}}$ bonds. However, the oxides of Ir and Rh surface do not exist below 0.1 V and -0.03 V [103]. Thereby permitting the ammonia adsorption onto Ir and Rh, while allowing the H$_{\text{upd}}$ and HER to proceed on the Pt surface.

### 5.3.2.3. Effect of Catalyst Loading on HER Kinetics

From Table 5-7, increasing the bimetal catalyst loading [Me/(Me + C)] from ~15% (by weight) to 30% (by weight), results in an increase in the overpotentials and a decrease in $i_0$ for all the bimetallic catalysts. From SEM images (Figure 5-1), the increase in the loading results in the deposition of the catalyst over another layer of catalyst, subsequently masking it. This results in a foil-like deposition for the electrode, which in turn results in a poor triple-phase boundary, thereby resulting in a reduced catalytic activity for HER. Figures 5-6A through 5-6D show the change in the intercrystallite distance (ICD) and hydrogen evolution current density with catalyst loading at overpotential of 100 mV. The HER current densities at 100 mV were compared to evaluate the operating potential window of the catalyst. The HER current densities for Pt, Ru, Rh, and Ni in the presence of ammonia at overpotential 100 mV were estimated to be 0.107, 0.174, 0.117, and 0.010 mA cm$^{-2}$, respectively. Although a slight decrease in the current density is observed with the addition of 1 M ammonia bimetals continued to
exhibit higher HER activity compared to the respective unalloyed metals. The decrease in the HER could be attributed to the fact that ammonia masks the surface of the alloying metal thereby leaving it inactive for HER. Pt-Ir exhibits the HER highest activity and the smallest drop in the activity of HER in the presence of 1 M ammonia. The ICD in nm was calculated as shown in Equation 13, where $\rho$ is the electrocatalyst density in g nm$^{-3}$, $D_p$ is the particle size of the electrocatalyst deposit in nm, $SA_c$ is the specific area of the carbon support in nm$^2$ g$^{-1}$, and $y$ is the catalyst loading in % (by weight) [105].

$$ICD = \frac{1}{30.75} \sqrt{\frac{\pi \rho D_p^3 SA_c (1 - y)}{y}}$$

(13)

For all the electrocatalysts, the catalytic activity at 100 mV overpotential and the ICD decreased with increase in loading. The decrease in ICD causes a poor triple phase boundary between the solid catalyst, the liquid reactant and gaseous products. As suggested by Watanabe et al., the catalysts with smaller ICD [83, 105] exhibited a lower electrocatalytic activity. The maximum activity for HER in the presence of ammonia was achieved with Pt-Ir catalyst with loading of 12.2% and ICD of 7.2 nm.

Other factors such as the Pt-Pt bond length affects the lattice strain, which in-turn affects the Fermi energy of the material, thereby affecting the electrocatalytic activity of the catalyst [41, 106]. The Pt-Pt bond length varies with the composition and the alloying material and was calculated as described previously by Shao et al. [106]. However the trend in the Pt-Pt bond length variation with the composition and alloying material is unclear.
Figure 5-6. Effect of loading on the HER activity at an overpotential of 100 mV (obtained from LSV data in Figure 5-4) and on the ICD for bimetals (A) Pt-Ir (B) Pt-Ru (C) Pt-Rh and (D) Pt-Ni. The ICD and the current density vary inversely with the loading. The low HER activity at higher loadings is attributed to the decrease in the ICD.

Figures 5-7A through 5-7D show the change in overpotential and Pt-Pt bond length with Pt content in the alloy. The overpotential of all bimetals in the presence of ammonia followed the same trend as observed for the overpotentials without ammonia. The maximum electrocatalytic activity for HER using Pt-Ir, Pt-Ru, Pt-Rh, and Pt-Ni is at 68%, 40%, 46%, and 88% Pt, respectively. In addition, it can be seen that the overpotential varies inversely to the Pt-Pt bond length. In other words, the activity of the catalyst is directly proportional to the Pt-Pt bond length [106]. Pt-Ir electrocatalyst with Pt-Pt bond length of 5.5 Å and a Pt content of 71% displayed the least overpotential for
HER. Nevertheless, in order to obtain a more exact composition for the catalyst, a surface response design of experiments needs to be undertaken.

![Figure 5-7](image)

**Figure 5-7.** Effect of Pt content in the alloy on the overpotential at -0.25 mA cm$^{-2}$ (obtained from LSV data in Figure 5-4, where A, B, C, and D represent Pt-Ir, Pt-Ru, Pt-Rh, and Pt-Ni, respectively) and Pt-Pt bond length. The Pt-Pt bond length is inversely related to the overpotential for HER. A Pt content of 71% for the Pt-Ir electrocatalyst displayed the least overpotential and therefore the highest activity for HER in 5 M KOH with 1 M ammonia.

5.4. Conclusion

Metals and bimetals of the type Pt$_x$M$_{(1-x)}$ (where, M=Ru, Rh, Ir, and Ni) were successfully electrodeposited on CFP. The electrodes were characterized and tested for their electrocatalytic activity for HER in 5 M KOH in the presence and absence of 1 M ammonia. The following conclusions can be drawn.
1. The presence of ammonia improves the HER catalytic activity on Rh. On the other hand, it has a detrimental effect on the catalytic activity of Pt, Ru, and Ni.

2. The synergistic effect of bimetals offers enhanced electrocatalytic activity for HER, in the Tafel region, when compared with the unalloyed constituent metals. In the presence of ammonia, the adsorption of ammonia is selective to the more electropositive alloying metal, thereby leaving base Pt sites free for HER.

3. The presence of hydroxides on surface of Ru and Ni and therefore causes ammonia to compete for adsorption on Pt sites in addition to the adsorption on the alloying material, resulting in the $H_{\text{upd}}$ potential to shift in the negative direction and in turn causing an increase in the HER overpotential for Pt-Ru and Pt-Ni.

4. Increasing the catalyst loading results in a decrease in the activity toward HER, which is attributed to a poor triple phase boundary, which is confirmed from the decrease in ICD.

5. Based on the electrocatalytic activity of HER at an overpotential of 100 mV, the Pt-Ir electrocatalyst with 13% loading and 68% Pt content with an ICD of 7.2 nm displayed the largest potential window for operation, without a significant loss in current density in the presence of ammonia.

5.5. References

CHAPTER 6: EFFICACY OF POTASSIUM POLY(ACRYLATE) GEL ELECTROLYTE AS A SUBSTITUTE TO AQUEOUS ELECTROLYTES FOR ALKALINE AMMONIA ELECTROLYSIS

(It should be noted that part of the contents of this chapter have been published in Electrochimica Acta [58]. R.P. and G.G.B. developed the idea and designed the experiments. R.P. performed the experiments and data analyses. R.P. and G.G.B. discussed the results. R.P. and G.G.B. co-wrote the paper.)

6.1. Introduction

Ammonia is predominantly present in domestic, industrial, and agricultural wastes, which are discharged into the larger water bodies causing ground water contamination [1-8]. Ammonia electrolysis offers a cost-effective, environmentally-friendly and an efficient technology to remediate ammonia from wastes, thereby preventing groundwater contamination while simultaneously producing hydrogen [1, 9-16]. Furthermore, ammonia electrolysis can be used to manufacture amperometric sensors for detecting ammonia[17]. The wide range of potential applications has led to a substantial increase in interest among researchers in the development of this technology.

The electro-oxidation of ammonia requires ammonia to be in its molecular form. At pH below 9, the fraction of ammonia present as ammonium-ions is greater than molecular ammonia therefore it occurs mainly through an indirect process [18]. However, at a higher pH, it occurs via a direct electro-oxidation process as shown in Equations 1-3 [10]. An increase in the pH results in an increase in the rate of ammonia electro-
oxidation, Faradaic efficiency, and yield [2]. The pH dependence of ammonia electro-oxidation is more pronounced at higher ammonia concentrations[2]. At the same time, the solubility of ammonia is reduced at higher alkali concentrations [19, 20].

\[
\begin{align*}
\text{Anode:} & \quad 2\text{NH}_3 + 6\text{OH}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O} + 6\text{e}^- \quad E^0 = -0.770 \text{ V vs SHE} \quad (1) \\
\text{Cathode:} & \quad 6\text{H}_2\text{O} + 6\text{e}^- \rightarrow 3\text{H}_2 + 6\text{OH}^- \quad E^0 = -0.828 \text{ V vs SHE} \quad (2) \\
\text{Overall:} & \quad 2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 \quad E^0 = 0.058 \text{ V} \quad (3)
\end{align*}
\]

It has been widely accepted that ammonia electro-oxidation follows the Gerischer mechanism which requires OH\(^-\) ions to be adsorbed on the surface [15]. However, it has also been postulated that the OH\(^-\) ions could be preferentially adsorbed on Pt thereby preventing the adsorption of ammonia and acting as a catalytic poison to the electro-oxidation of ammonia[14].

Most of the studies in ammonia electrolysis have used aqueous KOH with ammonia as the electrolyte[14]. However, for its application as a wastewater remediation process, it is required to separate the KOH from the remediated stream after electrolysis. Moreover, the presence of aqueous 5 M KOH with ammonia increases the density of the electrolyte by 200 g l\(^-1\), thereby increasing the power required to pump the electrolyte into the electrolytic cell [21, 22]. It has also been noted that aqueous alkali is corrosive and known to cause leaks, therefore, it is vital to identify an alternative electrolyte for the process[23].

Solid Polymer Electrolytes (SPE’s) are widely used in fuel cells and seem to be a viable option for aqueous alkaline electrolysis, as they:

1. Avoid any recovery costs associated with the addition and separation of KOH from the remediated stream.
2. Facilitate the ammonia to stay in the solution phase.

3. Remove any parasitic power associated with pumping the viscous KOH.

4. Make the system more compact, thereby making the technology adaptable to portable applications.

However, alkaline SPE’s are plagued with low ionic conductivities and poor durability, which are clearly summarized by Arges et al., [24]. In comparison, Alkaline Polymer Gel Electrolytes (APGE’s) have ionic conductivities in the same order as its aqueous counterpart [25, 26]. APGEs are also widely used in electrochemical sensors, electrochemical capacitors, solid state sensors, Ni-Metal Hydride [27-29], Ni-H$_2$ [30], Ni-Cd [25, 31], Ni-Zn [25, 30, 32], Zn-Air batteries [33], other alkaline batteries [31, 34], and Fuel cells [35]. Therefore APGE’s could be the next best alternative to aqueous electrolytes. Table 6-1 provides a list of polymer electrolytes along with their ionic conductivities and compositions. Table 6-1 shows that PAA based electrolytes have higher ionic conductivities than other APGE’s.

It has been reported that the polymer synthesized with 7 % (by weight) PAA-K and 6 M KOH displayed the highest ionic conductivity [29]. It has also been reported that the potassium salt of poly acrylic acid (PAA-K) based APGE’s have a KOH retention of at least 90% and have been successfully used for urea electrolysis [36]. This shows that using PAA-K as an alternative to aqueous KOH for ammonia electrolysis could prove beneficial.
Table 6-1.

Comparison of the ionic conductivities of various APGEs available in the literature

<table>
<thead>
<tr>
<th>No.</th>
<th>Polymer</th>
<th>Copolymer and other additive</th>
<th>Maximum ionic conductivity at room temperatures (S cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PVA + KOH</td>
<td>-</td>
<td>(8.5 \times 10^{-4})</td>
</tr>
<tr>
<td>2.</td>
<td>PVA + KOH</td>
<td>PC + (\alpha\text{-Al}_2\text{O}_3)</td>
<td>~10(^{-3})</td>
</tr>
<tr>
<td>3.</td>
<td>PVA + KOH</td>
<td>ZrO(_2)</td>
<td>0.267</td>
</tr>
<tr>
<td>4.</td>
<td>PVA + KOH</td>
<td>PECH</td>
<td>(10^{-3} – 10^{-2})</td>
</tr>
<tr>
<td>5.</td>
<td>PVA + KOH</td>
<td>PEO</td>
<td>(10^{-7} – 10^{-2})</td>
</tr>
<tr>
<td>6.</td>
<td>PVA + Li salt</td>
<td>-</td>
<td>(9.2 \times 10^{-3})</td>
</tr>
<tr>
<td>7.</td>
<td>PEO + KOH</td>
<td>-</td>
<td>(5.1 \times 10^{-3} – 10^{-2})</td>
</tr>
<tr>
<td>8.</td>
<td>PEO + KOH</td>
<td>PECH</td>
<td>(10^{-3})</td>
</tr>
<tr>
<td>9.</td>
<td>PEO + LiClO(_4)</td>
<td>PECH</td>
<td>(10^{-3})</td>
</tr>
<tr>
<td>10.</td>
<td>(PAA-K) + KOH (Gel1)</td>
<td>-</td>
<td>~0.6</td>
</tr>
<tr>
<td>11.</td>
<td>PAA + KOH (Gel2)</td>
<td>MBA</td>
<td>0.288</td>
</tr>
</tbody>
</table>

This chapter aims on testing this hypothesis. The following three objectives were pursued:

1. To evaluate the performance of PAA-K for the anodic Ammonia Electro-oxidation Reaction (AER) and compare it to aqueous 5 M KOH electrolyte.

2. To evaluate the performance of PAA-K for the cathodic water reduction reaction or Hydrogen Evolution Reaction (HER) and compare it to aqueous 5 M KOH electrolyte.

3. To compare the rate of hydrogen production and conversion of ammonia for the Ammonia Electrolytic Cell (AEC) using PAA-K and aqueous 5 M KOH electrolyte.
6.2. Experimental

All the chemicals used in this study were of analytical grade. All the experiments were carried out at ambient temperatures and were repeated in order to check for reproducibility. The errors reported in the chapter were calculated by error propagation using errors from the instrument and standard deviation in the measurements.

6.2.1 PAA-K Synthesis

PAA-K, 7% (by weight) was synthesized, by mixing the partial potassium salt of poly acrylic acid of 99% purity, obtained from Sigma Aldrich, with 500 ml of 6 M KOH as described earlier [29]. 6 M KOH was made from KOH pellets (purity ≥85%) purchased from Fisher Scientific.

6.2.2. Ionic Conductivity

The ionic conductivity for 5 M KOH and PAA-K was measured by AC impedance spectroscopy. The resistance of the electrolyte was determined by placing the conductivity cell in the corresponding electrolyte, by applying an AC current with a frequency range between 10 kHz and 10 Hz at the open circuit potential using a Solartron 1252A frequency response analyzer coupled with a Solartron 1287 potentiostat with an electrochemical interface. The conductivity cell was calibrated using standard potassium chloride solutions.
6.2.3. Ammonia and pH measurements

Ammonia concentrations were measured at the beginning and end of each galvanostatic test, while pH was measured at the beginning and end of each Cyclic Voltammetry (CV) test. One milliliter of the electrolyte at the electrode surface was sampled and diluted to bring the ammonia concentration and pH within the measuring range of the instrument. Both the ammonia concentration and pH were measured using a high performance ammonia Ion Selective Electrode (ISE) (No. 9512HPBNWP) and a pH electrode (No. 9172BNWP) respectively, in conjunction with an ISE/pH/mV/ORP meter (Model 710Aplus) which were obtained from Orion Research. The ISE and pH were calibrated with standard solutions prior to its use. The detection limit of the ammonia ISE was 0.01 ppm.

6.2.4. Electrochemical Characterization

CV tests were used to investigate the compatibility of PAA-K to both anodic AER and cathodic HER. Galvanostatic tests were used to evaluate the performance of the AEC. The electrolyte solutions were prepared from triple distilled water, analytical grade potassium hydroxide pellets of purity ≥85% (Fisher Scientific), and 14.8 M ammonium hydroxide (Fisher Scientific).

6.2.4.1. Electrode Synthesis

Pt-Ir was chosen as the electrocatalyst due to the high sensitivity of Pt, Ir and Pt-Ir to AER [10, 13, 37, 38] and HER [39-41]. The electrodes were synthesized by co-
electrodepositing Pt and Ir onto 2 cm by 2 cm titanium gauze (18 mesh, 99.99% purity from Alfa Aesar) and untreated Toray TGP-H-30 Carbon Fiber Paper (CFP) substrates [12, 13]. Instead of the two CFP sandwiched with titanium gauze as reported previously [13], only one CFP was used, in order to establish contact between ammonia, OH⁻ ions in the gel electrolyte, and the active sites of the catalyst when assembled in a cell as described in sections 6.2.4.2 and 6.2.4.3. The electrodeposition was carried out, using the optimized conditions for ammonia electrolysis, from a bath consisting of 2.4 g L⁻¹ H₂PtCl₆ and 4.8 g L⁻¹ IrCl₃ (both 99.99% pure obtained from Alfa Aesar) in 1 M HCl, prepared using 5.95-6.05 N HCl (from Fisher) and HPLC grade ultrapure water (from Fisher). Electrodeposition was carried out at 78°C with a potential of -0.12 V vs Ag/AgCl (saturated with KCl) and a 20 cm² Pt foil (0.01 cm thick, 99.999% pure from ESPI Metals) counter electrode was used [12]. The loading of each electrode was determined gravimetrically and kept at 1.25±0.10 mg cm⁻², as this was reported to have the maximum electrode activity for the electro-oxidation of ammonia [2]. Identical Pt-Ir electrodes were synthesized by using the same starting bath concentration and the same charge for plating.

6.2.4.2. Cyclic Voltammetry

A laboratory scale electrode cell assembly as shown in Figure 6.1(A) was set up for CV studies. An acrylic spacer compartment (5 cm x 5 cm x 0.5 cm with a 2 cm x 2 cm window cut in the middle) was used for containing the gel electrolyte, which was placed between the working and the auxiliary electrodes and held between two end-
plates, identical to the spacer compartment. The purpose of the window in the end plates was to allow the electrodes to be in contact with the electrolyte giving access to the reference electrode fitted within a glass body luggin capillary. This whole assembly was then immersed into a beaker containing the electrolyte test solution. Therefore the current resulting from the CV test is due to the ions traveling through the gel and the shunt current due to the ions traveling from the back of one electrode to another can be neglected.

Each set of electrodes was tested with the aqueous electrolyte before being tested with the PAA-K. When testing the aqueous electrolyte, the spacer was left empty while assembling the set-up, so that it would be occupied by the aqueous electrolyte once introduced. The CV experiments were carried out with a Solartron 1287 with an electrochemical interface. A pair of Pt-Ir electrodes served as working and counter electrodes. The reference electrode was an Hg/HgO saturated with KOH (20% by weight), purchased from Koslow Scientific. A scan rate of 10 mV s\(^{-1}\) was used. The CV was repeated until a sustained periodic state was achieved.

6.2.4.3. Galvanostatic polarization

A two electrode cell assembly shown in Figure 6-1(B) was used for the galvanostatic tests. The set up used here was similar to the one used for the CV studies, except that there were no windows in the end plates, gaskets were placed between each electrode and the end plate to hold the test solution. Another gasket was placed between electrodes to hold the gel or the aqueous electrolyte. Polypropylene separators from
Celgard® (25 µm porous product no. 3401) cut to 6 cm x 4.5 cm were used on either side of the gel compartment, in order to prevent the gases generated at the electrodes from entering the gel. Gaskets were made from 6 cm x 4.5 cm x 0.32 cm ethylene propylene diene monomer rubber (Durometer rating 50 A, from McMaster-Carr) with 5.5 cm x 4 cm window cut in the middle. Two 0.1 cm elbow shaped threaded holes were drilled on the top of each end plate to inject the test solution and allow the release of the gases during the electrolysis, as shown in Figure 6-1(B). The assembly was held together in place by screws and the threaded tube fittings were attached to the top of these holes. These fittings were then connected to graduated gas collection cylinders purchased from H-Tec with the help of a Tygon® tubing (ID 0.25 inch and wall thickness 0.0625 inch).

Figure 6-1. (A) Setup used for cyclic voltammetry experiments (B) Setup used for diffusion studies and galvanostatic experiments.
An Arbin BT2000 battery cycler was used to carry out the galvanostatic experiments. Pt-Ir electrodes were used as working and counter electrodes. The current was applied between the working and counter electrodes in steps of 10 mA increasing progressively, while the voltage was continuously monitored. The duration for each step was three minutes.

The durability and the performance of the APGE’s were studied by applying a constant current of 125 mA between the working and counter electrodes for one hour. A voltage of 1 V was set to terminate the experiment. The current and cut-off voltage were chosen such that they were high enough to allow ammonia electrolysis and low enough to prevent the water electrolysis at the anode and also prevent the anode from reaching the poisoning potential, the potential at which the electrode surface gets blocked and thereby preventing further adsorption of reacting species [14, 15]. The anode and cathode gases generated during this experiment were collected separately using two gas collection cylinders. The diffusivity and the moles of ammonia lost from the anode compartment were estimated by measuring the ammonia concentration at the anode after maintaining the cell at Open Circuit Voltage (OCV) for one hour.

6.2.5. Gas Chromatography

The anode and cathode side gases that were collected during the constant current experiments were analyzed by a SRI8610 gas chromatograph (GC) equipped with two columns (molecular sieve 13 X and HayeSep D) and a thermal conductivity detector. Argon was used as the carrier gas with a flow rate of 25 ml min⁻¹. The GC was calibrated
prior to use, by standard gases from Airgas. The injector temperature was kept at 130°C and the oven temperature was maintained at 50°C for a stabilizing period of three minutes. The oven temperature was then increased at a rate of 5° min⁻¹ until it reached 150 °C.

6.3. Results and Discussion

6.3.1. Ionic Conductivity studies and pH measurement

The conductivity cell was calibrated using standard potassium chloride solutions and a cell constant of 0.3062 cm⁻¹ was determined. The ionic resistance of the PAA-K and 5 M KOH was obtained from the high frequency intercept in the impedance spectroscopy complex-plane plot. The conductivity is then estimated using the formula:

\[ \text{Conductivity} = \frac{\text{Cell Constant (cm}^{-1})}{\text{Solution Resistance (W)}} \]

The ionic conductivity for the PAA-K is 0.5870 S cm⁻¹ which is close to aqueous 5 M KOH (0.6155 S cm⁻¹), consistent to the values reported in the literature [29]. The pH for the aqueous 5 M KOH and PAA-K in the absence of ammonia was 15.13 and 14.86, respectively. In the presence of 1 M ammonia there was no change in the pH. The values agree with the pH estimated from correlations after accounting for the solubility of ammonia in 5 M KOH [42, 43] and dissociation into \( \text{NH}_4^+ \) and \( \text{OH}^- \) ions and change in activity of water reported in the literature [20, 44].
6.3.2. Ammonia Diffusivity

While estimating the conversion, yield, and efficiency of the AEC, it is important to correct the ammonia concentration for the ammonia lost through diffusion. It is therefore required to estimate the diffusivity of ammonia and number of moles of ammonia transported to the cathode. Besides, the presence of ammonia in the cathode compartment could potentially deteriorate the Nafion membrane in a proton exchange membrane fuel cell when transported along with the hydrogen generated [45, 46].

The diffusion flux and diffusivity were calculated using the formula:

\[ J = \frac{N_{c,f} - N_{c,i}}{A t} \]

where, \( J \) is the diffusion flux (mol cm\(^{-2}\) s\(^{-1}\)), \( N_{c,i} \) is the initial moles of ammonia at the cathode, \( N_{c,f} \) is the final moles of ammonia at the cathode (mol), \( A \) is the cross sectional area (cm\(^2\)), and \( t \) is the time (s) and from Fick’s first law of diffusion the diffusion flux can be written as follows:

\[ J = -D \frac{\Delta C}{\Delta X} \]

where, \( D \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)), \( \Delta C \) is the difference in concentration of ammonia between the anode and the cathode (mol cm\(^{-3}\)), and \( \Delta X \) is the thickness of the gel or distance between the two electrodes (cm). The ammonia concentrations at the anode and cathode compartments were analyzed before and after a stabilization time of one hour and reported in Table 6-2.
Table 6-2.

Comparison of diffusion flux and diffusion coefficient of ammonia in aqueous 5 M KOH with PAA-K electrolytes measured at OCV.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Compart ment</th>
<th>Volume of Feed (± 0.1 ml)</th>
<th>[NH₃](± 1 ppm)</th>
<th>NH₃ loss (± 0.1 x10⁻⁴ moles)</th>
<th>NH₃ Crossover rate (x 10⁻⁸ moles cm⁻² s⁻¹)</th>
<th>D* (±0.3347 x 10⁻⁵ cm² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous 5 M KOH*</td>
<td>Anode</td>
<td>9.0</td>
<td>17000</td>
<td>9100</td>
<td>4.6</td>
<td>6.335±0.197</td>
</tr>
<tr>
<td></td>
<td>Cathode</td>
<td>9.0</td>
<td>0</td>
<td>8700</td>
<td>-5.1</td>
<td></td>
</tr>
<tr>
<td>PAA(7%)*</td>
<td>Anode</td>
<td>6.0</td>
<td>17100</td>
<td>14500</td>
<td>1.5</td>
<td>0.910±0.028</td>
</tr>
<tr>
<td></td>
<td>Cathode</td>
<td>6.0</td>
<td>0</td>
<td>1250</td>
<td>-0.7</td>
<td></td>
</tr>
</tbody>
</table>

Based on the measured ammonia concentration, the ammonia flux or rate of ammonia cross-over to the cathode in the presence of the separator is 6.33x10⁻⁸ moles cm⁻² s⁻¹ and the diffusivity of ammonia in 5 M KOH is 1.9x10⁻⁵ cm² s⁻¹, this value is reasonably close to the 2.1x10⁻⁵ cm² s⁻¹ reported in the literature [47]. On the other hand the diffusivity of ammonia in PAA-K was reduced by a factor of 10. The ammonia concentration diffused to the cathode for the aqueous electrolyte was 5.1 millimoles per mole of ammonia. However, only 0.7 millimoles was transported to the cathode when PAA-K was used, implying that the 0.8 moles of ammonia could have been absorbed by the PAA-K.

6.3.3. Electrochemical Studies

The cyclic voltammograms for anodic AER and cathodic HER were evaluated with PAA-K and compared to those achieved with aqueous 5 M KOH. All the potentials shown in the voltammograms were reported versus Reversible Hydrogen Electrode
(RHE) to exclude the effect of change in pH between electrolytes. Galvanostatic experiments were performed to evaluate the rate of hydrogen generation and ammonia conversion for the electrolytes of interest.

6.3.3.1. Ammonia Electro-oxidation Reaction (AER) with PAA-K

The comparisons of the cyclic voltammograms for PAA-K with aqueous 5 M KOH on Pt-Ir electrodeposited on titanium gauze in the presence and absence of ammonia are shown in Figure 6-2. The cyclic voltammogram for aqueous 5 M KOH electrolyte in the absence of ammonia presents a broad wave from 0.19 V to 0.53 V. This region has been predominantly referred to as the hydrogen ionization region and the reversible peaks in this region are: hydrogen desorption and ionization [39, 41, 48, 49].

Since the peaks in this region have been observed to vary with the type of anion and the concentration of the solution, the OH⁻ ion electrosorption is believed to contribute to the peak A1 as well [50-52]. In addition, the OH⁻ electrosorption for different phases of platinum have been found to occur at different potentials [49, 53, 54], indicating that the OH⁻ adsorption on polycrystalline platinum can take place either in the hydrogen ionization region, anion adsorption region, the surface-oxide formation region or across a combination of regions [51].

A distinctive reversible peak labeled A1 is observed at 0.4 V, when aqueous 5 M KOH was used in the absence of ammonia. This peak corresponds to the reversible OH⁻ electrosorption. However, when PAA-K was used as the electrolyte the OH⁻ electrosorption peak (G1 occurring at 0.49 V) shifted to more positive potentials along
with the irreversible platinum oxides formation region. The 90 mV shift in the positive direction could be attributed to the lower OH\textsuperscript{-} ion concentration and the presence of fewer sites for OH\textsuperscript{-} ion adsorption.

From Figure 6-2, it can also be observed that the CV for aqueous 5 M KOH in the presence of ammonia presents two peaks viz., A3 at 0.32 V and A2 at 0.75 V. They correspond to the reversible adsorption of OH\textsuperscript{-} ions and electro-oxidation of ammonia, respectively. The peak A3 is stronger than the A1 OH\textsuperscript{-} adsorption peak, indicating the possibility of co-adsorption of ammonia and OH\textsuperscript{-} ions. However, the peak corresponding to the co-adsorption of ammonia and OH\textsuperscript{-} ions at 0.32 V disappeared when PAA-K was used. This suggests that most of the electrode surface is preoccupied and vacant electrocatalytic sites are limited for the adsorption of the reactants.

In addition, it could be noted that the onset and peak potential for the electro-oxidation of ammonia with aqueous 5 M KOH electrolytes are 0.48 V and 0.75 V (A2), respectively, whereas with PAA-K are 0.58 V and 0.82 V (G2), respectively. The Tafel slopes for aqueous 5 M KOH calculated from CV data for the AER is 98.14 mV decade\textsuperscript{-1} at low overpotentials, which doubled at high overpotentials in correlation with previous studies [55, 56]. However the Tafel slope for PAA-K is 185.3 mV decade\textsuperscript{-1}. Despite having an ionic conductivity as high as aqueous 5 M KOH, the onset potential for ammonia electro-oxidation shifted 100 mV in a positive direction and the net charge for the AER, after accounting for the charge associated with the double layer, is reduced by a factor of 3.5 from 1.4 mC cm\textsuperscript{-2} to 0.4 mC cm\textsuperscript{-2} when PAA-K was used. This reduction in the charge for AER and the positive shift in potential could be partially attributed to: 1.
The surface limitation caused by the polymer covering parts of the active surface; and 2. Low OH\(^-\) ion concentration, which in turn causes a lower mobility for ammonia.

![Cyclic voltammograms comparing the electro-oxidation of ammonia on Pt-Ir electrodeposited on titanium gauze substrate with aqueous 5 M KOH and PAA-K. The normalized current density for CVs in the absence of ammonia (dotted lines) has been multiplied by a factor of 16 for visual clarity. The results show that, upon using PAA-K the onset potential as well as the peak potential for OH\(^-\) ion electrosorption and ammonia electro-oxidation shift to more positive potentials. The charge for AER, using the PAA-K electrolyte, decreased by a factor of 3.5 when compared to the aqueous electrolyte.](image)

**Figure 6-2.** Cyclic voltammograms comparing the electro-oxidation of ammonia on Pt-Ir electrodeposited on titanium gauze substrate with aqueous 5 M KOH and PAA-K. The normalized current density for CVs in the absence of ammonia (dotted lines) has been multiplied by a factor of 16 for visual clarity. The results show that, upon using PAA-K the onset potential as well as the peak potential for OH\(^-\) ion electrosorption and ammonia electro-oxidation shift to more positive potentials. The charge for AER, using the PAA-K electrolyte, decreased by a factor of 3.5 when compared to the aqueous electrolyte.

The reason for the AER current density attaining a peak at 0.75 V (A2), for aqueous 5 M KOH, despite the absence of any mass transport limitation, is reported and verified to be the poisoning of the electrocatalyst surface due to chemisorption of intermediates of the reaction, thereby preventing any further electro-oxidation of ammonia [14, 15, 37, 38, 47, 55, 57]. On the other hand, the delay in the occurrence of
the AER peak with PAA-K could be a result of a milder physical adsorption of the polymer on the electrocatalyst surface, which is desorbed at potentials above 0.75 V, opening up new sites for ammonia electro-oxidation. The positive shift in the poisoning potential allows for a wider potential window for which the electrode is active for ammonia electrolysis. In order for PAA-K to be used as an electrolyte, it has to allow for the interaction of the OH⁻ ions and ammonia at the active surface of the catalyst.

Figure 6-3. Cyclic voltammograms comparing the electro-oxidation of ammonia on Pt-Ir electrodeposited on CFP substrate with aqueous 5 M KOH and PAA-K. The normalized current density for CVs in the absence of ammonia (dotted lines) has been multiplied by a factor of 8 for visual clarity. It can be observed that the CFP substrate based electrodes when compared to Ti substrate, let to an increase in the specific current densities. The charge for AER, using the PAA-K electrolyte, decreased by a factor of 2.6 when compared to the aqueous electrolyte

In order to provide a larger surface area for the oxidation of ammonia and minimize the surface blockage of the catalyst by the polymer, CFP were used as the
substrates for the electrodes. Figure 6-3 reveals the comparisons of cyclic voltammograms for PAA-K with aqueous 5 M KOH on Pt-Ir electrodeposited on CFP substrates with the presence and absence of ammonia. From Figure 6-3, it can be observed that the ammonia electro-oxidation current obtained with CFP electrodes is higher than that obtained for Ti substrate electrodes. Though the ammonia electro-oxidation peak current for PAA-K is lower compared to the aqueous KOH electrolyte counterpart, it is higher by a factor of four compared to Ti substrate electrodes. In addition the net charge for AER obtained with CFP based electrodes were 4.9 mC cm⁻² and 1.9 mC cm⁻² for the aqueous 5 M KOH and the PAA-K systems, respectively. The AER charge obtained with PAA-K decreased by a factor of 2.6 as opposed to the 3.5 for the electrodes with Ti substrate.

Figure 6-4. Cyclic voltammograms comparing the cathodic reduction of water on Pt-Ir electroplated on CFP substrate with aqueous 5 M KOH and PAA-K. It can be seen that the onset of HER with PAA-K starts at a less negative potential when compared with aqueous 5 M KOH electrolyte.
In addition, the peak at 0.30 V corresponding to the co-adsorption of ammonia and OH\(^-\) ions with PAA-K, for the electrodes synthesized with CFP substrate is prominent when compared to the electrodes synthesized with Ti gauze substrate. The onset potential for ammonia electro-oxidation is 0.51 V for the PAA-K as opposed to 0.48 V for the aqueous electrolyte bringing the shift in the starting potentials to 30 mV. The potential shift was lower when compared with the 100 mV shift obtained with the electrodes synthesized with Ti gauze substrate. The increase in the ammonia electro-oxidation peak intensity and the lower potential shift in the positive direction make the CFP substrates a better choice for ammonia electro-oxidation with PAA-K.

6.3.3.2. Hydrogen Evolution Reaction (HER) with PAA–K

Figure 6-4 illustrates the comparison of cyclic voltammograms for the HER in Pt-Ir electroplated on CFP in the presence and in the absence of ammonia using aqueous 5 M KOH with PAA-K, respectively. It can be observed that the onset potential for the HER with aqueous 5 M KOH is 0.03 V, whereas for PAA-K it was found to be occurring at 0.09 V. This implies that using PAA-K facilitates hydrogen generation at a potential which is 60 mV less cathodic than that of its aqueous counterpart. The reason for this behavior could be attributed to the fact that PAA-K is a super-absorbent which causes the activity and pH to remain constant during the course of the experiment by compensating for any decrease in water activity and increase in pH as water is being electrolyzed. However for the 5 M KOH electrolyte the gas generation due to water electrolysis could cause the activity to decrease further and pH at the electrode surface to increase, in turn
causes the potentials to shift in the cathodic direction. However, a more detailed study needs to be performed in order to completely understand the contributions of the change in pH and activity of water for the less cathodic onset potential for HER in the presence of PAA-K. In addition, from the CV results, it can be observed that the presence of ammonia for both aqueous 5 M KOH and PAA-K does not have any significant effect on the HER.

6.3.3.3. Galvanostatic Studies

Figure 6-5 shows the comparison of cell voltages for the galvanostatic step experiments for ammonia electrolysis with PAA-K to 5 M aqueous KOH with ammonia performed in a two electrode cell system described earlier (Section 6.2.4.3).

![Figure 6-5. Comparison of the galvanostatic-step test results for ammonia electrolysis using aqueous 5 M KOH with PAA-K electrolytes. The dashed lines (---) represent the applied specific current density, while the solid lines (--) represent the voltage response of the cell. It can be seen from the cell voltage for the AEC using PAA-K electrolyte that the power consumption is slightly higher than the 5 M KOH electrolyte at 5 mA cm$^{-2}$ g$^{-1}$.](image)
Despite being an excellent choice for the HER and reducing the rate of electrode
deactivation at the anode, the cell voltage of the AEC with PAA-K reached 1 V at 10 mA cm\(^{-2}\) g\(^{-1}\) which is lower than the specific current achieved using aqueous 5 M KOH electrolyte. This could be due to the increase in the onset potential for AER of 50 mV or the decrease in the mobility of the ammonia in solution due to the absence of KOH, causing a concentration gradient at the electrode surface.

*Figure 6-6.* Comparison of voltage response of the AEC for constant current tests at 125 mA (6.5 mA cm\(^{-2}\) g\(^{-1}\)) with aqueous and PAA-K. The inset shows the comparison of the OCV as a function of time for the aqueous and PAA-K systems. The results indicate that the cell voltage for PAA-K electrolyte is higher than its aqueous counterpart by 100 mV initially and keeps increasing continuously.

In addition, there could be a trace of hydrogen diffused into the gel electrolyte disrupting the conductivity of the gel. It was found that the voltage response was similar to the response that was obtained before testing with PAA-K, implying that the electrodes were not deteriorated. Therefore, the continuous increase in the cell voltage could be attributed to different reasons: the disruption in the conductivity of the gel by the
entrapped gases, the ammonia concentration gradient at the electrode that arises due to the limited mobility of ammonia within the PAA-K, the decreased in the ammonia concentration with time, or all of these factors combined. The concentration of ammonia before and after the constant current experiments was analyzed using the ammonia ISE. The concentration was then corrected for diffusion.

Table 6-3.

Ammonia concentration at the anode compartment before and after constant current electrolysis at Pt-Ir (loading 1.25 mg cm$^{-2}$) for one hour at 0.125 A (conversion, rate of ammonia removal, power required and current efficiency for ammonia electrolysis were all calculated after correction for ammonia loss through diffusion).

<table>
<thead>
<tr>
<th>System</th>
<th>Volume of Feed (∓ 0.1 ml)</th>
<th>NH$_3$ Concentration (∓ 1 ppm)</th>
<th>Conversion (∓ 0.014 %)</th>
<th>Rate of NH$_3$ Consumed (∓ 0.11 mg cm$^{-2}$ h$^{-1}$)</th>
<th>Power Consumption per g of NH$_3$ (∓ 1.82W h)</th>
<th>Current Efficiency based on Ammonia Consumption (∓ 2 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous 5 M KOH Before</td>
<td>9.0</td>
<td>Before Electrolysis</td>
<td>After Electrolysis</td>
<td>Corrected for Diffusion</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17000</td>
<td>6400</td>
<td>14300</td>
<td>15.882</td>
<td>6.06</td>
</tr>
<tr>
<td>Aqueous 5 M KOH After</td>
<td>9.0</td>
<td>17100</td>
<td>6550</td>
<td>14450</td>
<td>15.497</td>
<td>5.95</td>
</tr>
<tr>
<td>PAA (7%)</td>
<td>6.0</td>
<td>17200</td>
<td>10300</td>
<td>12900</td>
<td>25.000</td>
<td>6.44</td>
</tr>
</tbody>
</table>

The conversion, rate of ammonia consumed, power consumption, and current efficiency were calculated as follows:

Conversion (%) = \( \frac{(C_{a,i} - C_{a,f})}{C_{a,i}} \times 100 \)

where \( C_{a,i} \) is the initial concentration of ammonia at the anode (M) and \( C_{a,f} \) is the final concentration of ammonia at the anode after correcting for diffusion (M).

Rate of ammonia reacted (mol cm$^{-2}$ h$^{-1}$) = \( \frac{(C_{a,i} - C_{a,f})}{A t} \) V
where \( V \) is the volume of solution taken (in liters), \( A \) is the geometric surface area of the electrode (cm\(^2\)), and \( t \) is the time (in hours).

\[
Power Consumed \left( \text{W h g}^{-1} \right) = \frac{I \bar{E} t}{(C_{a,i} - C_{a,f}) V M}
\]

where \( I \) is the current applied (A), \( \bar{E} \) is the average cell voltage response (V), and \( M \) is the molecular weight of ammonia (17.03 g).

\[
h_{NH3, \text{Current}} (\%) = \frac{N_{\text{expt}}}{N_{\text{theo}}} \times 100
\]

where \( h_{NH3, \text{Current}} \) is the current efficiency based on ammonia consumption, \( N_{\text{expt}} \) is the experimental moles of ammonia consumed given by \((C_{a,i} - C_{a,f}) V M\), and \( N_{\text{theo}} \) is the moles of ammonia consumed based on Faraday’s law.

The conversion, power consumption for ammonia electrolysis, and current efficiency are summarized in Table 6-3. The gases generated at the anode and cathode were collected during each constant current experiment and then analyzed.

Based on the results presented in Table 6-3, it can be understood that the conversion for ammonia, the rate of ammonia consumed, and current efficiency are higher with the gel electrolyte. However, previous CV results explain that the ammonia electrolysis had been retarded when PAA-K was used as the electrolyte in lieu of aqueous 5 M KOH. Nevertheless, the electrodes when used with PAA-K, encounter catalytic poisoning at a higher potential when compared with the PAA-K electrolyte leading to the higher conversion and efficiency.
The volume of the gases generated at the cathode, the results of the GC analysis, and efficiencies are reported in Table 6-4. From the gas collection and gas chromatography results the current and energy efficiencies for hydrogen generation were calculated as follows:

\[
h_{H_2, \text{Current}}(\%) = \frac{V_{H_2} \rho_{H_2}}{M_{H_2, \text{theo}}} \times 100
\]

\[
h_{H_2, \text{Energy}}(\%) = \frac{1.55}{I \overline{\varepsilon} t / (V_{H_2} r_{H_2})} \times 100
\]

Where \( h_{H_2, \text{Current}} \) is the current efficiency, \( h_{H_2, \text{Energy}} \) is the energy efficiency based on hydrogen produced, \( V_{H_2} \) is the volume of hydrogen collected, \( r_{H_2} \) is the density of hydrogen at standard, temperature and pressure, and \( M_{H_2, \text{theo}} \) is the theoretical mass of hydrogen produced based on Faraday’s law.

**Table 6-4.**

*Gas analysis and efficiency calculations for the production of hydrogen during the constant current electrolysis of ammonia on Pt-Ir (loading 1.25 mg cm\(^{-2}\)) CFP electrodes at 0.125 A*

<table>
<thead>
<tr>
<th>System</th>
<th>Gas Volume at Cathode (± 1 ml)</th>
<th>Cathode Gas Analysis (± 0.01%)</th>
<th>Hydrogen Volume (±1 ml)</th>
<th>Current Efficiency (± 1.93 %)</th>
<th>Energy Efficiency (± 0.58 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous 5 M KOH Before</td>
<td>46</td>
<td>98.37</td>
<td>1.84</td>
<td>45</td>
<td>87.20</td>
</tr>
<tr>
<td>PAA (7%)</td>
<td>50</td>
<td>100.00</td>
<td>0.00</td>
<td>50</td>
<td>96.36</td>
</tr>
<tr>
<td>Aqueous 5 M KOH After</td>
<td>48</td>
<td>99.59</td>
<td>1.41</td>
<td>48</td>
<td>92.12</td>
</tr>
</tbody>
</table>
It can be seen that the amount of hydrogen generated at the cathode, when aqueous 5 M KOH was used as the electrolyte, is less than the volume of hydrogen that could be expected based on the conversion of ammonia. It can also be seen that traces of nitrogen are present in the gases collected at the cathode side. The only possible explanation for the nitrogen being detected at the cathode side is that the nitrogen generated at the anode may have crossed over to the cathode compartment of the electrolytic cell. Similarly, part of the hydrogen that was generated at the cathode could have diffused to the anodic compartment of the electrolytic cell thereby causing the volume of the hydrogen to be lower. On the other hand, when PAA-K was used as the electrolyte the volume of hydrogen collected was the closest to the volume of hydrogen expected from Faraday’s law calculation. The absence of nitrogen in the gas chromatography results for the gases generated at the cathode side reflects the absence of nitrogen crossover to the cathode.

6.4. Conclusions

A systematic study to compare the performance of PAA-K electrolytes with KOH on the electrolysis of ammonia was carried out. It was found that the diffusivity of ammonia in PAA-K electrolyte/polypropylene separator (0.27×10^{-5} cm^2 s^{-1}) decreased by a factor of 10 when compared with aqueous 5 M KOH electrolyte/polypropylene separator, thereby reducing the amount of ammonia crossing over to the cathode side of the ammonia electrolytic cell.
Cyclic voltammetry results for the ammonia electro-oxidation reaction with PAA-K revealed that the carbon fiber paper substrates offer a surface area large enough to maintain a good sorption of ammonia and OH\textsuperscript{-} ions in the active catalyst for electrolyzing ammonia. The use of PAA-K as an electrolyte increased the onset potential for ammonia electro-oxidation to more anodic potentials while simultaneously reducing its reaction rate.

The onset potential for the hydrogen evolution reaction in the presence of PAA-K is reduced to less cathodic potentials, consequently increasing the rate of hydrogen production before anode electrocatalysts poisoning occurs. Thereby, it allows for a wider potential window for operation of the ammonia electrolytic cell. Galvanostatic studies showed that the use of PAA-K caused an increase in the conversion of ammonia from 15.882±0.002\% to 25.000±0.004\%, while the current efficiency for ammonia removal increased from 92±1\% to 97±2\%.

Further, the use of PAA-K prevented the diffusion of gases generated from one compartment to another compartment of the ammonia electrolytic cell. In order for PAA-K to be used in lieu of the aqueous KOH electrolyte for ammonia electrolysis, further research is required to improve the mechanical strength of the polymer.

6.5. References

CHAPTER 7: CONCLUSION AND FUTURE SCOPE

7.1. Conclusions

The major contributions of this study to the field of electrochemical science and engineering are listed below:

1. It has been confirmed that the HER follows the Volmer-Heyrovsky-Tafel mechanism.
2. The presence of ammonia causes a decrease in the electrocatalytic activity of catalysts, Pt, Ru, and Ni for the HER. On the other hand, the presence of ammonia increases the electrocatalytic activity of Rh for the HER.
3. The presence of ammonia has helped identify the role of the $H_{\text{upd}}$ on the kinetics of HER, a reaction that has been probed for centuries. $H_{\text{upd}}$ enhances the electrocatalytic activity of HER on catalysts Pt, Ru, and Ni, while hindering the reaction on Rh.
4. Alloying Pt with Ir, Ru, Rh, and Ni results in an increase in the electrocatalytic activity for HER due to the preferential adsorption of ammonia on the more electropositive alloying material thereby leaving the Pt sites free for HER.
5. The kinetic activity of HER in the presence of ammonia follows the trend Pt-Ir > Pt-Rh > Pt-Ru > Pt-Ni > Rh > Pt > Ru > Ni. Pt-Ir with 13 % catalyst loading and a Pt content of 68 % displayed the highest activity for HER in the presence of ammonia.
6. The use of PAA-K as a substitute to aqueous KOH electrolyte resulted in an increased conversion of ammonia from 16 % to 25 %, while the current efficiency increased from 92 ± 1 % to 97 ± 2 %.

7.2. Future Scope

7.2.1 Alternative Electrode Design

Understanding the reason for surface limitation at the anode would help design better electrocatalysts for the anodic ammonia electro-oxidation reaction. In addition, developing a carbon nanotube or graphene based substrate for both anode and cathode electrodes will provide higher electrochemical active surface area and therefore higher reaction rates.

7.2.2. Alternative Electrolyte and Cell design

Investigation of polymerization techniques such as cross-linking and copolymerizing of polyacrylic acid (PAA) is necessary to decrease swelling, enhance the mechanical stability. Furthermore, this will facilitate the development of a stable alkaline anion exchange membrane will in turn aid the construction of a membrane electrode assembly (MEA). The MEA offers lower solution resistance and enables the rapid transport of the OH⁻ ions to the anode, thereby decreasing the transport losses associated with the system.
APPENDIX A: ENERGY AND ELECTRICITY FLOW CHART FOR USA(YEAR: 2011)

Figure A1. 2011 Energy flow diagram (quadrillion BTU). Source: Annual Energy Review 2011 (DOE/EIA 0384 September 2012 Pg.37)

Figure A2. Electricity Generation and Consumption Flow Diagram (quadrillion BTU) Source: Annual Energy Review 2011 (DOE/EIA 0384 September 2012, Pg 219)
APPENDIX B: CARBON CYCLE AND ATMOSPHERIC CO$_2$ LEVELS

Figure B1: Carbon Cycle. Source: www.NSIDC.org

Figure B2. Keeling Curve Depicting Atmospheric CO$_2$ levels over a period of 50 years. Source: www.esrl.noaa.gov
Figure B3. 2009 CO$_2$ emissions by different countries in million metric ton
APPENDIX C: PROPERTIES OF AMMONIA

Table C1.


<table>
<thead>
<tr>
<th>Hydrogen Content</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ weight fraction</td>
<td>17.65</td>
<td>wt.%</td>
<td>H₂ volume density</td>
</tr>
<tr>
<td><strong>Solid Phase</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting point</td>
<td>-78</td>
<td>°C</td>
<td>Latent heat of fusion (1 atm at triple point)</td>
</tr>
<tr>
<td><strong>Liquid Phase</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor pressure (21°C)</td>
<td>8.88</td>
<td>bar</td>
<td>Liquid density (1 atm @ boiling point)</td>
</tr>
<tr>
<td>Boiling point (@ 1.0 atm)</td>
<td>-33.5</td>
<td>°C</td>
<td>Liquid/gas equivalent (1 atm and 15°C)</td>
</tr>
<tr>
<td>Latent heat of vaporization (1 atm @ boiling point)</td>
<td>1371.2</td>
<td>kJ/kg</td>
<td></td>
</tr>
<tr>
<td><strong>Critical temperature</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Gas Phase</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Critical temperature</td>
<td>132.4</td>
<td>°C</td>
<td>Critical pressure</td>
</tr>
<tr>
<td>Gas density (1 atm at boiling point)</td>
<td>0.86</td>
<td>kg/m³</td>
<td>Gas density (1 atm at 15°C)</td>
</tr>
<tr>
<td>Compressibility (Z) (1 atm at 15°C)</td>
<td>.9929</td>
<td></td>
<td>Specific gravity (air=1) (1 atm at 20°C)</td>
</tr>
<tr>
<td>Specific volume 1 atm at 20°C</td>
<td>1.411</td>
<td>m³/kg</td>
<td>Viscosity</td>
</tr>
<tr>
<td>Heat capacity at constant pressure (Cp) (1 atm at 15°C)</td>
<td>.037</td>
<td>kJ/(mol.K)</td>
<td>Heat capacity at constant pressure (Cv) (1 atm at 15°C)</td>
</tr>
<tr>
<td>Critical Density</td>
<td>0.24</td>
<td>g/ml</td>
<td>Entropy, Gas @ 25°C, 1 atm</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>22.19</td>
<td>mW/(mK)</td>
<td></td>
</tr>
<tr>
<td><strong>Misc</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water solubility (1 atm at 0°C)</td>
<td>862</td>
<td>vol/vol</td>
<td>Autoignition temperature</td>
</tr>
<tr>
<td>Lower flammable limit in air</td>
<td>15%</td>
<td>by volume</td>
<td>Upper flammable limit in air</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>17.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Determination of Electrodeposition Potential

A CV of the substrate in the plating solution at 10 mV s\(^{-1}\) was performed to determine the metal-ion reduction potential. Figures D1.A through D1.E show the cyclic voltammograms of the CFP substrates in the electrodeposition solutions of Pt, Rh, Ru, Ir, and Ni respectively. The voltammogram (Figure D1.A) for the CFP substrate in Pt solution shows a broad plateau marked A2 followed by a peak A1 and a sharp reduction current, corresponding to the Pt(IV) to Pt(II) reduction, the Hydrogen Under Potential Deposition (H\(_{\text{upd}}\)) on freshly deposited Pt surface, and hydrogen evolution respectively. Upon careful observation, a slight bump submerged in plateau-A2 conforming to the Pt(II) to Pt reduction, as mentioned previously. As for Rh, there is no clear deposition peak corresponding to the Rh (III) reduction to Rh, as it is shadowed in the current resulting from the HER.\(^2,3\) The dominant nature of the H\(_{\text{upd}}\) peak and HER currents in the CV from Figure D1.A to D1.D is a result of the high HCl concentration used in this study.\(^1\) The potentials chosen for deposition are marked by dotted lines in the CV (-0.1V, 0.01 V, -0.2 V and -0.8 V for Pt, Rh, Ru, Ir, and Ni respectively) such that any current loss to hydrogen evolution could be minimized in order to achieve reasonable electrodeposition efficiencies.\(^4\) The deposition rate obtained at these potentials for Pt and Rh is comparable to those reported in the literature.\(^2,5\) The XRD results for the electrodes synthesized are given in Fig D2. The deposition occurred in the metallic phase and can be confirmed from the peaks present in the XRD results. The orientations of the polycrystalline catalysts are labeled based on their respective peak positions.
Figure D1. Cyclic voltammograms for CFP substrates in (A) platinum, (B) rhodium, (C) ruthenium, (D) iridium, and (E) nickel plating solutions obtained at a scan rate of 10 mVs⁻¹. Dashed lines represent the CV in the absence of metal salts, while solid lines represent the CV with the presence of the metal salt. Cyclic voltammograms were used to determine the plating potentials for Pt, Rh, Ru, and Ni respectively, on carbon fiber paper.
**Figure D2.** XRD images for electrodeposited Pt, Rh, Ru, and Ni electrodes along with CFP substrate. The synthesized catalysts are present in the metallic phase.
APPENDIX E: ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) AND EQUIVALENT CIRCUIT FITTING

EIS is a powerful technique in facilitating the characterization of various complicated electrochemical processes ranging from simple electrode reactions to complicated systems such as corrosion, batteries, fuel cells, and electrolyzers. This technique has been used to measure the impedance using alternating currents with a wide range of frequencies usually superimposed over a DC potential. The resulting impedance spectra could be used to estimate independent contributions of the uncompensated solution resistance, pseudocapacitance, polarization resistance, charge transfer resistance and thereby the faradaic impedance of an electrochemical reaction which in turn can be used to estimate the kinetic parameters including rate constants in the mechanism for fast electron transfer reactions. EIS, particularly when expressed with equivalent circuits, gives a detailed physical insight into normally abstract details about an electrochemical reaction.

Figure F1 shows the flow chart adopted to estimate the rate constants for the Volmer, Heyrovsky, and Tafel steps for the HER. The equivalent circuit fits were estimated by using the Complex Non-linear Least Squares (CNLS) fitting algorithm available in Z-view software. The criteria for the goodness of fit for a particular model was chi-squared values < 0.015, sum-squared values < 1.5%, and the error associated with each circuit element < 5%. The smaller chi-squared and sum-squared values using the calc-modulus weighting procedure, implies a close fit of the model to the experimental values.
**Figure E1.** Flow chart for the numerical procedure adopted to estimate the kinetic parameters for the HER (k_1, k_{-1}, k_2, k_3, and Θ). Inset to Figure 4., illustrates the equivalent circuit parameters (solution resistance R_s and faradaic impedance Z_f) from a Nyquist plot for an electrochemical reaction without diffusion.
**APPENDIX F: EDX IMAGES FOR BIMETALS**

**Figure F1.** A1 through D1 represents the EDX images (intensity (cps) versus binding energy (keV)) for bimetals Pt-Ir, Pt-Rh, Pt-Ru, and Pt-Ni at a loading of ~0.6 mg cm\(^{-2}\) and figures A2 through D2 represents the EDX images for bimetals Pt-Ir, Pt-Rh, Pt-Ru, and Pt-Ni at a loading of ~1.9 mg cm\(^{-1}\).