## INVESTIGATION OF MATERIALS FOR THE ELECTROCHEMICAL DECOMPOSITION OF AMMONIA

By

Daniel J. Little

## A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Chemistry–Doctor of Philosophy

#### ABSTRACT

## INVESTIGATION OF MATERIALS FOR THE ELECTROCHEMICAL DECOMPOSITION OF AMMONIA

#### By

#### Daniel J. Little

The ability to store renewable energy in the form of chemical bonds in fuels is essential for the realization of a clean energy future. There have been decades of work on the subject of using renewable energy for the electrochemical splitting of water molecules to form hydrogen gas (H<sub>2</sub>) as a fuel. However, development of infrastructure for the efficient transportation and storage of large quantities of the low-density H<sub>2</sub> remains as a major challenge preventing a commercial disruption. Instead of reducing protons (H<sup>+</sup>) from water to produce H<sub>2</sub>, therefore, an alternative solution would be to couple the oxidation of water to the reduction of nitrogen gas (N<sub>2</sub>) from the air and produce ammonia (NH<sub>3</sub>). NH<sub>3</sub> is a higher-density fuel for which the transportation and storage infrastructure is already in place at a national industrial scale.

There is plenty of ongoing research into the synthesis of NH<sub>3</sub> from renewable N<sub>2</sub> and H<sub>2</sub>, but there have been relatively few studies into efficiently splitting it back apart to recover the H<sub>2</sub> fuel. Furthermore, what work has been done in NH<sub>3</sub> splitting has largely been in aqueous conditions, which are corrosive to the transportation and storage infrastructure and involve an inherent loss of energy density compared to liquid ammonia (NH<sub>3</sub>(*l*)). In this work, we investigate the half reactions involved the electrochemical splitting of anhydrous NH<sub>3</sub>(*l*), and propose new Earth-abundant anode and cathode materials to replace the traditionally used noble metals.

For all who have supported me along the pathway of academic achievement.

#### ACKNOWLEDGEMENTS

First, I would like to thank my wife, Kayli, my parents, Jeannine and John, my sister, Sarah, and the rest of my family for their love and support through my academic career. Without them I would have never gotten to where I am today, quite literally in the case of my parents. Their willingness to put up with my eccentricities throughout my entire life has been the catalyst for the development of my scientific career.

I would like to acknowledge all of the educators-both in science and otherwisewho have inspired me, bared with me, and otherwise facilitated my career in chemistry. The lessons I learned from them will never be forgotten, though I am going to continue my pursuit to be a science educator whether they like it or not.

I owe a lot of gratitude to Ben Levine, and the members of his research group during the summer and fall of 2012: Garrett Meek, Yinan Shu, and Scott Fales for their willingness to introduce me to theoretical chemistry and continue to support me even after I discovered it was not my area of interest. They have all been excellent friends and colleagues, willing to answer the many questions I posed to them during my tenure as a graduate student. I owe my excitement and willingness to use computer programming to assist my chemical experimentation to them, which likely saved me months of time over these five years.

Credit is due to all of the "Ammoniaks"-members of the ammonia fuel collaboration-especially Jason Thornton, Arianna Savini, Dillon Edwards, Faezeh Habib Zadeh, and of course Tom Hamann and Mitch Smith. I could make an extensive list of

iv

things that I learned from working with each one of them-though I will not do so here for the convenience of the reader. Still, they, and the other collaborators, helped build me from a first-year graduate student who did not understand which electrode was which, into the scientist I am now.

Of course I must thank all of the members of the Hamann lab, past and present, for accepting me into their group, putting up with my slightly obsessive tendencies, and always being there to talk about both chemistry, and things completely unrelated to chemistry. Obviously I learned much from those ahead of me in the Ph.D. program, but I actually learned just as much from teaching things to the newer members and answering their questions. I am a better scientist today having worked in such a supportive research group, and I plan to take group dynamic and mechanic ideas into my future career.

I need to acknowledge the constructive, collaborative mentality of all of the other students, postdocs, and faculty of the fourth floor. The ability to freely discuss researchin addition to non-research-with others in the department is critical to the success of the entire department. On that note, I think it is important to acknowledge all of the women and men who make the Michigan State Department of Chemistry work-from administrators, to support staff, to those who keep the building clean, and those who fix the elevators all too frequently. They do not receive enough credit for what they do, and academic research would be nearly impossible without their hard work.

For acknowledgements specific to the experiments within, I need to first thank Dr. Eli Fahrenkrug and the Electron Microbeam Analysis Laboratory at the University of

Michigan for assistance with the Auger Electron Spectroscopy measurements. Also, I would like to thank Dr. Kai Sun and the Michigan Center for Materials Characterization for assistance with and use of the Kratos XPS, which is supported by the University of Michigan College of Engineering and NSF grant #DMR-0420785. I would also like to specifically thank Hamed Hajibabaei for assistance with the SEM at the Composite Materials and Structures Center, and Dr. Kathryn Severin for use of the ICP-OES in the AP Labs of the Michigan State University Department of Chemistry. All of the work presented in this dissertation was supported financially by Michigan State University.

#### PREFACE

I jumped at the ammonia project back in the fall of 2012 because it was clear that in the worst-case scenario, I would be engaged for five years and learn all of the skills needed to be a successful, independent researcher, and in the best-case scenario I would change the world.

That sounds dramatic, but it is definitely true. I believe that in order to make my research as a chemist truly meaningful, I should work on projects that are both extremely innovative, and also attempt to solve the most important problems in the world we live in. As I see it, the problem-of-choice is giving access to clean energy for everyone on Earth, consequently helping to solve problems of politics, economics, and the environment all at once. Thus, when starting my graduate work in chemistry, I was drawn to Professor Tom Hamann's research group to study photoelectrochemistry: the conversion of sunlight into useful electricity or fuels.

When interviewing with Professor Hamann, however, I was introduced to a new project, on which I would be the first graduate student, that offered me the potential to do ground-breaking research in a virtually unexplored field: liquid ammonia electrolysis. The idea was to use ammonia as a fuel in place of—or at least as a transportation and storage medium for—renewable hydrogen gas. There are likely hundreds if not thousands of research groups worldwide—both academic and industrial—studying the renewable formation of hydrogen from water splitting, but this project actually sought to answer the question, "Then what?" The public already has apprehension about moving

vii

away from traditional hydrocarbon fuels, and design and implementation of new hydrogen infrastructure will be expensive and complicated.

So I jumped on board into a new research project where it was completely unclear what I would learn, what I would do, and whether or not what I was attempting to do would actually work. I owe a lot of credit to Professor Hamann, Professor Mitch Smith, and coworkers like Dr. Jason Thornton, Dr. Arianna Savini, and Faezeh Habib Zadeh and other collaborators on "the ammonia project" who helped me learn all of the information in the chapters that follow. While I know my research by itself is not exactly world-changing, it opens the door for future students on the ammonia project collaboration, and our combined work can come together as something spectacular.

## TABLE OF CONTENTS

LIST OF TABLES	xi
LIST OF FIGURES	xii
KEY TO ABBREVIATIONS	xviii
CHAPTER 1: THE POTENTIAL ROLE OF AMMONIA IN A RENEWABLE ENERGY FUTURE Energy and the Global Climate Ammonia as an Energy Carrier The State of Ammonia Electrolysis Research APPENDICES Appendix 1.1: Calculation of E <sub>cell</sub> for the Electrolysis of Liquid Ammonia	1 2 4 8 15 16
Appendix 1.2: Background Theory for 2-Electrode and 3-Electrode Measurements Appendix 1.3: Discussion of the Term "Onset Potential" REFERENCES	18 21 23
CHAPTER 2: EXPERIMENTAL DESIGN FOR THE ELECTROCHEMICAL INVESTIGATION OF ANHYDROUS AMMONIA Electrochemical Experimentation in Stock Liquid Ammonia Distillation of Liquid Ammonia for Electrochemistry in	27 28
Rigorously Dry Conditions Evaluation of Electrochemical Headspace	31
Via Gas Chromatography Elemental Analysis of the Electrochemical Cell Contents	34
Voltammetry in <i>N N</i> -Dimethylformamide	37
Sampled Time Voltammetry Fabrication of Working Electrodes from	38
Transition Metal Wires	39
Determination of the Electrochemically Active Electrode	-
Surface Area	40
Instrumentation	42
KEFEKENCES	43

CHAPTER 3: IDENTIFYING THE PROBLEMS WITH LIQUID AMMONIA	
ELECTROLYSIS ON PLATINUM ELECTRODES	
Introduction	
Experimental	
Results and Discussion	
Voltammetry in Liquid Ammonia	
Voltammetry in <i>N</i> , <i>N</i> -Dimethylformamide	
Conclusions	
REFERENCES	
CHAPTER 4: INVESTIGATION OF IRON NITRIDE AS AN	
EARTH-ABUNDANT ELECTROCATALYST FOR	
THE OXIDATION OF LIQUID AMMONIA	64
Introduction	65
Experimental	67
Results and Discussion	
Conclusions	
REFERENCES	
CHAPTER 5: EVALUATION OF AMORPHOUS COBALT PHOSPHIDE	
AS AN EARTH-ABUNDANT AMMONIUM	
REDUCTION ELECTROCATALYST	
Introduction	
Experimental	91
Results and Discussion	
Conclusions	103
REFERENCES	105
CHAPTER 6: CONCLUSIONS AND FUTURE WORK	107
Introduction	108
Ammonia Oxidation Catalysts	109
Ammonium Reduction Catalysts	111
REFERENCES	114

# LIST OF TABLES

Table 1.1:	Energy density comparison of various fuels and
Table 5.1:	Average electrochemical performance of fifteen similar $CoP_x$ electrodes compared to a Pt disk in 0.1 M NH <sub>4</sub> NO <sub>2</sub> in NH <sub>2</sub> () 100

## LIST OF FIGURES

Figure 1.1:	An ammonia fuel cycle involving the reduction of N <sub>2</sub> coupled with H <sub>2</sub> O oxidation (lower left), the splitting of NH <sub>3</sub> to N <sub>2</sub> and H <sub>2</sub> (top), and the oxidation of H <sub>2</sub> as a fuel (lower right) (Reproduced from Little <i>et al.</i> ) <sup>23</sup>	7
Figure 1.2:	Electrode configuration diagrams for a 2-electrode (a) and 3-electrode (b) experiment. In the 3-electrode case, the working, reference, and counter electrodes are labeled W.E., R.E., and C.E. respectively. In both cases, the red "V <sub>A</sub> " represents where a potential is applied, the green "V <sub>M</sub> " represents where a potential is measured, and the blue "I <sub>M</sub> " represents where the current is measured	18
Figure 1.3:	Illustration of how the onset potential would be calculated from a sample curve	22
Figure 2.1:	Diagram of the electrochemical cell used for voltammetry in $NH_3(I)$ as well as in DMF with dissolved $NH_3(g)$	29
Figure 2.2:	Diagram of the custom Ag/AgNO <sub>3</sub> reference electrode for use in NH <sub>3</sub> ( <i>I</i> ) solutions	30
Figure 2.3:	Powder XRD spectrum of KNH <sub>2</sub> synthesized from KH and liquid NH <sub>3</sub> . A reference spectrum for KNH <sub>2</sub> is shown in the red, dotted line. The large amorphous feature at 20° is due to the sample holder, which included a dome to maintain a nitrogen atmosphere for the powder. (Reproduced from Little <i>et al.</i> ) <sup>4</sup>	31
Figure 2.4:	Diagram of the $NH_3(I)$ distillation flask including two glass valves for the gas inlet and outlet, as well as a black, plastic screw-cap containing a white Teflon septum.	32

Figure 3.1:	The electrolysis of $NH_3(I)$ using platinum disk electrodes. Panes (a) and (b) show successive cyclic voltammograms with 1.0 M $NH_4PF_6$ and 1.0 M KPF <sub>6</sub> as electrolytes, respectively, while pane (c) shows STVs for both conditions. The STV for 1.0 M KNH <sub>2</sub> is also depicted in pane (c)
Figure 3.2:	AES spectra of a Pt electrode cleaned electrochemically in sulfuric acid (a), and of a similar electrode cleaned electrochemically and then anodically poisoned in 1.0 M $NH_4PF_6$ in liquid ammonia (b). Sputtering with Ar <sup>+</sup> allowed for depth-profiling
Figure 3.3:	(a) STVs of NH <sub>3</sub> ( <i>I</i> ) comparing current densities at varying potential using three different concentrations of either NH <sub>4</sub> PF <sub>6</sub> (triangles) or KPF <sub>6</sub> (circles) as the supporting electrolyte, as well as 1.0 M KNH <sub>2</sub> (black squares). For all STVs, the markers represent actual points of data, and there are straight lines connecting them for trend clarity. (b) CVs in NH <sub>3</sub> ( <i>I</i> ) with 1 M NH <sub>4</sub> PF <sub>6</sub> electrolyte (red) and 1 M KPF <sub>6</sub> electrolyte (green) with a Pt disk working electrode at 100 mV/s
Figure 3.4:	Cathodic CVs in $NH_3(I)$ of 1.0 M KPF <sub>6</sub> (green) and 1.0 M $NH_4PF_6$ (black). Also included are STVs measured at 1 and 100 ms in 1.0 M $NH_4PF_6$ (dark red and light red triangles respectively), and at the same times in 1.0 M KPF <sub>6</sub> (dark blue and light blue circles respectively)
Figure 3.5:	(a) STVs showing electrolysis of NH <sub>3</sub> dissolved in DMF using platinum disks as both the anode and the cathode. The red curve has 0.1 M NH <sub>4</sub> PF <sub>6</sub> , while the green curve has 0.1 M TBAPF <sub>6</sub> . (b) CV (red) and STV (blue) of the anodic current with NH <sub>3</sub> dissolved in 0.1 M NH <sub>4</sub> PF <sub>6</sub> in DMF. In black is the CV without dissolved NH <sub>3</sub> . In green is the CV with NH <sub>3</sub> dissolved in 0.1 M TBAPF <sub>6</sub> . (c) CVs (black and green with NH <sub>4</sub> PF <sub>6</sub> and TBAPF <sub>6</sub> respectively) and STVs of the cathodic current with NH <sub>3</sub> dissolved in DMF. The black and light and dark red curves contain 0.1 M NH <sub>4</sub> PF <sub>6</sub> as the supporting electrolyte, while the light and dark blue curves contain 0.1 M TBAPF <sub>6</sub> . (5)

Figure 3.6:	(a) Quasi-reversible redox wave for $NH_4^+$ in DMF. (b) Cathodic waves measured in 0.1 M $NH_4PF_6$ with increasing concentrations of $HCIO_4$ using a Pt disk electrode in DMF	.57
Figure 3.7:	Tafel plot of the CV shown in black in Figure 3.5(c). The value of $\alpha$ close to 0.5 indicates a likely 1-electron reaction, quasi-reversible reaction.	. 58
Figure 3.8:	Diagram showing where improvements can be made by either avoiding electrode poisoning (indicated by arrow with "poison" icon), or via catalysis (indicated by arrows with "catalysis" ions). The formal potentials for $NH_4^+$ reduction, $H^+$ reduction, and $NH_3$ oxidation are indicated on the top black scale. Both the STV (red) and CV (green) were recorded using a Pt disk electrode in 0.1 M $NH_4PF_6$ in DMF	. 60
Figure 4.1:	(a) CV of a Pt disk electrode in distilled NH <sub>3</sub> ( <i>I</i> ) (black), and five successive CVs of a Pt disk electrode in distilled NH <sub>3</sub> ( <i>I</i> ) after the addition of degassed Millipore water to make the solution 10 % water (colors). (b) CVs of an Fe disk electrode in the same conditions as (a), except that only 1 % water was added. The vertical black arrows indicate the order of successive anodic scans. Dashed boxes indicate the overpotential required to reach 10 mA cm <sup>-2</sup> current. Small, black, diagonal arrows indicate the scan direction. All curves were measured at 100 mV s <sup>-1</sup> with 0.1M KPF <sub>6</sub> as the supporting electrolyte	.69
Figure 4.2:	Successive CVs of distilled $NH_3(I)$ on an Fe disk electrode with the order of the scans indicated by the vertical black arrow. All scans were measured at 100 mV s <sup>-1</sup> with 0.1 M KPF <sub>6</sub> as supporting electrolyte	.71
Figure 4.3:	Chronoamperograms conducted on an Fe disk at seven different potentials near the onset of the anodic wave shown in Figure 4.2. Potentials here are reported versus NHE, and verified using electron solvation between experiments. All scans used a 0.1 M KPF <sub>6</sub> electrolyte. Periodic sudden jumps in the current seen	1

at the highest four potentials are due to the effervescence of

evolved gas bubbles, thus suddenly changing the exposed	
surface area72	2

- Figure 4.4: Current efficiencies for the dissolution of an Fe disk electrode in distilled NH<sub>3</sub>(*l*) as a function of the net charge passed at the working electrode during the experiment. Potentials of 1.2, 1.4, or 1.6 V versus NHE were applied for varying amounts of time and the current was integrated to obtain the total charge passed. For all points, 0.1M NH<sub>4</sub>NO<sub>3</sub> was used as the supporting electrolyte to avoid the presence of fluorine from the PF<sub>6</sub><sup>-</sup> anion.... 73

Figure 4.6:	Anodic current of the Pt disk electrode in distilled NH <sub>3</sub> ( <i>I</i> ) before	
	and after dissolution of Fe electrode. Five essentially overlapping	
	scans are depicted7	7

- Figure 4.7: SEM images of Fe foil after use as an anode in 0.1 M NH<sub>4</sub>NO<sub>3</sub> in dry NH<sub>3</sub>(*I*)......78
- Figure 4.8: The surface area of an Fe disk electrode as a function of the number of wide cathodic scans measured. The surface area was measured from CV capacitance between each of the wide scans. 78
- Figure 4.10: XPS of the Nitrogen 1s region (a), the Fe 2p region (b), and the Oxygen 1s region (c) of an in situ modified Fe electrode surface... 80

Figure 4.11:	Raman spectrum of in situ modified iron anode after exposure to the air on the lab bench overnight
Figure 4.12:	Steady-state sampled time voltammograms (STVs) of anodic behavior of Pt and in situ modified Fe in distilled $NH_3(I)$ . All points are sampled from 180 seconds into a chronoamperogram at the respective potential and are connected with straight lines
Figure 5.1:	SEM images of the Cu disk substrate, (a) and (b), and $CoP_x$ disk electrode corresponding to the curves shown in Figures 5.3, 5.8, and 5.9, (c) and (d)
Figure 5.2:	SEM images of a $CoP_x$ film deposited on a Cu disk substrate by holding -1.1 V versus Ag/AgCl rather than application of the pulsed deposition method
Figure 5.3:	Cathodic <i>J-V</i> curves in 0.1 M $NH_4NO_3$ in $NH_3(I)$ with a Pt disk (black) or $CoP_x$ disk (blue). Linear sweeps were measured at 100 mV s <sup>-1</sup> , and current densities were calculated using the electrochemically active surface area
Figure 5.4:	Composite of <i>J-V</i> curves in 0.1 M $NH_4NO_3$ in $NH_3(I)$ from fifteen $CoP_x$ electrodes fabricated by the pulsed deposition method
Figure 5.5:	Comparison of the $\mu$ moles of H <sub>2</sub> measured in the headspace of the electrochemical cell (red diamonds) with the theoretical maximum amount of H <sub>2</sub> if the Faradaic efficiency for H <sub>2</sub> evolution were 100 % (blue circles)
Figure 5.6:	First and second cathodic cyclic voltammograms of a $CoP_x$ electrode in 0.1 M NH <sub>4</sub> NO <sub>3</sub> in NH <sub>3</sub> ( <i>I</i> ) showing the large cathodic wave only evident on the first scan of each CoP <sub>x</sub> electrode, indicated by the black arrow
Figure 5.7:	Cyclic voltammogram of a $CoP_x$ electrode in 0.1 M NH <sub>4</sub> NO <sub>3</sub> in NH <sub>3</sub> ( <i>I</i> ) showing hysteresis due to H <sub>2</sub> bubble formation. The scan direction is indicated by the black arrows

Figure 5.8:	Chronoamperogram of the same $CoP_x$ electrode shown in Figure 5.3 measured at -1.67 V versus NHE in 0.1 M NH <sub>4</sub> NO <sub>3</sub> in NH <sub>3</sub> ( <i>I</i> )
Figure 5.9:	Cathodic Tafel plots corresponding to the <i>J-V</i> curves depicted in Figure 5.3 in 0.1 M $NH_4NO_3$ in $NH_3(I)$ with a Pt disk (black) or $CoP_x$ disk (blue). Tafel fits are shown in dashed red lines
Figure 5.10:	Cathodic <i>J-V</i> curves in 0.1 M $NH_4PF_6$ in DMF with a Pt disk (black) or $CoP_x$ disk (blue). Linear sweeps were measured at 100 mV s <sup>-1</sup> , and current densities were calculated using the electrochemically active surface area
Figure 5.11:	Cathodic Tafel plots corresponding to the <i>J-V</i> curves depicted in Figure 5.10 in 0.1 M $NH_4PF_6$ in DMF with a Pt disk (black) or $CoP_x$ disk (blue). Tafel fits are shown in dashed red lines
Figure 6.1:	The electrolysis of $NH_3(I)$ with a 0.1 M $NH_4NO_3$ electrolyte using $FeN_x$ and $CoP_x$ as the anode and cathode respectively (Spartan green), compared to two Pt electrodes (red)

## **KEY TO ABBREVIATIONS**

AES	Auger Electron Spectroscopy
Ag	Elemental silver
Ag⁺	Silver(I) cation
AgCl	Silver chloride
AgNO <sub>3</sub>	Silver nitrate
Ar	Elemental argon
Ar <sup>+</sup>	Argon ion
C <sub>3</sub> H <sub>8</sub>	Propane
C <sub>8</sub> H <sub>18</sub>	Octane
CH₄	Methane
cm	Centimeters (1 x 10 <sup>-2</sup> meters)
CO <sub>2</sub>	Carbon dioxide
CoP	Cobalt phosphide
CoP <sub>x</sub>	Amorphous cobalt phosphide
Cu	Elemental copper
CV	Cyclic Voltammogram, or Cyclic Voltammetry
DMF	N,N-Dimethylformamide
e <sup>-</sup>	Electron

E <sub>rxn</sub>	The thermodynamic minimum cell potential needed to drive a reaction
EDS	Energy Dispersive X-ray Spectroscopy
F	Faraday constant
Fe	Elemental iron
$[Fe(NH_3)_6][Cl_2]$	Iron(II) hexamine chloride complex
Fe₄N	Iron nitride
FeN <sub>x</sub>	Amorphous iron nitride
GDP	Gross Domestic Product
GT	Gigatons (1 x 10 <sup>9</sup> metric tons)
Н	Elemental hydrogen
H⁺	Free proton
H•	Hydrogen atom
H <sub>2</sub>	Molecular hydrogen
H <sub>2</sub> ( <i>g</i> )	Molecular hydrogen in the gas state
H <sub>2</sub> O	Water
HCIO <sub>4</sub>	Perchloric acid
Не	Elemental Helium
lr	Elemental iridium
kg	Kilogram (1 x 10 <sup>3</sup> grams)

KH	Potassium hydride	
KPF <sub>6</sub>	Potassium hexafluorophosphate	
kΩ	Kiloohms (1 x 10 <sup>3</sup> ohms)	
L	Liters	
Li	Elemental lithium	
mA	Milliamps (1 x 10 <sup>-3</sup> amps)	
MJ	Megajoules (1 x 10 <sup>6</sup> joules)	
n	Integer number of electrons	
Ν	Elemental nitrogen	
N <sub>(ad)</sub>	Nitrido "poison" species adsorbed on an electrode surface	
N <sub>2</sub>	Molecular nitrogen	
N <sub>2</sub> ( <i>g</i> )	Molecular nitrogen in the gas state	
$N_2H_{x+y,(ad)}$	Hydrazido species adsorbed on an electrode surface $(x,y = 1 \text{ or } 2)$	
N <sub>x</sub> H <sub>y,(ad)</sub>	Unspecified ammonia oxidation intermediate $(x,y = 1 \text{ or } 2)$	
N <sub>x</sub> H <sub>y-1,(ad)</sub>	Unspecified ammonia oxidation intermediate $(x,y = 1 \text{ or } 2)$	
$N_xH^{-}_{y-1,(ad)}$	Unspecified ammonia oxidation intermediate $(x,y = 1 \text{ or } 2)$	
NH <sub>(ad)</sub>	Imido species adsorbed on an electrode surface	
NH <sub>2,(ad)</sub>	Amido species adsorbed on an electrode surface	
$\rm NH_2^-$	Amide anion	
$NH_3$	Ammonia	

- NH<sub>3,(ad)</sub> Ammonia molecule adsorbed on an electrode surface
- $NH_3(g)$  Ammonia in the gas state
- NH<sub>3</sub>(*I*) Ammonia in the liquid state
- NH<sub>3</sub>(*aq*) Saturated solution of ammonia in water
- NH4<sup>+</sup> Ammonium ion
- NH<sub>4</sub><sup>0•</sup> Neutral, reduced ammonium Rydberg radical species
- NH<sub>4</sub>Br Ammonium bromide
- NH<sub>4</sub>Cl Ammonium chloride
- NH<sub>4</sub>I Ammonium iodide
- NH<sub>4</sub>NO<sub>3</sub> Ammonium nitrate
- NH<sub>4</sub>PF<sub>6</sub> Ammonium hexafluorophosphate
- NHE Normal Hydrogen Electrode
- Ni Elemental nickel
- NO<sub>3</sub><sup>-</sup> Nitrate anion
- NO<sub>x</sub> Unspecified nitrogen oxide molecule
- M Molar (moles solute divided by liters solvent)
- mM Millimolar (millimoles of solute divided by liters of solvent)
- mV Millivolts (1 x 10<sup>-3</sup> volts)
- O Elemental oxygen

O <sub>2</sub>	Molecular oxygen		
OH <sup>-</sup> <sub>(ad)</sub>	Hydroxide species adsorbed on an electrode surface		
$PF_6^-$	Hexafluorophosphate anion		
рН	Negative base ten logarithm of the molar concentration of protons		
PH <sub>3</sub>	Phosphine		
Pt	Elemental platinum		
PtCl₄●xNH <sub>3</sub>	Ammoniated platinum(IV) chloride complex		
PV	Photovoltaic		
Rh	Elemental rhodium		
S	Seconds		
S°	Standard entropy of a chemical species		
SCE	Standard Calomel Electrode		
STP	Standard Temperature and Pressure (25 degrees Celsius and 1 atmosphere)		
STV	Sampled Time Voltammogram, or Sampled Time Voltammetry		
Т	Temperature		
TBAPF <sub>6</sub>	Tetrabutylammonium hexafluorophosphate		
TCD	Thermal Conductivity Detector		
TW	Terra-watts (1 x 10 <sup>12</sup> watts)		
V	Volts		

XPS	X-ray Photoelectron Spectroscopy
XRD	(Thin film) X-ray Diffraction
α	Butler-Volmer reaction barrier symmetry coefficient
°C	Degrees Celsius
$\Delta G^{\circ}_{f}$	Gibbs free energy for the formation of a chemical species under standard conditions
$\Delta G_{rxn}$	Change in Gibbs free energy for a chemical reaction
<sup>n K</sup> ∆G <sub>rxn</sub>	Change in Gibbs free energy for a chemical reaction at a specified temperature "n" Kelvin
∆H° <sub>f</sub>	Change in enthalpy for the formation of a chemical species under standard conditions
$\Delta S^{\circ}_{f}$	Change in entropy for the formation of a chemical species under standard conditions
μF	Microfarads (1 x 10 <sup>-6</sup> farads)

# CHAPTER 1:

THE POTENTIAL ROLE OF AMMONIA IN A RENEWABLE ENERGY FUTURE

## **Energy and the Global Climate**

Carbon dioxide (CO<sub>2</sub>) acts as a prominent greenhouse gas in the Earth's atmosphere due to its high transparency to the incident solar visible radiation, and a high absorptivity for infrared radiation emitted from the surface of the Earth.<sup>1</sup> According to data from the Vostok ice core, the CO<sub>2</sub> concentration in the atmosphere has been in equilibrium between 200 and 300 ppm for the past 420,000 years.<sup>2</sup> However, due to what are almost certainly anthropogenic causes, the CO<sub>2</sub> concentration has been increasing exponentially since the industrial revolution to over 400 ppm today, and the rate of increase is not slowing.<sup>3</sup> Climate scientists expect this increased atmospheric concentration of CO<sub>2</sub> to increase the global mean surface temperature by 2-5 °C,<sup>4</sup> and this predicted increase in the average temperature is already occurring. All of the five hottest years on record, (global average since 1880), have occurred since 2010, and all of the twelve hottest years on record have occurred since 1998.<sup>5</sup> The risks associated with such climate change could include mass extinctions and destabilization of global and regional food and water supplies.<sup>4</sup>

The combustion of fossil fuels for energy–either for production of electricity, or in the transportation, industrial, or residential and commercial sectors–is the largest source of greenhouse gas emission.<sup>6</sup> It has been demonstrated that the global average energy consumption can be closely modeled as proportional to human population, global average gross domestic product (GDP) per capita, and the global energy intensity, or energy consumption per unit GDP.<sup>7,8</sup> Due to increased conservation and improvements in efficiency due to technology, the total global energy intensity has actually been

steadily decreasing for the past century, and this trend is projected to continue.<sup>8</sup> However, the global population is projected to increase to between 9 and 10 billion by the year 2050 (from about 7.5 billion today), and it is not in the best interest of any country to intentionally decrease its own per capita GDP.<sup>9</sup> Since the rate of increase of the global population and per capita GDP is faster than the decrease in energy intensity, the global energy consumption is projected to increase to 26 TW (from 18 TW today) by the year 2040.<sup>10,11</sup> 86 % of the energy consumed globally today is derived from the combustion of fossil fuels, with approximately equal portions of oil, natural gas, and coal consumed.<sup>8,10,11</sup> By most estimates, there are no foreseeable supply constraints that will limit continued consumption of fossil fuels.<sup>4,11</sup> However, relying on fossil fuel combustion to meet the world's increasing energy demand will result in an associated increase in carbon dioxide (CO<sub>2</sub>) emissions from 33 GT today to a projected 46 GT in 2040.<sup>4</sup> Thus, in order to mitigate the worst possible outcomes of climate change, large-scale, carbonneutral alternative energy resources must be implemented in the coming decades.

Solar energy is by far the largest energy resource available, and efficient photovoltaic (PV) technologies comprised of Earth-abundant elements already exist. While their relatively high cost compared to fossil fuels has hampered their commercial implementation, conventional PV's are on the verge of reaching grid-parity, and next generation PV's may prove disruptive in overcoming the cost-efficiency paradigm. Intrinsic limitations of solar energy, however, are its diffusivity and geographic, seasonal, and daily variability. Thus, in order to effectively utilize the power of the sun,

efficient and scalable methods to concentrate, store and transport solar energy are most likely required.

## Ammonia as an Energy Carrier

The above has motivated research in artificial photosynthetic systems that use solar photons to drive the water splitting reactions, thereby storing solar energy in the bonds of molecular hydrogen (H<sub>2</sub>). H<sub>2</sub> gas formed from photoelectrochemical water splitting could be used with either conventional combustion engines or in fuel cells, with either process featuring only water as the byproduct-thus eliminating greenhouse gasses from the fuel cycle. However, while the specific energy, (energy per unit mass), of  $H_2$  is unrivaled,  $H_2$  gas has a relatively low energy density (energy per unit volume). Table 1.1 shows a comparison of various potential fuel sources, as well as a commercial lithium ion battery technology. Using state-of-the-art carbon fiber storage tanks a volumetric energy density of only 5.3 MJ  $L^{-1}$  can be achieved for H<sub>2</sub> gas at 700 bar pressure.<sup>12</sup> This is over a six-fold reduction from the 34.4 MJ L<sup>-1</sup> for gasoline.<sup>13</sup> Extreme cryogenic temperatures are needed to liquefy H<sub>2</sub>, and large volumes of hydrogen cannot be stored at high pressures. Consequently, the storage and transportation of hydrogen represents a significant technical challenge that needs to be overcome before it can become a widely-used fuel.

One possible avenue to store and transport hydrogen is to convert it to ammonia (NH<sub>3</sub>). Synthesis of NH<sub>3</sub> (largely via the Haber-Bosch process) is already one of the

Energy Source	Specific Energy / MJ kg <sup>-1</sup>	Energy Density / MJ L <sup>-1</sup>
Gasoline (C <sub>8</sub> H <sub>18</sub> )	46.7	34.4
Propane (C <sub>3</sub> H <sub>8</sub> , 14 bar)	48.9	19.0
Natural Gas	55.5	10.4
Hydrogen (H <sub>2</sub> ) (700 bar, Carbon fiber tank)	142	5.3
Ammonia (NH <sub>3</sub> , 10 bar)	22.5	13.6
Tesla Powerwall 2 (Commercial Li Ion Battery)	0.405	0.361

**Table 1.1:** Energy density comparison of various fuels and commercial lithium ion batteries.<sup>12–14</sup>

largest industrial processes worldwide, and as a result, the infrastructure for the storage and transport of NH<sub>3</sub> already exists. It is held in tanks at the 50,000 ton scale for up to years at a time, and is shipped via conventional ground transportation or via pipeline.<sup>15</sup> Pipeline networks dedicated to NH<sub>3</sub> are already in place in the United States, and existing natural gas pipelines can be used to transport NH<sub>3</sub> as well with minimal modifications.<sup>15</sup> NH<sub>3</sub> is also already distributed and sold commercially primarily for use in agriculture as fertilizer. Safety protocols are already in place for these processes involving NH<sub>3</sub>, and independent safety evaluations have been performed for NH<sub>3</sub> fuel systems, concluding the level of risk to be similar-to or less-than that of natural gas or propane.<sup>16,17</sup>

Unlike hydrogen, NH<sub>3</sub> can be liquefied easily under 10 bar of pressure, which leads to an energy density of 13.6 MJ  $L^{-1}$ –almost three-fold larger than H<sub>2</sub>. In addition, NH<sub>3</sub> can be decomposed back to nitrogen and hydrogen thermodynamically with less than 10% of the energy needed for splitting H<sub>2</sub>O.<sup>18,19</sup> NH<sub>3</sub> "splitting" would generate

hydrogen that could be utilized in hydrogen fuel cells. The inter-conversion of hydrogen and ammonia therefore potentially offers a more efficient route to store and transport hydrogen than compression. Alternatively, NH<sub>3</sub> itself could potentially be used in direct ammonia fuel cells.<sup>20–22</sup>

Figure 1.1 shows a graphical depiction of a possible ammonia fuel cycle.<sup>23</sup> This cycle is completely closed and contains only oxygen ( $O_2$ ) and nitrogen ( $N_2$ ) from the air and water ( $H_2O$ ) in addition to NH<sub>3</sub>. If the N<sub>2</sub> reduction process in the lower-left corner, and the NH<sub>3</sub> splitting reaction at the top are driven using renewable energy, then there are no greenhouse gas emissions or any other pollutants involved with this cycle. Hydrogen fuel cell cars like the one suggested in the lower-right corner are already available for consumers today. Additionally, there is extensive ongoing research into the catalytic synthesis of NH<sub>3</sub> using renewable energy, as suggested in the lower-left Bosch process.<sup>24–26</sup>

The large point of uncertainty for the realization of the fuel cycle in Figure 1.1 is the NH<sub>3</sub> splitting process at the top. If that reaction cannot be done efficiently with minimal greenhouse gas emissions, then the entire cycle would be unreasonable for implementation. There is a large body of promising work on the thermal decomposition, or "cracking", of NH<sub>3</sub> using solid-state catalysts.<sup>27</sup> However, these catalysts generally incorporate expensive noble metals and require operation temperatures around 300 °C or greater to achieve sufficient conversion. More importantly, thermal cracking in this



**Figure 1.1:** An ammonia fuel cycle involving the reduction of N<sub>2</sub> coupled with H<sub>2</sub>O oxidation (lower left), the splitting of NH<sub>3</sub> to N<sub>2</sub> and H<sub>2</sub> (top), and the oxidation of H<sub>2</sub> as a fuel (lower right). (Reproduced from Little *et al.*)<sup>23</sup>

way is a continuous-flow process, which is not conducive to the inherently intermittent nature of solar (or wind) energy, or the periodic increases and decreases in fuel demand over the course of the day and year. What is preferred, therefore, is an electrochemical reactor that can switch between active and idle states quickly rather than needing to run continuously

Such a reactor would drive the splitting of  $NH_3$  through electrolysis-where a potential is applied across two electrodes in contact with  $NH_3$  in solution-evolving  $N_2$  at the positive electrode or "anode", and evolving  $H_2$  at the negative electrode or "cathode". The magnitude of the potential needed to drive the electrolysis is equal to

0.077 V-the thermodynamic minimum for the reaction-plus some additional potential called an "overpotential". Overpotential is needed to push the reaction in the forward direction as there is no net reaction when the overpotential is zero. For a particular catalyst/electrode, a larger overpotential corresponds to a larger driving-force for the reaction to proceed, and thus generally a faster rate of reaction, measured as current. Therefore, a small amount of overpotential is fundamentally required in electrolysis, but more efficient catalysts can increase the current without increasing the potential.

## The State of Ammonia Electrolysis Research

The electrolysis of NH<sub>3</sub> to H<sub>2</sub> and N<sub>2</sub> has been studied primarily only in aqueous solution. Vitse *et al.* used an alloy of platinum and iridium to catalyze the electrolysis of a 1 M aqueous ammonia (NH<sub>3</sub>(*aq*)) solution and obtained current densities between 400 and 500 mA cm<sup>-2</sup> with only 500 mV of applied overpotential.<sup>19</sup> Under these aqueous conditions, the reduction of the H<sub>2</sub>O solvent is the source of the H<sub>2</sub> product, and hydroxide ions (OH<sup>-</sup>) have been reported to participate in the oxidation of NH<sub>3</sub>(*aq*) as proton acceptors as suggested by the mechanism below in Equations (1.1) through (1.5)–originally postulated by Gerischer and Mauerer.<sup>28</sup>

$$\mathsf{NH}_{3,(ad)} + \mathsf{OH}_{(ad)}^{-} \longrightarrow \mathsf{NH}_{2,(ad)} + \mathsf{H}_2\mathsf{O} + e^{-}$$
(1.1)

$$\mathsf{NH}_{2,(ad)} + \mathsf{OH}_{(ad)}^{-} \underbrace{\longrightarrow} \mathsf{NH}_{(ad)} + \mathsf{H}_{2}\mathsf{O} + \mathsf{e}^{-}$$
(1.2)

$$NH_{x,(ad)} + NH_{y,(ad)} \longrightarrow N_2H_{x+y,(ad)} \quad (x,y = 1 \text{ or } 2)$$
(1.3)

$$N_2H_{x+y,(ad)} + (x+y)OH_{(ad)} \longrightarrow N_2 + (x+y)H_2O + (x+y)e^-$$
 (1.4)

$$NH_{(ad)} + OH_{(ad)}^{-} \longrightarrow N_{(ad)} + H_2O + e^{-} (N_{(ad)} = poison)$$
(1.5)

After investigating the NH<sub>3</sub>(*aq*) oxidation voltammograms carefully as a function of pH, Katsounaros *et al.* were able to conclude that the rate determining process involves decoupled electron and proton transfers—as opposed to the proton-coupled electron transfer processes suggested by Gerischer and Mauerer.<sup>29</sup> Thus, in the revised mechanism, either equation (1.1) or (1.2) should be replaced by equations (1.6) and (1.7). Even in the revised mechanism it is widely accepted that OH<sup>-</sup> plays a critical role in the NH<sub>3</sub>(*aq*) oxidation mechanism by acting as a base and accepting the protons as they are removed from the nitrogen species.

$$N_{x}H_{y,(ad)} + OH^{-} = (N_{x}H_{y-1})^{-}_{(ad)} + H_{2}O$$
(1.6)

$$(\mathsf{N}_{x}\mathsf{H}_{y-1})^{-}_{(ad)} = \mathsf{N}_{x}\mathsf{H}_{y-1,(ad)} + e^{-}$$
(1.7)

An important point to emphasize in the oxidation of  $NH_3(aq)$  is the formation of  $N_{(ad)}$  as shown in (1.5). The reactions of (1.3) and (1.5) are competing pathways, and thus at sufficiently high positive overpotential,  $N_{(ad)}$  formation occurs faster than N–N bond formation leading to a poisoned anode surface. This is observed in voltammetry as a peak followed by a sharp decline in anodic current as potential is swept in the positive direction.<sup>30</sup> The "poisoned" electrode is then ineffective for further oxidation of  $NH_3(aq)$ . However, poisoned anodes can then be restored, generally, by sweeping to, or the application of, sufficiently negative potentials.<sup>30</sup> This is because the  $N_{(ad)}$  poison species exists exclusively on the surface of the anode, and thus does not cause a significant change in electrode morphology or bulk composition.

The cathodic half reaction during NH<sub>3</sub>(*aq*) electrolysis is the reduction of H<sub>2</sub>O to H<sub>2</sub> as shown in equation (1.8), making NH<sub>3</sub>(*aq*) electrolysis further analogous to H<sub>2</sub>O electrolysis under basic conditions. Thus noble metal proton reduction catalysts effective for H<sub>2</sub>O electrolysis are also generally effective as cathodes for NH<sub>3</sub>(*aq*) electrolysis.<sup>31</sup> Since this reaction occurs at the same potential as simple proton reduction–after accounting for changes in pH–the thermodynamic potential needed to drive the entire cell (both half reactions), E<sub>rxn</sub>, is minimized.

$$H_2O + e^{-} \underbrace{\longrightarrow}_2 H_2 + OH^{-}$$
(1.8)

Since both anodic and cathodic half reactions are affected by the presence of water, (or OH<sup>-</sup>), the electrolysis of NH<sub>3</sub>(*aq*) is not directly analogous to the electrolysis of liquid ammonia (NH<sub>3</sub>(*h*)). Still, there is information that can be gleaned from the larger body of NH<sub>3</sub>(*aq*) electrolysis research. For instance, the problem of anodic poisoning as shown in (1.5), where at sufficiently positive overpotentials the rate of N<sub>(ad)</sub> formation exceeds that of N–N bond formation, can potentially be a problem regardless of solvent. The formation of the N<sub>(ad)</sub> poison species is a significant barrier for NH<sub>3</sub>(*aq*) oxidation as it sets a maximum anodic overpotential limit that practical devices cannot exceed.<sup>29,32</sup> In general, however, the electrolyses of NH<sub>3</sub>(*aq*) and NH<sub>3</sub>(*l*) should be treated as different processes, and it is dangerous to make assumptions about NH<sub>3</sub>(*l*) based upon what is known in aqueous conditions.

For practical considerations, if the electrolysis efficiencies were identical,  $NH_3(l)$  would be desired over  $NH_3(aq)$  for implementation into the energy framework. A saturated  $NH_3(aq)$  solution is approximately 14 M at STP, whereas  $NH_3(l)$  is 40 M-

nearly triple the energy density. Further, the alkaline NH<sub>3</sub>(*aq*) solutions are corrosive to metallic storage and transport infrastructure, whereas there is already a substantial existing pipeline system for the distribution of NH<sub>3</sub>(*l*). In addition, electrolysis of NH<sub>3</sub>(*l*) eliminates the possibility of forming NO<sub>x</sub> compounds as unwanted side products.<sup>30,33</sup> If the liquid state is sustained using decreased temperatures–such as -65 °C in the case of our NH<sub>3</sub>(*l*) experiments–there is a thermodynamic penalty, raising E<sub>rxn</sub> from 0.077 V to 0.10 V (calculation *vide infra*). However, practical devices could operate at ambient temperature simply by using elevated pressure to sustain the NH<sub>3</sub>(*l*).<sup>18,34</sup>

In contrast to the electrolysis of  $NH_3(aq)$ , the electrolysis of  $NH_3(l)$  has received almost no attention. The primary example is a paper by Hanada *et al*, who reported 7.2 mA cm<sup>-2</sup> from the electrolysis of  $NH_3(l)$  with 2.0 V applied between two platinum electrodes at 9.63 bar and 25°C.<sup>18</sup> This was only achieved with a relatively high concentration (1 M) potassium amide (KNH<sub>2</sub>) electrolyte, which in solid form is known to detonate. They demonstrated using gas chromatography that H<sub>2</sub> and N<sub>2</sub> are the products generated at the cathode and anode respectively, and attributed these products to the reduction of  $NH_3$  and oxidation of amide ( $NH_2^-$ ). However, this mechanism was not substantiated. While they showed that increasing the concentration of  $NH_2^-$  increased the rate of  $NH_3(l)$  electrolysis, they did not report controls where the  $NH_2^-$  concentration was changed but the ionic strength of the solution was held constant. In addition, since only two electrodes were used, the overpotentials for each of the half reactions were not identified.

As will be discussed in detail in Chapter 3, we were able to demonstrate that the half reactions of the electrolysis of  $NH_3(I)$  on Pt electrodes are the reduction of ammonium ( $NH_4^+$ ) and the oxidation of  $NH_3$ .<sup>23</sup> In fact, the reduction of  $NH_3$  in  $NH_3(I)$  is impossible with a Pt cathode as electron solvation–a process where free electrons are dissolved directly into solution–occurs at more positive potentials.<sup>35</sup> We also demonstrated that  $NH_2^-$  electrolytes actually decrease the rate of  $NH_3$  oxidation by showing much larger anodic currents using either  $NH_4^+$  or "neutral" electrolytes.

These findings were later confirmed by Dong *et al*, who studied the electrolysis of NH<sub>3</sub>(*l*) using ammonium halide electrolytes, as well as ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), and potassium amide (KNH<sub>2</sub>).<sup>36</sup> They found that anodic current increased by switching from ammonium chloride (NH<sub>4</sub>Cl), to bromide (NH<sub>4</sub>Br), to iodide (NH<sub>4</sub>I), and that NH<sub>4</sub>NO<sub>3</sub> had a similar performance to NH<sub>4</sub>I. KNH<sub>2</sub> drastically underperformed all three of the above, however, in agreement to what we observed, and what Hanada *et al.* reported.<sup>18,23</sup> Dong *et al.* were able to further improve anodic performance by switching to a nanostructured rhodium-platinum-iridium (Rh-Pt-Ir) alloy which reduced the anodic overpotential by approximately 0.7 V.<sup>36</sup> However, they report that while the geometric areas of their Pt electrode and Rh-Pt-Ir electrode are the same, the nanostructured Rh-Pt-Ir electrode has an electrochemical active surface area over 360 times larger.

In 2016, Goshome *et al.* also reported the electrolysis of  $NH_3(l)$  with an  $NH_4Cl$  electrolyte, investigating the activity of both Pt and stainless steel anodes.<sup>34</sup> They achieved current densities similar to our report and that of Dong *et al*, though they also saw significant anodic dissolution after sustaining a cell potential of 2 V for 8 hours in

the case of stainless steel, or 50 hours in the case of Pt. They determined the dissolution products to be  $[Fe(NH_3)_6][CI]_2$  and  $PtCI_4 \bullet xNH_3$  respectively via powder x-ray diffraction (XRD). However, only one variety of stainless steel was tested as an anode, and the type used was not specified in the paper. Also, chemical processes occurring at the anode could not be studied specifically due to the lack of a reference electrode.

There has also been some work studying the NH<sub>3</sub> electrolysis reaction pathways using alternative solvents. Buzzeo et al. studied both the oxidation and reduction half reactions for the case of NH<sub>3</sub> dissolved in N,N-dimethylformamide (DMF) or the ionic liquid 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide on Pt electrodes.<sup>37</sup> They concluded that the oxidation of  $NH_3$  and reduction of  $H^+$  were the important half reactions. However, their electrochemical cell incorporated silver а wire pseudoreference electrode, making it difficult to quantitatively compare reaction potentials. Still, the technique demonstrates the possibility of learning mechanistic information about NH<sub>3</sub> electrolysis through the use of an organic solvent.

The objective of our research is to more closely explore both the anodic and cathodic half reactions of the electrolysis of  $NH_3(I)$ , identify the chemical problems hindering the efficiency of the overall process, and suggest solutions to those problems involving sustainable, Earth-abundant materials. First, the electrolysis of  $NH_3(I)$  using Pt as both the anode and cathode is investigated as a function of the relative concentrations of  $NH_4^+$  and  $NH_2^-$  in the electrolyte. By coupling the  $NH_3(I)$  results with data from the electrolysis of  $NH_3(g)$  dissolved in DMF, the half reactions occurring at each electrode are clarified and the requirements of large overpotentials for each are
discussed. Second, a new  $NH_3(I)$  electrolyte preparation method is introduced and discussed, and the characteristics of an Earth-abundant Fe/FeN<sub>x</sub> anode material will be highlighted. Then, electrodeposited CoP<sub>x</sub> is presented as an Earth-abundant alternative cathode material. Finally, possible future research directions are suggested that should clarify the route toward better NH<sub>3</sub> splitting catalysis.

APPENDICES

#### Appendix 1.1: Calculation of E<sub>cell</sub> for the Electrolysis of Liquid Ammonia

The thermodynamic potential for electrolysis,  $E_{cell}$ , is related to the free energy change of the reaction,  $\Delta G_{rxn}$ , by (1.9) where n is the number of electrons involved in the electrochemical reaction, and F is Faraday's constant.

$$\mathsf{E}_{\mathsf{cell}} = \frac{-\Delta \mathsf{G}_{\mathsf{rxn}}}{\mathsf{nF}} \tag{1.9}$$

The reaction of interest is the decomposition of ammonia (NH<sub>3</sub>), shown by (1.10).

$$\mathsf{NH}_{3}(I) \longrightarrow \frac{1}{2}\mathsf{N}_{2}(g) + \frac{3}{2}\mathsf{H}_{2}(g) \tag{1.10}$$

This decomposition reaction is simply the inverse of the formation of NH<sub>3</sub> from its elements at standard state. The free energy change of formation ( $\Delta G^{\circ}_{f}$ ) is related to the changes in entropy ( $\Delta S^{\circ}_{f}$ ) and enthalpy ( $\Delta H^{\circ}_{f}$ ) by (1.11):

$$\Delta G^{o}_{f} = \Delta H^{o}_{f} - T\Delta S^{o}_{f} \tag{1.11}$$

NH<sub>3</sub> is not liquid under standard conditions (T = 298 K and 1 atm pressure), however, where values for  $\Delta H^{\circ}_{f}$  and  $\Delta S^{\circ}_{f}$  are available. Thus, E<sub>cell</sub> at the temperature of this study, 203 K, was estimated by using  $\Delta H^{\circ}_{f}$  and  $\Delta S^{\circ}_{f}$  at 298 K, (which are easily obtained from tabulated values)<sup>38</sup> and a temperature of 203 K in equation (1.11).  $\Delta S^{\circ}_{f}$  is determined from S° for the reactant and both products as shown in (1.12) through (1.14).<sup>38</sup>

$$\Delta S_{f}^{\circ} = \left[\frac{1}{2}S^{\circ}(N_{2}(g)) + \frac{3}{2}S^{\circ}(H_{2}(g))\right] - S^{\circ}(NH_{3}(I))$$
(1.12)

$$\Delta S_{f}^{o} = \left[\frac{1}{2}\left(191.6 \text{ J mol}^{-1} \text{ K}^{-1}\right) + \frac{3}{2}\left(130.7 \text{ J mol}^{-1} \text{ K}^{-1}\right)\right] - \left(103.3 \text{ J mol}^{-1} \text{ K}^{-1}\right)$$
(1.13)

$$\Delta S_{f}^{\circ} = 188.6 \text{ J mol}^{-1} \text{ K}^{-1}$$
 (1.14)

Plugging into (1.11):

$$^{203 \text{ K}}\Delta G_{rxn} \approx (67200 \text{ J mol}^{-1}) - (203 \text{ K})(188.6 \text{ J mol}^{-1} \text{ K}^{-1}) = 28900 \text{ J mol}^{-1}$$
 (1.15)

Plugging the result from (1.15) into (1.9):

$$\mathsf{E}_{cell} = \frac{-\frac{203 \text{ K}}{\Omega} G_{rxn}}{\mathsf{nF}} = \frac{-(28900 \text{ J mol}^{-1})}{(3)(96485 \text{ C mol}^{-1})} = -0.100 \text{ V} = -100 \text{ mV}$$
(1.16)

#### Appendix 1.2: Background Theory for 2-Electrode and 3-Electrode Measurements

In different parts of this project, electrochemical measurements were made that employed either two electrodes, an anode and cathode, as depicted in Figure 1.2(a), or three electrodes with the addition of a reference electrode as depicted in Figure 1.2(b). Cells employing only two electrodes have the advantage of more closely resembling practical devices, but it is far simpler to investigate specific electrochemical reactions with the addition of the reference electrode. For the sake of clarity, we will discuss some important differences between the two experiments.



**Figure 1.2:** Electrode configuration diagrams for a 2-electrode (a) and 3-electrode (b) experiment. In the 3-electrode case, the working, reference, and counter electrodes are labeled W.E., R.E., and C.E. respectively. In both cases, the red "V<sub>A</sub>" represents where a potential is applied, the green "V<sub>M</sub>" represents where a potential is measured, and the blue "I<sub>M</sub>" represents where the current is measured.

In the 2-electrode configuration there is a positively charged "anode", which is where an oxidation reaction occurs, and a negatively charged "cathode" where a reduction reaction occurs. Experimentally, a potentiostat is used to apply a known potential between the anode and cathode–as indicated by the red " $V_A$ " in Figure 1.2. Then, the electrons flowing into the anode, through the circuit, and then out of the cathode are measured as a current–as indicated by the blue " $I_M$ ". In order for Faradaic current to flow in this configuration, the potential applied between the anode and cathode must be greater than the thermodynamically limiting  $E_{cell}$ , which for the case of NH<sub>3</sub> electrolysis is specified in equation (1.16). After that point, further increasing the potential will result in an increase in the measured current. This additional potential is called "overpotential".

Unfortunately, in the 2-electrode configuration it is impossible to determine whether the anodic or cathodic reaction is rate limiting, i.e. requires more overpotential to increase the current. Thus, for most electrochemical experiments a 3-electrode configuration is used. Here a "working" electrode–"W.E." in Figure 1.2(b)–can serve as either the anode or the cathode as its potential is set with respect to a "reference" electrode, "R.E.". A reference electrode is actually an electrochemical half-cell that will hold a fixed potential so long as only a small magnitude current flows through the cell. For that reason, a third "counter" electrode–"C.E." in Figure 1.2(b)–is used to complete the circuit for current measurements.

The potential difference between the working and reference electrode is known, and since the potential of the reaction in the reference electrode is constant, the potential at the surface of the working electrode specifically is known, providing the advantage over the 2-electrode configuration. The potential at the counter electrode is unknown in this configuration, as the potentiostat simply allows it to become any potential necessary to allow current to flow through the circuit and prevent excess

charge from building up at the working electrode. In the 3-electrode configuration, either oxidation or reduction reactions can occur at the working electrode, depending upon the potential with respect to the reference, and thus the current/overpotential relationship for each half-reaction can be studied independently.

#### Appendix 1.3: Discussion of the Term "Onset Potential"

The term "onset potential" is frequently used in discussions comparing catalytic efficiencies of different materials. However, the term is not rigorously defined. In fact, as the scale of a plot is continually magnified, an electrolysis *J-V* curve will continue to hold the same shape, making it arbitrary to define where the "onset" of the wave is on the potential axis.

In Chapter 3, due to the current density frequently reaching a linear, ohmic regime where the slope is dictated by the solution resistance, the "onset potential" is defined as the point where a line drawn through the linear portion of a redox wave of the *J-V* curve would intersect with the baseline. A sample of this method is depicted in Figure 1.3. With this definition, it is possible for two CV curves to have similar onset potentials, but significantly different current densities at their onsets. Therefore, materials will also be compared by the overpotentials required to reach a certain current density, particularly in Chapters 4 and 5. These current densities are chosen arbitrarily as well, however this is a convenient method for compensating for different shapes of catalytic curves.

A common method to quantitatively compare the shapes of two CV or *J*-*V* curves is through the use of a Tafel slope.<sup>39</sup> In this method, the base-ten logarithm of the absolute value of the current density is plotted as a function of potential, making it simpler to compare the exponentially-curved regions of two CV or *J*-*V* plots. The slope of the linear region of a Tafel plot indicates the additional overpotential required to

create a ten-fold increase in the magnitude of current, and can also serve as a useful metric for quantitatively comparing the performances of two different materials.



**Figure 1.3:** Illustration of how the onset potential would be calculated from a sample curve.

REFERENCES

#### REFERENCES

- (1) Harries, J. E.; Brindley, H. E.; Sagoo, P. J.; Bantges, R. J. *Nature* **2001**, *410*, 355–357.
- Petit, J. R.; Jouzel, J.; Raynaud, D.; Barkov, N. I.; Barnola, J.-M.; Basile, I.; Bender, M.; Chappellaz, J.; Davis, M.; Delaygue, G.; Delmotte, M.; Kotlyakov, V. M.; Legrand, M.; Lipenkov, V. Y.; Lorius, C.; PÉpin, L.; Ritz, C.; Saltzman, E.; Stievenard, M. *Nature* 1999, *399*, 429–436.
- (3) Tans, P.; Keeling, R. Atmospheric CO2 at Mauna Loa Observatory https://scripps.ucsd.edu.
- (4) Field, C. B.; Barros, V. R.; Dokken, D. J.; Mach, K. J.; Mastrandrea, M. D.; Bilir, T. E.; Chatterjee, M.; Ebi, K. L.; Estrada, Y. O.; Genova, R. C.; Girma, B.; Kissel, E. S.; Levy, A. N.; MacCracken, S.; Mastrandrea, P. R.; White, L. L. *Climate Change 2014: Impacts, Adaptation and Vulnerability. Contributions of the Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: Cambridge, United Kingdom and New York, NY, USA, 2014.
- (5) NOAA National Centers for Environmental Information. *State of the Climate: Global Analysis for Annual 2016*; 2017.
- (6) United States Environmental Protection Agency. *Draft Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2015*; 2017.
- (7) Kates, R. W. *Environment* **2000**, *42*, 10–19.
- (8) Lewis, N. S.; Nocera, D. G. Proc. Natl. Acad. Sci. U. S. A. 2006, 103, 15729– 15735.
- (9) United Nations Department of Economic and Social Affairs, P. D. *World Population Prospects: The 2015 Revision*; 2015.
- (10) BP Statistical Review of World Energy, June 2016; 2016.

- (11) U.S. Energy Information Administration. *International Energy Outlook 2016*; 2016.
- Hua, T.; Ahluwalia, R.; Peng, J.-K.; Kromer, M.; Lasher, S.; McKenney, K.; Law,
   K.; Sinha, J. *Technical Assessment of Compressed Hydrogen Storage Tank* Systems for Automotive Applications; 2010.
- (13) Zamfirescu, C.; Dincer, I. J. Power Sources 2008, 185, 459–465.
- (14) Powerwall 2 https://www.tesla.com/powerwall.
- (15) Bartels, J. R. A feasibility study of implementing an Ammonia Economy, Iowa State University, 2008.
- (16) Duijm, N. J.; Markert, F.; Paulsen, J. L. *Safety Assessment of Ammonia as a Transport Fuel*; Roskilde, Denmark, 2005.
- (17) Quest Consultants Inc. Comparative Quantitative Risk Analysis of Motor Gasoline, LPG, and Anhdryous Ammonia as an Automotive Fuel; Norman, OK, 2009.
- (18) Hanada, N.; Hino, S.; Ichikawa, T.; Suzuki, H.; Takai, K.; Kojima, Y. *Chem. Commun. (Camb).* **2010**, *46*, 7775–7777.
- (19) Vitse, F.; Cooper, M.; Botte, G. G. J. Power Sources 2005, 142, 18–26.
- (20) Afif, A.; Radenahmad, N.; Cheok, Q.; Shams, S.; Kim, J. H.; Azad, A. K. *Renew. Sustain. Energy Rev.* **2016**, *60*, 822–835.
- (21) Boggs, B. K.; Botte, G. G. J. Power Sources 2009, 192, 573–581.
- (22) Lan, R.; Tao, S. *Electrochem. Solid-State Lett.* **2010**, *13*, B83.
- (23) Little, D. J.; Smith, III, M. R.; Hamann, T. W. *Energy Environ. Sci.* **2015**, *8*, 2775–2781.
- (24) Tanabe, Y.; Nishibayashi, Y. Chem. Rec. 2016, 1–29.
- (25) Shipman, M. A.; Symes, M. D. Catal. Today 2016, 1–12.

- (26) Bandy, J. A.; Zhu, D.; Hamers, R. J. *Diam. Relat. Mater.* **2016**, *64*, 34–41.
- (27) Yin, S. F.; Xu, B. Q.; Zhou, X. P.; Au, C. T. Appl. Catal. A Gen. 2004, 277, 1–9.
- (28) Gerischer, H.; Mauerer, A. *Electroanal. Chem. Interfacial Electrochem.* **1970**, *25*, 421–433.
- (29) Katsounaros, I.; Chen, T.; Gewirth, A. A.; Markovic, N. M.; Koper, M. T. M. *J. Phys. Chem. Lett.* **2016**, *7*, 387–392.
- (30) Le Vot, S.; Reyter, D.; Roué, L.; Bélanger, D. J. Electrochem. Soc. 2012, 159, F91.
- (31) Palaniappan, R.; Ingram, D. C.; Botte, G. G. *J. Electrochem. Soc.* **2014**, *161*, E12–E22.
- (32) Li, Z.-F.; Wang, Y.; Botte, G. G. *Electrochim. Acta* **2017**, *228*, 351–360.
- (33) Bunce, N. J.; Bejan, D. *Electrochim. Acta* **2011**, *56*, 8085–8093.
- (34) Goshome, K.; Yamada, T.; Miyaoka, H.; Ichikawa, T.; Kojima, Y. *Int. J. Hydrogen Energy* **2016**, 2–7.
- (35) Itaya, K.; Malpas, R. E.; Bard, A. J. Chem. Phys. Lett. 1979, 63, 411–415.
- (36) Dong, B.-X.; Tian, H.; Wu, Y.-C.; Bu, F.-Y.; Liu, W.-L.; Teng, Y.-L.; Diao, G.-W. *Int. J. Hydrogen Energy* **2016**, *41*, 14507–14518.
- (37) Buzzeo, M. C.; Giovanelli, D.; Lawrence, N. S.; Hardacre, C.; Seddon, K. R.; Compton, R. G. *Electroanalysis* **2004**, *16*, 888–896.
- (38) Jolly, W. L. Chem. Rev. 1952, 50, 351–361.
- (39) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; 2nd ed.; Wiley and Sons Inc., 2000.

# CHAPTER 2:

## EXPERIMENTAL DESIGN FOR THE ELECTROCHEMICAL INVESTIGATION OF

ANHYDROUS AMMONIA

#### **Electrochemical Experimentation in Stock Liquid Ammonia**

Anhydrous ammonia (Airgas) was liquefied at ambient pressure by passing the gas directly into a pre-assembled electrochemical cell like the one shown in Figure 2.1 submerged in a bath of dry ice in methanol. All electrochemical experiments were conducted in this bath, which was kept between -70 and -65 °C. After a sufficient amount of  $NH_3(I)$  was collected—as designated by a horizontal mark on the side of the cell-the flow of  $NH_3(g)$  at the inlet was replaced by a gentle flow of dry N<sub>2</sub>. The outlet was connected to a silicon oil bubbler at all times. An amount of ammonium hexafluorophosphate  $(NH_4PF_6)$ (Fluka, 98%, recrystallized), potassium hexafluorophosphate (KPF<sub>6</sub>) (Acros, 99%, recrystallized), or ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) (Jade Scientific, reagent, dried and stored under vacuum) required to produce an NH<sub>3</sub>(*I*) solution of the desired electrolyte concentration was added to the electrochemical cell, along with all electrodes as shown in Figure 2.1, and the cell was sealed using virgin, rubber septa.

The two-electrode electrolysis of  $NH_3(I)$  was performed using two identical platinum metal (Pt) disks as the anode and cathode. Three-electrode voltammetry in  $NH_3(I)$  was performed using one of the Pt disk working electrodes, a high surface area Pt mesh as a counter electrode, and a custom-made silver/silver nitrate (Ag/AgNO<sub>3</sub>)



**Figure 2.1:** Diagram of the electrochemical cell used for voltammetry in  $NH_3(l)$  as well as in DMF with dissolved  $NH_3(g)$ .

reference electrode. (The cell in Figure 2.1 depicts the three-electrode setup.) The Ag/AgNO<sub>3</sub> reference–as shown in the diagram in Figure 2.2–was fabricated by melting a glass Pasteur pipette around a small piece of Pt wire at one end, and filling the inside of the pipette with a methanol solution of 0.1 M tetrabutylammonium perchlorate (TBAP) (Fluka, 99%), and 0.01 M AgNO<sub>3</sub> (Jade Scientific, Reagent ACS). A silver wire was then inserted into the open end of the pipette, sealed in place using a rubber septum, and connected to the potentiostat.<sup>1</sup> The resulting reference held a sufficiently stable potential in any solvent it was tested in, including NH<sub>3</sub>(*l*). The potential of the reference electrode was measured versus a commercial saturated calomel electrode (SCE), allowing all electrochemical measurements to be reported versus NHE after

conversion.<sup>2</sup> Unless otherwise noted, all cyclic voltammograms (CVs) were conducted at a scan rate of 100 mV s<sup>-1</sup>.



**Figure 2.2:** Diagram of the custom  $Ag/AgNO_3$  reference electrode for use in  $NH_3(I)$  solutions.

Special care was taken when conducting voltammetry in NH<sub>3</sub>(*I*) with potassium amide (KNH<sub>2</sub>). KNH<sub>2</sub> was synthesized as reported by Hanada *et al.* from anhydrous ammonia and potassium hydride (KH) (Alfa Aesar, 30% w/w in mineral oil), and was kept under a nitrogen atmosphere at all times.<sup>3</sup> Characterization of the resulting powder is shown in Figure 2.3. NH<sub>3</sub>(*I*) was formed *in situ* inside a sealed flask containing KNH<sub>2</sub>,

and was quenched with isopropanol immediately following electrochemical measurements.



**Figure 2.3:** Powder XRD spectrum of KNH<sub>2</sub> synthesized from KH and liquid NH<sub>3</sub>. A reference spectrum for KNH<sub>2</sub> is shown in the red, dotted line. The large amorphous feature at 20° is due to the sample holder, which included a dome to maintain a nitrogen atmosphere for the powder. (Reproduced from Little *et al.*)<sup>4</sup>

#### Distillation of Liquid Ammonia for Electrochemistry in Rigorously Dry Conditions

From Chapter 4 and on,  $NH_3(I)$  was first thoroughly dried before use. To accomplish this, anhydrous ammonia (Airgas) was liquefied at ambient pressure by condensing the gas in a custom flask submerged in a methanol/dry ice bath as depicted in Figure 2.4. When a sufficient amount of  $NH_3(I)$  was collected (approximately 200 mL), about 1 cm<sup>3</sup> of metallic sodium was added to the flask through the center neck, resulting

in the characteristic deep-blue color of solvated electrons that indicates the removal of trace water in the liquid. The flask was then lifted out of the bath, one end of a cannula was inserted in the sealed electrochemical cell, and then other was inserted through the virgin septum, keeping the tip above the  $NH_3$  solution. As the flask warmed, dry  $NH_3(g)$  was transferred to sealed electrochemical cell.



**Figure 2.4:** Diagram of the  $NH_3(I)$  distillation flask including two glass valves for the gas inlet and outlet, as well as a black, plastic screw-cap containing a white Teflon septum.

The methodology for electrochemical experiments conducted with distilled  $NH_3(I)$  was similar to that of the stock  $NH_3(I)$  experiments, except that after assembly and before solvent condensation, the cell was then purged of air by carefully pulling a vacuum and refilling the flask with dry nitrogen using a Schlenk line, repeated three

times. This way, all electrochemical experiments could be reasonably considered free of air and water contamination. When conducting gas chromatography experiments, argon gas (Airgas, 99.99%) or helium gas (Airgas, 99.99%) was used to fill the headspace of the cell in place of nitrogen so that the nitrogen gas evolved during the reaction could be measured.

From Chapter 4 and on, a custom Ag/AgCl reference electrode was used in place of the Ag/AgNO<sub>3</sub> reference previously described. The Ag/AgCl reference electrode was designed similarly to the Ag/AgNO<sub>3</sub> reference, however the electrolyte was saturated in both ammonium chloride (NH<sub>4</sub>Cl) (Fischer, >99.6%) and NH<sub>3</sub>(*g*) in methanol. The silver wire was first mechanically polished, cleaned in 3 M nitric acid, and then pre-coated with AgCl by applying 0.4 mA cm<sup>-2</sup> in a 0.1 M solution of hydrochloric acid.<sup>5</sup> The wire was then sealed in the solution and allowed to reach equilibrium over three days. The completed reference was demonstrated to be stable in NH<sub>3</sub>(*l*) by measuring the potential for electron solvation to be -2.67  $\pm$  0.01 V over a period of hours.<sup>6</sup> Potentials measured with this reference were converted to NHE by measuring the reversible redox wave for ferrocene in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) (Aldrich, 98%, recrystallized), which has been reported at 0.31 V versus SCE.<sup>2</sup> This was confirmed via measurements with a commercial SCE electrode. SCE values were then converted to NHE by adding 241 mV.<sup>2</sup>

#### **Evaluation of Electrochemical Headspace Via Gas Chromatography**

Gas chromatography (GC) was conducted using an Agilent 7820A GC System incorporating a 30 m HP-PLOT/U column for separating NH<sub>3</sub> from N<sub>2</sub> and H<sub>2</sub>, and a 50 m long 5Å Molsieve for separating N<sub>2</sub> and H<sub>2</sub> from each other, and a thermal conductivity detector (TCD). The thermal conductivity detector was calibrated for N<sub>2</sub> and H<sub>2</sub> by injecting known quantities of pure N<sub>2</sub> or pure H<sub>2</sub> using either a 100  $\mu$ L or 25  $\mu$ L syringe. The TCD senses changes in the thermal conductivity of the gas in the outlet due the presence of analyte mixed with the carrier gas, and thus the sensitivity for different gasses depends on the carrier gas chosen. Since He and H<sub>2</sub> have very similar thermal conductivities, the TCD sensitivity for H<sub>2</sub> is very low when He is used as a carrier gas–though it is very high when Ar is used as the carrier. The opposite is true for N<sub>2</sub> detection. The choice of carrier gas thus impacts the quantity of product required for detection and should be carefully considered before carrying out an experiment.

The GC system also featured a pneumatic bypass valve which allowed for flow through both the Plot/U and Molesieve columns to the detector when "off", or straight from the Plot/U column to the detector, bypassing the Molesieve, when "on". This feature is important as larger molecules such as NH<sub>3</sub>, H<sub>2</sub>O, or CO<sub>2</sub> take an extremely long time–up to hours–to pass through the 5Å Molsieve and then experience extreme peak broadening. Thus, the separation procedure involves injection with the bypass valve "off", then switching the valve to "on" after the non-dipole-containing gases (H<sub>2</sub>, He, N<sub>2</sub>, O<sub>2</sub>, and Ar) have passed the valve onto the Molsieve. (Of course, Ar is significantly larger and heavier than the others, but still quickly passes onto the

Molsieve because in is non-polar.) These non-dipole-containing gases then sit stagnant on the Molsieve while the remaining gases elute from the Plot/U directly to the detector. After this elution step is complete, the bypass valve is turned back to "off" and the remaining gases elute in increasing order of their size.

A sample port incorporating a low-bleed rubber septum and septum injector nut (Vici Valco) was connected to one of the narrow, quarter-inch necks of the electrochemical flask via a Swagelok Ultra-torr Vacuum Fitting. Gaseous samples were extracted from the headspace of the cell using a Hamilton 500  $\mu$ L Model 1750 Sample-Lock syringe. In order to not overfill the GC inlet, only 100  $\mu$ L samples were extracted and injected. Even with the Sample-Lock feature of the syringe (a Teflon valve that allowed for manual sealing of the syringe), great care was taken to inject samples into the GC as quickly as possible after extraction from the cell headspace. This was done to minimize any sample leakage and N<sub>2</sub> contamination from the atmosphere into the sample.

The complete separation method took approximately 30 minutes, and as a result samples were extracted from the cell headspace every 30 minutes. During bulk electrolysis experiments, the potential of interest was applied for 30-minute intervals between injections, instead of continuously, in order to easily identify the charge passed between each separation and quantification of the headspace.

In order to subtract any N<sub>2</sub> originating from air contamination, several samples of laboratory air were injected through the GC in order to precisely identify the N<sub>2</sub>:O<sub>2</sub> ratio from the air. Since the headspace of the cell was thoroughly purged with vacuum and

Ar, the initial partial pressure of  $O_2$  in the cell was assumed to be 0. Thus, the area of the  $O_2$  peak in the gas chromatograph could be attributed exclusively to air contamination. Therefore, when analyzing the GC data, the fraction of the  $N_2$  peak proportional to the  $O_2$  peak was subtracted, and the remainder was assumed to result from electrochemical  $N_2$  production.

#### Elemental Analysis of the Electrochemical Cell Contents Via ICP-OES

Elemental analysis of the liquid-phase of the  $NH_3(I)$  electrochemical cell was conducted through Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES). After all electrochemical experiments were complete, the  $NH_3(I)$  solution was carefully poured into a vial and left in the fume hood to slowly evaporate to dryness. The remainder of the cell was rinsed with three 5 mL aliquots of Millipore water, which were poured into a separate vial for collection. (Three 5 mL aliguots of Millipore water was sufficient for collection of trace dissolved nickel or copper which are reported to dissolve at 100% Faradaic efficiency with positive applied bias.7-12) These two vials were guantitatively diluted by a factor of 250 in 2% nitric acid (HNO<sub>3</sub>) in order to be certain of the total volume and sufficiently dilute the supporting electrolyte to avoid salt depositions in the ICP instrument. A standard "Fe stock" solution was made by dissolution of a precisely known amount of iron(III) nitrate (Spectrum, 99%) into 2% HNO<sub>3</sub> using a 100.0 mL volumetric flask. A standard dilution series for iron (Fe) guantification was then generated using aliguots of the "Fe stock" measured with a 100-1000 µL Eppendorf pipettor and additional volumetric flasks.

In order to conduct the ICP-OES measurements, we were required to switch to  $NH_4NO_3$  as the supporting electrolyte instead of the  $NH_4PF_6$  or  $KPF_6$  used previously. This decision was made to prevent any source of fluorine– $PF_6^-$  in this case–from being injected into the instrument. Nitrate ( $NO_3^-$ ) was chosen as the replacement anion to avoid halide ions that can be oxidized at the very positive potentials we employed.  $NH_4NO_3$  is also very soluble in  $NH_3(I)$ , the nitrogen is already in its highest oxidation state so it cannot be oxidized further, and since all samples for ICP-OES are dissolved in 2% nitric acid ( $HNO_3$ ), using  $NO_3^-$  as the supporting anion keeps the analyte as simple as possible. In order to keep the findings consistent, all electrochemical experiments involving the investigation of Fe electrode corrosion in Chapter 4–specifically those preceding ICP-OES, XPS, and GC–were conducted with 0.1 M  $NH_4NO_3$  as the supporting electrolyte.

#### Voltammetry in *N*,*N*-Dimethylformamide

Electrochemical experiments conducted in *N*,*N*-Dimethylformamide (DMF) used the same electrodes as in  $NH_3(I)$  with respect to both the two-electrode and threeelectrode configurations. The electrolytes in DMF consisted of varying concentrations of either  $NH_4PF_6$  or  $TBAPF_6$ , depending on the desired concentration of  $NH_4^+$ . When dissolved  $NH_3$  was required, anhydrous  $NH_3$  gas (Airgas) was bubbled for 2-3 minutes until the solution was saturated.

#### Sampled Time Voltammetry

In voltammetry experiments, where the potential is changed as a function of time, both potential and time are convoluted together in the resulting CV or *J-V* curve. Thus, deviations in the standard Butler-Volmer-esque shape of a voltammogram indicate chemical changes occurring over time. However, when the working electrode surface is chemically changing as a function of both time and potential-such as in the case of anodic poisoning (Chapter 3), dissolution (Chapter 4), or the formation of a catalytic film (Chapter 4)-it is necessary to be able to experimentally deconvolute potential and time. In order to accomplish this, Sampled Time Voltammetry (STV) was sometimes used in place of simple CV or linear sweep voltammetry. Instead of simply sweeping the potential at a linear scan rate, a sequence of chronoamperograms at regular potential intervals was used. The current from each of the chronoamperograms was extracted at a constant point and plotted as a function of potential, thus generating a J-V curve where all points were collected after the same length of time. The key advantage of this method is that the working electrode can be freshly regenerated between each chronoamperogram so that at each point the only variables across the entire experiment are the potential applied and the resulting current.

Unless otherwise noted, the current from the point 1 ms into each chronoamperogram was plotted as a function of potential. A time of 1 ms is large enough to ensure a negligible contribution from charging current, but also a relatively small degree of electrode fouling (assuming solution resistance of 1 k $\Omega$  and an

electrode capacitance of 20  $\mu$ F cm<sup>-2</sup>, the contribution from charging current should be below 1 mA after only 10<sup>-5</sup> s).

#### Fabrication of Working Electrodes From Transition Metal Wires

Unless otherwise mentioned, all working electrodes used were manufactured by attaching a small piece of wire of the element of interest, (iron, copper, etc.), to a relatively longer piece of Cu wire insulated with polyvinyl chloride. A polypropylene pipette tip was then melted with a heat gun around the end of interest, enveloping all conductive wire tightly in plastic. The very end was then removed carefully with an electric belt sander resulting in a small disk electrode of the desired element. Disk electrodes were then polished using 1000 grit sandpaper followed by a typical commercial electrode polishing pad utilizing 50 nm alumina particle paste (BASi). The Pt working electrode was made similarly to the Fe electrodes, except that the Pt wire (0.5 mm, 99.99%, Aldrich) was fixed permanently in borosilicate glass. The disk and surrounding glass were finely ground, and before each electrode polishing pad. The disk-end of the Pt electrode was curved to a 90-degree angle–as depicted on the left of Figure 2.1–to encourage electrochemically formed bubbles to become detached.

The Fe plate electrodes used in Chapter 5 were manufactured by mechanically bending a long piece of the aforementioned Fe wire to attach it to a 0.5 x 0.5 cm piece of Fe foil (0.25 mm thick, 99.99%, Alfa Aesar). No epoxy, adhesive, nor anything not

composed of Fe was used so that only Fe was exposed to the solution. The Fe plate could easily be detached from the wire for instrumental characterization.

The Pt mesh counter electrode used in nearly all electrochemical experiments was manufactured similarly to the Fe plate electrode, except that the Pt wire mechanically attached to the Pt mesh was only approximately 1 cm long. The 1 cm Pt wire was mechanically attached to a piece of insulated Cu wire, and the junction between the wires was covered with melted polypropylene plastic to insulate all Cu from being exposed to the solution.

#### **Determination of the Electrochemically Active Electrode Surface Area**

For most macroscopic electrodes, like those used in this study, there can be a significant difference between the geometric active surface area and the electrochemically active surface area. This is due to micro- or nanostructures of the electrode surface that provide additional active sites for electrochemical reactions without an increase in the macroscopic size of the electrode. In this study, current densities as a function of both geometric and electrochemically active surfaces are employed, as appropriate, and identified in the text.

When required, the electrochemically active surface areas of electrodes were determined by measuring the double-layer charging current as a function of CV scan rate. When the Faradaic current at the working electrode is essentially zero, the electrode can be modeled as a parallel-plate capacitor where the magnitude of the current at a constant scan rate is proportional to the capacitance per unit active area of

the electrode. For the well-studied system of a platinum electrode in an aqueous electrolyte, the double-layer capacitance by this approximation is about 20  $\mu$ F cm<sup>-2</sup>. We took advantage of this information to approximate the electrochemically active surface areas of FeN<sub>x</sub> electrodes and CoP<sub>x</sub> electrodes in Chapters 4 and 5 respectively.

When determining the growth of the electrochemical surface area of the Fe/FeN<sub>x</sub> electrode in  $NH_3(I)$  in Chapter 4, we made the very coarse assumption that the double-layer capacitance would be approximately the same as a platinum electrode in water. This is undoubtedly untrue, but since we were only interested in comparing the change of one Fe/FeN<sub>x</sub> electrode, rather than compare one electrode to another, both the trend of electrochemically active surface area increasing with successive anodic scans, and the magnitude of that increase, should still be correct.

We employed a more quantitative approach to compare the electrochemically active surface areas of Pt and CoP<sub>x</sub> electrodes in DMF solutions in Chapter 5. We could not isolate a region without significant Faradaic current for a CoP<sub>x</sub> in aqueous solution due to either H<sub>2</sub> evolution processes, or film dissolution, depending on the potential region. First, the electrochemically active surface area of our Pt electrode was determined in an aqueous solution using the 20  $\mu$ F cm<sup>-2</sup> assumption. Then, that electrode was transferred to the DMF solution, and the dependence of the charging current on the scan rate was re-evaluated. Since the surface area of that Pt electrode was known from the aqueous measurement, the double-layer capacitance of the Pt electrode in DMF could be calculated. Then, this value was used to model the

capacitance of a  $CoP_x$  electrode in DMF so that the electrochemically active surface area of all  $CoP_x$  electrodes could be approximated in the DMF solution.

#### Instrumentation

All electrochemical experiments were conducted using either a Gamry Reference 600 potentiostat, or a Metrohm µAutolabIII. Elemental analysis of the electrochemical solution was measured using a Varian 710-ES Axial ICP-OES. X-ray Photoelectron Spectroscopy (XPS) was measured with a Kratos Axis Ultra XPS. Raman spectroscopy was conducted using a Renishaw inVia Raman Microscope employing a RL532C100 laser source. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) measurements were recorded using a Carl Zeiss Variable Pressure SEM EVO LS25 with an Ametek EDAX Apollo X Energy Dispersive X-ray Detector. REFERENCES

#### REFERENCES

- (1) East, G. A.; del Valle, M. A. J. Chem. Educ. 2000, 77, 97.
- (2) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; 2nd ed.; Wiley and Sons Inc., 2000.
- (3) Hanada, N.; Hino, S.; Ichikawa, T.; Suzuki, H.; Takai, K.; Kojima, Y. *Chem. Commun. (Camb).* **2010**, *46*, 7775–7777.
- (4) Little, D. J.; Smith, III, M. R.; Hamann, T. W. *Energy Environ. Sci.* **2015**, *8*, 2775–2781.
- (5) Sawyer, D. T.; Sobkowiak, A.; Roberts, J. L. *Electrochemistry for Chemists*; Second.; John Wiley & Sons, Inc.: New York, 1995.
- (6) Itaya, K.; Malpas, R. E.; Bard, A. J. Chem. Phys. Lett. 1979, 63, 411–415.
- (7) Bergstrom, F. W. J. Am. Chem. Soc. **1924**, 46, 2631–2636.
- (8) Jolly, W. L. J. Am. Chem. Soc. 1956, 78, 4849–4849.
- (9) Vijh, A. K. J. Electrochem. Soc. 1972, 119, 861.
- (10) Brown, O. R.; Thornton, S. A. J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases **1974**, *70*, 14.
- (11) Brown, O. R.; Thornton, S. A. J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases **1974**, *70*, 1269.
- (12) Heusler, K. E.; Kutzmutz, S. J. Electroanal. Chem. Interfacial Electrochem. **1990**, 285, 93–101.

# CHAPTER 3:

### IDENTIFYING THE PROBLEMS WITH LIQUID AMMONIA ELECTROLYSIS

### ON PLATINUM ELECTRODES

*Electrolysis of Liquid Ammonia for Hydrogen Generation*, Little, D. J.; Smith, III, M. R.; Hamann, T. W. *Energy Environ. Sci.* **2015**, *8*, 2775–2781. - Adapted by permission of The Royal Society of Chemistry

#### Introduction

As of June, 2015, the only two reports in the literature investigating the electrolysis of liquid ammonia ( $NH_3(I)$ ) were from the lchikawa group who reported 7.2 mA cm<sup>-2</sup> from the electrolysis of  $NH_3(I)$  with 2.0 V applied between two platinum electrodes at 9.63 bar and 25°C.<sup>1,2</sup> This was only achieved with a relatively high concentration (1 M) potassium amide ( $KNH_2$ ) electrolyte, which can detonate in solid form. They demonstrated using gas chromatography that hydrogen gas ( $H_2$ ) and nitrogen gas ( $N_2$ ) were the products generated at the cathode and anode respectively, and attributed these products to the reduction of  $NH_3$  and oxidation of  $NH_2^-$ . However, this mechanism was not substantiated. In addition, the two-electrode cell in those studies could not determine separate overpotentials for the anodic and cathodic reactions.

With these reports as a starting point, we began investigating the electrolysis of ammonia ( $NH_3$ )-both as  $NH_3(I)$  and as  $NH_3$  dissolved in *N*,*N*-dimethylformamide (DMF)-using platinum electrodes, with and without a third reference electrode. This allowed us to identify the anodic and cathodic reactions occurring, as well as the standard reduction potentials and overpotentials associated with these reactions, and the current controlling processes. As a result, comparable electrolysis efficiencies were realized with simpler and safer electrolytes. This allowed us to identify the specific reaction barriers that needed to be surmounted in order to improve the electrolysis efficiency of ammonia splitting.

#### Experimental

Electrochemical experiments were conducted in both  $NH_3(I)$  and DMF as described in Chapter 2. In this chapter, the  $NH_3(I)$  was prepared without distillation over sodium, and the Ag/AgNO<sub>3</sub> reference electrode was used. All electrochemical experiments were conducted using a Metrohm  $\mu$ Autolab(III) using the Nova 1.7 software package.

#### **Results and Discussion**

#### Voltammetry in Liquid Ammonia

Figure 3.1 shows the cyclic voltammetry (CV) curves corresponding to the electrolysis of  $NH_3(l)$ . The potential between the two disks was cycled between 0 and 2.0 V at 100 mV s<sup>-1</sup> several successive times. From the curves depicted in Figure 3.1(a) for  $NH_4PF_6$  and 3.1(b) for  $KPF_6$ , it is clear that the overall current decreases over the course of the experiment, particularly during the first scan, for both  $NH_4PF_6$  and  $KPF_6$  electrolytes. This is characterized both by the 2-fold decrease in the maximum current at 2.0 V from scan 1 to scan 2, and also by the very large hysteresis in scan 1. This behavior suggests that the surface of at least one of the Pt electrodes is changed over the course of the experiment making it less active for the respective electrolysis half



**Figure 3.1:** The electrolysis of  $NH_3(I)$  using platinum disk electrodes. Panes (a) and (b) show successive cyclic voltammograms with 1.0 M  $NH_4PF_6$  and 1.0 M  $KPF_6$  as electrolytes, respectively, while pane (c) shows STVs for both conditions. The STV for 1.0 M  $KNH_2$  is also depicted in pane (c).

reaction. We attribute this fouling to a poisoned state which builds up on the platinum surface during the ammonia oxidation half reaction, *vide infra*, analogous to species originally suggested by Gerischer and Mauerer, and then confirmed by others for the oxidation of NH<sub>3</sub> in aqueous solution.<sup>5–7</sup> Indeed, after intentionally poisoning a planar Pt electrode, a strong surface and near-surface nitride signal was detected by Auger electron spectroscopy (AES) as shown in Figure 3.2. The CVs of the poisoned electrode

(scans 2-5) are similar to that reported for the 1.0 M KNH<sub>2</sub> electrolyte by Hanada *et* al.,<sup>1,2</sup> however with a slightly smaller current density.



**Figure 3.2:** AES spectra of a Pt electrode cleaned electrochemically in sulfuric acid (a), and of a similar electrode cleaned electrochemically and then anodically poisoned in 1.0 M NH<sub>4</sub>PF<sub>6</sub> in liquid ammonia (b). Sputtering with Ar<sup>+</sup> allowed for depth-profiling.

The anodic poisoning of the Pt electrodes represents a major hurdle preventing the accurate determination of the rate of ammonia electrolysis on Pt. Thus, in order to determine the CV response for ammonia electrolysis in the absence of electrode fouling, sampled time voltammetry (STV) measurements were employed. The current onset potential is similar, but with an order of magnitude larger current density. The STV with 1.0 M KNH<sub>2</sub> was also measured, which showed similar performance to the other two electrolytes.

During the electrolysis on two electrodes, the potential drop between the anode and cathode must be the sum of the thermodynamic potential for the reaction,  $E_{rxn}$ , and the overpotentials for both the oxidation and reduction half reactions in order for the
reaction to be driven at a desired rate. But it is impossible to determine both the oxidation and reduction overpotentials without the addition of a third, reference electrode. In order to avoid fouling of the working electrode as seen in Figures 3.1(a) and (b), and also to prevent large-amplitude noise resulting from the formation of bubbles at the surface of the working electrode at high overpotentials, a similar STV procedure to that described above was conducted with a three-electrode cell. The anodic behavior from the STV measurements for three different concentrations of NH<sub>4</sub>PF<sub>6</sub> and KPF<sub>6</sub> electrolytes, as well as 1.0 M KNH<sub>2</sub> are plotted in Figure 3.3(a). After measuring the curve of 1.0 M KPF<sub>6</sub>, sodium amide (NaNH<sub>2</sub>) was added to the solution until saturated (approximately 6 mM), and the STV was re-measured. Figure 3.3(a) shows the resulting data.



**Figure 3.3:** (a) STVs of  $NH_3(l)$  comparing current densities at varying potential using three different concentrations of either  $NH_4PF_6$  (triangles) or  $KPF_6$  (circles) as the supporting electrolyte, as well as 1.0 M KNH<sub>2</sub> (black squares). For all STVs, the markers represent actual points of data, and there are straight lines connecting them for trend clarity. (b) CVs in  $NH_3(l)$  with 1 M  $NH_4PF_6$  electrolyte (red) and 1 M  $KPF_6$  electrolyte (green) with a Pt disk working electrode at 100 mV/s.

The magnitude of current density at a given potential increases roughly proportionally with the concentration of both KPF<sub>6</sub> and NH<sub>4</sub>PF<sub>6</sub> electrolytes. The anodic waves for both electrolytes are linear between 0.7 and 2.2 V versus NHE. There is no significant difference between the behavior of the KPF<sub>6</sub> and NH<sub>4</sub>PF<sub>6</sub> electrolytes. Further, the addition of NH<sub>2</sub><sup>-</sup> to the KPF<sub>6</sub> electrolyte had no noticeable effect on the anodic current, as the sparingly soluble salt changed the ionic strength of the solution very little. These results are consistent with the rate of oxidation being limited by the solution resistance. This is in general agreement with the previous report by Hanada et al. of liquid ammonia electrolysis where the current density increased with increasing concentration of amide electrolyte.<sup>1</sup> In that paper, however, it was suggested that amide ions were oxidized at the anode and ammonia reduced at the cathode.<sup>1</sup> In Figure 3.3(a), there is ten-fold higher current with 1.0 M NH<sub>4</sub>PF<sub>6</sub> or KPF<sub>6</sub> as the electrolyte compared to when 1.0 M KNH<sub>2</sub> is used. The auto-ionization constant for NH<sub>3</sub> is approximately  $10^{-33}$  M<sup>2</sup>, thus the concentration of NH<sub>2</sub><sup>-</sup> in "neutral" NH<sub>3</sub>(*l*) is ~3 × 10<sup>-17</sup> M. In a NH<sub>3</sub>(*l*) solution with a 1.0 M  $NH_4^+$  electrolyte, the concentration of  $NH_2^-$  is ~10<sup>-33</sup> M. Upon the addition of 6 mM NaNH<sub>2</sub> to "neutral" NH<sub>3</sub>(*I*), the concentration of NH<sub>2</sub><sup>-</sup> is ~10<sup>-3</sup> M, and the concentration of NH<sub>2</sub><sup>-</sup> with 1.0 M KNH<sub>2</sub> is 10<sup>0</sup> M. If NH<sub>2</sub><sup>-</sup> were the species being oxidized, the solution of 1.0 M KNH<sub>2</sub> should show anodic current 10<sup>33</sup> larger than the solution of 1.0 M NH<sub>4</sub>PF<sub>6</sub>, where instead it is a factor of 10 smaller. This demonstrates that the overpotential for oxidation of NH<sub>3</sub> is the same as that for oxidation of NH<sub>2</sub><sup>-</sup>, both of which would produce a NH<sub>2(ads)</sub> species adsorbed on the electrode surface. The

overall reaction of  $NH_3$  (and  $NH_2^-$ ) to form  $N_2$  is a three electron-transfer process. This indicates that the rate-limiting step for  $N_2$  generation is not the first electron transfer.



**Figure 3.4:** Cathodic CVs in  $NH_3(I)$  of 1.0 M KPF<sub>6</sub> (green) and 1.0 M NH<sub>4</sub>PF<sub>6</sub> (black). Also included are STVs measured at 1 and 100 ms in 1.0 M NH<sub>4</sub>PF<sub>6</sub> (dark red and light red triangles respectively), and at the same times in 1.0 M KPF<sub>6</sub> (dark blue and light blue circles respectively).

The presence of  $NH_4^+$  has a much more profound effect on the cathodic current density at negative applied potentials in  $NH_3(l)$ . Figure 3.3(b) shows a cathodic wave with an onset of approximately -2.5 V versus NHE for the 1.0 M KPF<sub>6</sub> electrolyte which is consistent with the current attributed to producing solvated electrons by Itaya *et al.*<sup>8</sup> The formal potential for electron solvation was reported as -2.69 V versus Ag/AgNO<sub>3</sub>, and the onset of the wave in Figure 3.3(b) was measured as -2.69 V versus the custom

Ag/AgNO<sub>3</sub> reference. Clearly, NH<sub>3</sub> is not the species being reduced at the cathode. The cathodic current for the 1 M NH<sub>4</sub>PF<sub>6</sub> exhibits a wave beginning at approximately -1.1 V versus NHE; thus a current onset at ~1.4 V lower applied potential. The cathodic wave in the presence of NH<sub>4</sub><sup>+</sup> must be due to either the reduction of protons dissociated from  $NH_4^+$ , or the reduction of the  $NH_4^+$  ion directly to  $NH_4^{0+}$ . With  $NH_3(I)$  solvent, there is a negligible concentration of protons in the solvent, thus it is difficult to distinguish between these two mechanisms. Some insight can be gleaned from the measured STV curves, however, as the electrodes may have initial hydrogen species bound to the electrode surface from the acid treatment as suggested by Figure 3.4. The STV curves in both 1.0 M KPF<sub>6</sub> and 1.0 M NH<sub>4</sub>PF<sub>6</sub> exhibit a wave with an onset of approximately 0 V versus NHE, which is consistent with H(surface) reduction. This initial current decays to the steady-state CV of the respective electrolyte once the surface hydrogen species are consumed. Thus, we suggest reduction of the  $NH_4^+$  ion directly to  $NH_4^{0+}$  is the first electron transfer step, which controls the cathodic overpotential. From these results, we propose the electrolysis of  $NH_3(l)$  to occur via the following scheme (equations 3.1–3.5):

$$NH_{3} \xrightarrow{anode} \frac{1}{2}N_{2} + 3H^{+} + 3e^{-}$$
(3.1)

$$3H^+ + 3NH_3 \longrightarrow 3NH_4^+$$
 (3.2)

$$3NH_4^+ + 3e^- \xrightarrow{cathode} 3NH_4^{0\bullet}$$
(3.3)

$$3NH_4^{0\bullet} \longrightarrow 3NH_3 + \frac{3}{2}H_2$$
(3.4)

I:  $NH_3 \longrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$  (3.5)

Overall:

### Voltammetry in N,N-Dimethylformamide

In order to attain greater control over all redox active species in solution, the electrolysis of NH<sub>3</sub> was also conducted in DMF at room temperature. In DMF, the concentration of H<sup>+</sup> can be manipulated in addition to NH<sub>4</sub><sup>+</sup>, as well as the concentration of NH<sub>3</sub> (which is 4 M at saturation).<sup>9</sup> The electrolysis of a saturated NH<sub>3</sub> solution on two identical Pt disk electrodes-directly analogous to the electrolysis of Figure 3.1-is depicted in Figure 3.5(a). The CVs have a similar shape and current magnitude to those shown in Figure 3.1(c), although the difference between the currents in the TBAPF<sub>6</sub> and NH<sub>4</sub>PF<sub>6</sub> electrolytes in DMF is more pronounced than the difference between the KPF<sub>6</sub> and  $NH_4PF_6$  electrolytes in  $NH_3(I)$ . Specifically, the CVs for the electrolysis in the  $NH_4PF_6$  electrolyte in both DMF and  $NH_3(I)$  are very similar, the KPF<sub>6</sub> current density is slightly (but consistently) lower, and the current density with the TBAPF<sub>6</sub> electrolyte is significantly lower at high potentials. These discrepancies are likely due to differences in ion mobility, especially between the small  $NH_4^+$  cation and the bulky TBA<sup>+</sup> cation.<sup>10,11</sup> A decreased mobility results in decreased solution conductivity, and thus lower current densities at high potentials.

Analogous to the experiments in  $NH_3(l)$ , the oxidation and reduction half reactions were isolated using a three-electrode cell with a conventional Ag/AgNO<sub>3</sub> reference electrode. Figure 3.5(b) shows the CV and STV curves at positive potentials versus NHE with NH<sub>3</sub> dissolved in DMF. The STV has an onset of approximately 0.5 V versus NHE, while the CV waves do not begin until about 1 V. Both of these waves are attributed to the oxidation of dissolved NH<sub>3</sub> as there is no anodic activity under the same



**Figure 3.5:** (a) STVs showing electrolysis of NH<sub>3</sub> dissolved in DMF using platinum disks as both the anode and the cathode. The red curve has 0.1 M NH<sub>4</sub>PF<sub>6</sub>, while the green curve has 0.1 M TBAPF<sub>6</sub>. (b) CV (red) and STV (blue) of the anodic current with NH<sub>3</sub> dissolved in 0.1 M NH<sub>4</sub>PF<sub>6</sub> in DMF. In black is the CV without dissolved NH<sub>3</sub>. In green is the CV with NH<sub>3</sub> dissolved in 0.1 M TBAPF<sub>6</sub>. (c) CVs (black and green with NH<sub>4</sub>PF<sub>6</sub> and TBAPF<sub>6</sub> respectively) and STVs of the cathodic current with NH<sub>3</sub> dissolved in DMF. The black and light and dark red curves contain 0.1 M NH<sub>4</sub>PF<sub>6</sub> as the supporting electrolyte, while the light and dark blue curves contain 0.1 M TBAPF<sub>6</sub>.

conditions in the absence of dissolved  $NH_3$ . This large shift from the STV onset to the CV onset is attributed to the 1 ms pre-poisoned surface similar to what was seen in  $NH_3(I)$ .

Figure 3.5(c) shows the CV and STV curves at negative potentials versus NHE with  $NH_3$  dissolved in DMF. Two STV curves are shown which were obtained from the same set of measurements, sampled at different times: 1 ms and 100 ms. The STV curves sampled at 1 ms both have a current onset of approximately 0 V versus NHE, which is consistent with the assignment of initial reduction of surface adsorbed hydrogen species. The STV curve of the  $NH_4PF_6$  electrolyte at longer times is in good agreement with the CV, which both have current onsets of approximately -0.6 V versus NHE. The STV curve of the  $TBAPF_6$  electrolyte at longer times shows essentially zero current at any potential, which is consistent with the CV curve in the same electrolyte. These results agree with the assignment of the cathodic current arising from the direct reduction of the  $NH_4^+$  ion.

Voltammetry in DMF, instead of  $NH_3(l)$ , allows for further elucidation of the reduction of  $NH_4^+$ . Figure 3.6(a) shows a quasi-reversible CV of a solution containing 20 mM  $NH_4PF_6$  and 100 mM TBAPF<sub>6</sub> in DMF, corresponding to the reduction of  $NH_4^+$  and oxidation of the reduced product. A formal potential of -0.60 ± 0.04 V versus NHE was determined for  $NH_4^+$  in DMF, which is consistent with the position of the wave for  $NH_4^+$  reduction seen in aqueous conditions by Berkh *et al.*<sup>12</sup> However, to the best of our knowledge, this is the first quasi-reversible CV of  $NH_4^+$  reduction in non-aqueous conditions suitable for reporting a formal potential. The reduction potential of  $NH_4^+$  also coincides with the cathodic current onset potentials with  $NH_4^+$  shown in Figure 3.5(c). Tafel analysis of the black CV in Figure 3.5(c) suggests a single-electron transfer process, further indicating that the cathodic wave results from the direct reduction of

 $NH_4^+$  to  $NH_4^{0^+}$  (Figure 3.7). This is contrary to the mechanism reported by Buzzeo *et al*, who suggested that the reduction wave for  $NH_4PF_6$  in DMF is the result of reducing  $H^+$  that had dissociated from the  $NH_4^{+}$ .<sup>13</sup> Their cathodic CV actually has a similar shape to that of Figure 3.6(a), but since it is reported using a silver wire pseudo-reference, it is impossible to quantitatively compare the two plots.



**Figure 3.6:** (a) Quasi-reversible redox wave for  $NH_4^+$  in DMF. (b) Cathodic waves measured in 0.1 M  $NH_4PF_6$  with increasing concentrations of  $HCIO_4$  using a Pt disk electrode in DMF.

In order to confirm that the cathodic wave is not due to a coincidentally large reduction overpotential of protons that have dissociated from the weak acid, small aliquots of perchloric acid (HClO<sub>4</sub>), which can be thought of simply as a source of H<sup>+</sup>, were added to a solution with 0.1 M NH<sub>4</sub>PF<sub>6</sub> in DMF. The CVs of these solutions are depicted in Figure 3.6(b). A cathodic wave with an onset of about -0.1 V versus NHE becomes larger as the H<sup>+</sup> concentration is increased, and thus is attributed to the reduction of H<sup>+</sup> in solution. There is also a second cathodic wave with an onset of about



**Figure 3.7:** Tafel plot of the CV shown in black in Figure 3.5(c). The value of  $\alpha$  close to 0.5 indicates a likely 1-electron reaction, quasi-reversible reaction.

-0.7 V versus NHE whose magnitude with respect to baseline does not change with increasing H<sup>+</sup> concentration. If the mechanism for the reduction of  $NH_4^+$  first involved the dissociation of H<sup>+</sup>, followed by the reduction of H<sup>+</sup>, (like that previously reported),<sup>13</sup> increasing the concentration of H<sup>+</sup> would cause the cathodic wave to shift to more positive potentials, not just introduce a second wave. This wave is therefore attributed to the direct reduction of  $NH_4^+$  as shown in the equations 3.6 through 3.8:

$$3NH_4^+ + 3e^- \longrightarrow 3NH_4^{0\bullet}$$
(3.6)

$$3NH_4^{0\bullet} \longrightarrow 3NH_3 + 3H^{\bullet}$$
(3.7)

$$3H^{\bullet} \longrightarrow \frac{3}{2}H_2$$
 (3.8)

This scheme is also consistent with that of Berkh *et al.*, where they emphasized that the  $NH_4^{0^{\circ}}$  species could be stabilized by remaining adsorbed on the Pt electrode surface.<sup>12</sup> The net reaction shown in (3.6) through (3.8) corresponds to reactions (3.3) and (3.4) proposed for electrolysis of  $NH_3(I)$ . It is reasonable to extend this proposed mechanism of direct  $NH_4^+$  reduction as the overpotential determining step for the cathodic reaction in  $NH_3(I)$  as well, where even with the same 0.1 M  $NH_4PF_6$  the concentration of  $H^+$  is lower than in DMF by one order of magnitude. This reaction also largely accounts for the differences in overpotential between liquid ammonia electrolysis and aqueous ammonia electrolysis. In aqueous systems, the reduction of water to  $H_2$  determines the overpotential, and good catalysts for this reaction are well-developed. In  $NH_3(I)$  it is the reduction of  $NH_4^+$  to  $H_2$  which determines the cathodic overpotential, and to the best of our knowledge, no effort has been invested to catalyze this reaction.

### Conclusions

In order to make the electrolysis of NH<sub>3</sub> a feasible source of fuel for a hydrogen economy, several kinetic hurdles must be overcome. The first of these is the phenomenon of poisoning. An anode material must be found where the overpotential for ammonia oxidation is the same 1 s into the electrolysis as it is after 1  $\mu$ s. This may involve either a pretreatment of an existing electrode material to keep the surface identity constant, or development of a new anode material that is a superior catalyst for the oxidation of NH<sub>3</sub>. The overpotential gains from such a material are shown with the arrow labeled "Poison" in Figure 3.8.



**Figure 3.8:** Diagram showing where improvements can be made by either avoiding electrode poisoning (indicated by arrow with "poison" icon), or via catalysis (indicated by arrows with "catalysis" ions). The formal potentials for  $NH_4^+$  reduction,  $H^+$  reduction, and  $NH_3$  oxidation are indicated on the top black scale. Both the STV (red) and CV (green) were recorded using a Pt disk electrode in 0.1 M  $NH_4PF_6$  in DMF.

As seen in Figure 3.1(c), the electrolysis of NH<sub>3</sub> is already proceeding to a small degree after only 100 mV of applied potential (the first point collected in the STV). This is consistent with the formal potential of ammonia oxidation, which can be deduced from the difference of the formal potential for the reduction of protons (0.0 V versus NHE) and the free energy change of ammonia electrolysis. For this reason, the formal potential for NH<sub>3</sub> oxidation is 0.10 V versus NHE as shown on Figure 3.8.

Once electrode poisoning is no longer a concern, a catalyst is still needed to lower the overpotential for both  $NH_3$  oxidation, as well as  $NH_4^+$  reduction as much as

possible. The overpotential gains from this catalysis are shown with arrows labeled "Catalysis" in Figure 3.8. In addition, a catalyst needs to be developed that will allow for the reduction of  $H^+$  instead of the initial reduction  $NH_4^+$  to  $NH_4^{0^*}$ . That would allow for a sufficient rate of proton reduction closer to the thermodynamic limit of 0 V versus NHE. Catalytic materials for both of these reactions–based on Earth-abundant metals–are the subjects of subsequent chapters.

REFERENCES

#### REFERENCES

- (1) Hanada, N.; Hino, S.; Ichikawa, T.; Suzuki, H.; Takai, K.; Kojima, Y. *Chem. Commun. (Camb).* **2010**, *46*, 7775–7777.
- (2) Dong, B.-X.; Ichikawa, T.; Hanada, N.; Hino, S.; Kojima, Y. *J. Alloys Compd.* **2011**, *509*, S891–S894.
- (3) East, G. A.; del Valle, M. A. J. Chem. Educ. 2000, 77, 97.
- (4) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; 2nd ed.; Wiley and Sons Inc., 2000.
- (5) Gerischer, H.; Mauerer, A. *Electroanal. Chem. Interfacial Electrochem.* **1970**, *25*, 421–433.
- (6) De Vooys, a. C. a; Koper, M. T. M.; Van Santen, R. a.; Van Veen, J. a R. *J. Electroanal. Chem.* **2001**, *506*, 127–137.
- (7) Le Vot, S.; Reyter, D.; Roué, L.; Bélanger, D. *J. Electrochem. Soc.* 2012, *159*, F91.
- (8) Itaya, K.; Malpas, R. E.; Bard, A. J. *Chem. Phys. Lett.* **1979**, *63*, 411–415.
- (9) Gerrard, W. Solubility of Gases and Liquids: A Graphic Approach; 1976.
- (10) Izutsu, K. *Electrochemistry in Nonaqueous Solutions*; First.; Wiley-VCH: Weinheim, 2002.
- (11) Krumgalz, B. S. J. Chem. Soc. Faraday Trans. 1 1983, 79, 571.
- (12) Berkh, O.; Shacham-Diamand, Y.; Gileadi, E. *J. Electrochem. Soc.* **2008**, *155*, F223.
- (13) Buzzeo, M. C.; Giovanelli, D.; Lawrence, N. S.; Hardacre, C.; Seddon, K. R.; Compton, R. G. *Electroanalysis* **2004**, *16*, 888–896.

## CHAPTER 4:

# INVESTIGATION OF IRON NITRIDE AS AN EARTH-ABUNDANT ELECTROCATALYST FOR THE OXIDATION OF LIQUID AMMONIA

Adapted with permission from:

As Precious as Platinum: Iron Nitride for Electrocatalytic Oxidation of Liquid Ammonia,

Little, D. J.; Edwards, D. O.; Smith, M. R.; Hamann, T. W. ACS Appl. Mater. Interfaces

2017, 9, 16228–16235. Copyright 2017 American Chemical Society.

### Introduction

We showed previously that the electrolysis of liquid ammonia  $(NH_3(I))$  occurs on platinum (Pt) electrodes via the half reactions depicted in equations (4.1) through (4.3).<sup>1</sup> E<sup>0</sup> for (4.1) and (4.2) were reported to be 0.1 V and -0.6 V versus NHE respectively, resulting in an  $E_{cell}^{0}$  for the overall NH<sub>3</sub>(*I*) splitting process in (4.3) of 0.7 V. There is a large overpotential of over 1 V needed to drive the anodic half reaction (4.1) at the rates that would be required for on-site  $NH_3(I)$  electrolysis. This barrier arises from both anodic poisoning and a lack of efficient catalysts. Thus, the problem that we aim to address is the development of a highly-catalytic material that resists anodic poisoning. Further, if the electrolysis of NH<sub>3</sub> is going to be economically competitive in the energy market, the process must be as inexpensive as possible. Pt is the only anode material that has really been studied in depth for the electrolysis of  $NH_3(I)$ , however.<sup>1,2</sup> The most efficient NH<sub>3</sub> electrolysis device reported operates in aqueous conditions–which results in a loss of energy density compared to  $NH_3(I)$  and is corrosive to storage and distribution media-and uses precious metals such as platinum, ruthenium, and iridium for the anode.<sup>3,4</sup> Remarkably, the electrolysis of  $NH_3(I)$  using Earth-abundant materials, such as first-row transition metals, remains essentially unstudied.

$$4NH_{3} \xrightarrow{anode} \frac{1}{2}N_{2} + 3NH_{4}^{+} + 3e^{-}$$
(4.1)

$$3NH_4^+ + 3e^- \xrightarrow{cathode} \frac{3}{2}H_2^+ + 3NH_3^-$$
(4.2)

$$NH_{3} \xrightarrow{\text{overall}} \frac{1}{2}N_{2} + \frac{3}{2}H_{2}$$
(4.3)

Nickel (Ni)–the first-row transition metal in Group 10 above Pt–is a natural first choice for investigating Earth-abundant materials. A Ni/Ni(OH)<sub>2</sub> electrode was shown to be active for NH<sub>3</sub> oxidation in aqueous conditions.<sup>5</sup> Unfortunately, Ni corrodes easily with positive applied bias in NH<sub>3</sub>(*I*) forming the stable hexamine complex, [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+,6,7</sup> The neighbors of Ni in the first-row of the periodic table, cobalt (Co) and copper (Cu), also rapidly corrode in NH<sub>3</sub>(*I*) and form stable ammine complexes.<sup>8–11</sup> Interestingly, unlike the ammine complexes of Ni, Co, and Cu, iron hexamine is not very stable, converting to iron oxide upon exposure to air.<sup>12,13</sup> The high reactivity of iron hexamine makes iron (Fe) a potentially advantageous element for NH<sub>3</sub> catalysis, since the formation of stable amines could cripple catalytic rates. Also, there are known catalysts for the Haber-Bosch process–the formation of NH<sub>3</sub> from nitrogen and hydrogen–employing Fe.<sup>14</sup> However, to the best of our knowledge, there are no reports in the literature where elemental Fe is employed as an anode for the electrolysis of NH<sub>3</sub>.

By comparison, the corrosion behavior of various transition metals in NH<sub>3</sub>(*I*) have been better studied.<sup>6,15–18</sup> This work was largely motivated by the commercial interest in storing NH<sub>3</sub>(*I*) in stainless steel containers. Thus, corrosion studies have focused primarily on stainless steel components such as nickel, zinc, and iron. The Fe corrosion study by Ahrens *et al.* demonstrated two separate potential regions for corrosion (evolving Fe<sup>2+</sup> and Fe<sup>3+</sup> respectively) with a large, 0.5 V wide passive region between them.<sup>16</sup> They also discussed the possibility of nitridation of the Fe anode surface, which could possibly serve as a catalyst for NH<sub>3</sub> oxidation.

In 2016, Goshome *et al.* reported the electrolysis of NH<sub>3</sub>(*l*) with a 5 M ammonium chloride electrolyte using a stainless steel anode.<sup>19</sup> They observed similar electrolysis current density with stainless steel and Pt anodes, but reported that over time the steel anode corroded with positive applied bias to form [Fe(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> in solution. However, there are numerous varieties of stainless steel containing different additives in varied amounts. Therefore, mechanistic conclusions on the chemistry of electrolysis on stainless steel cannot be made without studying electrolysis using pure Fe anodes. Additionally, since the desired electrolysis was reported in addition to corrosion, it is important to identify all of the anodic chemical pathways in order to design the ideal electrode.

In this chapter, we compare the electrochemical behavior of elemental Pt and Fe anodes in stock  $NH_3(I)$  versus distilled  $NH_3(I)$ . These results illustrate how the presence of even a small amount of water in  $NH_3(I)$  can critically change the poisoning behavior of electrodes. The extent of different anodic processes on Fe–both corrosion and  $NH_3(I)$  oxidation–are determined for multiple potential regimes. Finally, an *in situ* modified Fe electrode with an anodic performance similar to Pt in  $NH_3(I)$  is characterized.

### Experimental

Electrochemical experiments were conducted in NH<sub>3</sub>(*I*) as described in Chapter 2. Before each experiment, the anhydrous ammonia was distilled over sodium before condensing in a pre-assembled electrochemical cell under inert atmosphere. The custom Ag/AgCl reference electrode with an electrolyte saturated with both NH<sub>4</sub>Cl and

dissolved  $NH_3(g)$  was used in all electrochemical experiments in this chapter. The Fe working electrodes used were manufactured using Fe wire (1.0 mm, 99.9%, Aldrich). All electrochemical experiments were conducted using a Gamry Reference 600 potentiostat.

### **Results and Discussion**

Figure 4.1(a) shows the anodic current density versus applied potential curves derived from cyclic voltammetry (CV) measurements which correspond to the oxidation of NH<sub>3</sub>(*I*) on a Pt disk electrode. Only one scan is shown in Figure 4.1(a) for Pt in pure distilled NH<sub>3</sub>(*I*) because successive scans all overlapped perfectly. When an aliquot of degassed Millipore water was added to the distilled NH<sub>3</sub>(*I*) to make the solution 10 % water, however, the previously reported poisoning behavior was reproduced, indicated by decreasing anodic current in successive scans.<sup>1</sup> This behavior was not evident in the pristine distilled NH<sub>3</sub>(*I*) electrolyte. We showed in Chapter 3 via Auger electron spectroscopy that the formation of a nitrogen-containing species accompanied the anodic poisoning of Pt in NH<sub>3</sub>(l). However, all experiments in that study were performed using stock  $NH_3(I)$ , rather than distilled, and the headspace of the flask was exposed to the air. It is now clear that water is crucial to the poisoning process. An additional anodic process involving both NH<sub>3</sub> and H<sub>2</sub>O at the Pt surface would be consistent with "nitrogen-containing". Indeed, adsorbed  $OH^-$  ions from  $H_2O$  have been proposed to have a role in the mechanism of anodic poisoning of Pt surfaces in aqueous NH<sub>3</sub> oxidation by Gerischer and Mauerer.<sup>20</sup> It appears this mechanism extends to the related process in  $NH_3(I)$  as well.



**Figure 4.1:** (a) CV of a Pt disk electrode in distilled NH<sub>3</sub>(*I*) (black), and five successive CVs of a Pt disk electrode in distilled NH<sub>3</sub>(*I*) after the addition of degassed Millipore water to make the solution 10 % water (colors). (b) CVs of an Fe disk electrode in the same conditions as (a), except that only 1 % water was added. The vertical black arrows indicate the order of successive anodic scans. Dashed boxes indicate the overpotential required to reach 10 mA cm<sup>-2</sup> current. Small, black, diagonal arrows indicate the scan direction. All curves were measured at 100 mV s<sup>-1</sup> with 0.1M KPF<sub>6</sub> as the supporting electrolyte.

From this result, we hypothesize that water is a required ingredient for electrode poisoning, and use of distilled  $NH_3(I)$  is essential for studying  $NH_3$  oxidation at transitional metal anodes. As can be seen in Figure 4.1(b), a polished Fe disk anode behaves profoundly different in distilled  $NH_3(I)$  than in the presence of trace amounts of water, even with an order of magnitude less water than was needed to illustrate the effect with Pt. In rigorously dry solutions, the current onset appears to be approximately the same as the Pt anode. In the presence of water, however, the Fe anodes are

poisoned until the measured current is extremely small. All further experiments were conducted in distilled (dry)  $NH_3(I)$ .

Interestingly, the CV response of Fe electrodes shown in Figure 4.1(b) does not correspond to the initial CV of a pristine electrode. Figure 4.2 shows the initial and subsequent CVs measured in distilled NH<sub>3</sub>(*I*) leading-up to that pictured in Figure 4.1(b). It is clear that in the absence of water, the anodic current is initially higher than in the presence of trace water, but then increases with successive scans and eventually reaches a constant, reproducible response. Note that even for this CV, there is a large hysteresis present at the foot of the wave. This indicates a kinetically slow process occurring at the electrode where the current takes several seconds to increase even when sufficient overpotential is applied.

The slow kinetics of this process are evident in the chronoamperograms in Figure 4.3, where several different specific potentials were held for 180 seconds each on a fresh Fe disk. Even at the highest overpotentials, the current takes several seconds to reach steady-state, but at the lowest overpotentials steady-state is barely reached by the full 180 seconds. Simple electron-transfer processes do not generally involve kinetics on a seconds time-scale, implying that the chemistry at the Fe surface is more complicated.

The most obvious process that can compete with  $NH_3(I)$  oxidation is the corrosion of the Fe electrode. A detailed study of the corrosion of Fe in  $NH_3(I)$  was published by



**Figure 4.2:** Successive CVs of distilled  $NH_3(I)$  on an Fe disk electrode with the order of the scans indicated by the vertical black arrow. All scans were measured at 100 mV s<sup>-1</sup> with 0.1 M KPF<sub>6</sub> as supporting electrolyte.

Ahrens *et al.*<sup>16</sup> Utilizing a distillation procedure similar to ours and Fe wire anodes, they identified two different corrosion processes for Fe in NH<sub>3</sub>(*l*): One process occurs at relatively low potentials (reported around 0 V versus TI/TICI, or approximately -0.34 V versus NHE)<sup>21</sup> where the anode dissolves into Fe<sup>2+</sup> ions in solution. A second process is seen at relatively high potentials (reported around 1 V versus TI/TICI, which is approximately 0.66 V versus NHE)<sup>21</sup> where the anode dissolves the anode dissolves as yellow/brown Fe<sup>3+</sup> ions in solution. In the potential range between these two processes–roughly 0.5 to 0.9 V versus TI/TICI–there is a passive region where corrosion is reported to not occur.

While it was mentioned that nitrogen (N<sub>2</sub>) evolution occurs simultaneously with



**Figure 4.3:** Chronoamperograms conducted on an Fe disk at seven different potentials near the onset of the anodic wave shown in Figure 4.2. Potentials here are reported versus NHE, and verified using electron solvation between experiments. All scans used a 0.1 M KPF<sub>6</sub> electrolyte. Periodic sudden jumps in the current seen at the highest four potentials are due to the effervescence of evolved gas bubbles, thus suddenly changing the exposed surface area.

the corrosion process that leads to  $Fe^{3+}$ , the authors did not comment on the relative efficiencies of the  $Fe^{3+}$  and  $N_2$  forming processes. We therefore determined the efficiency for  $Fe^{3+}$  dissolution by applying a given potential on an Fe electrode, measuring the molar quantity of Fe ions in solution, and comparing that to the number of electrons passed during the experiment. Figure 4.4 shows a plot of the current efficiency of anodic dissolution as a function of the net charge passed at the anode. A potential of 1.2, 1.4, or 1.6 V versus NHE was held at an Fe disk electrode in a solution of 0.1 M NH<sub>4</sub>NO<sub>3</sub> in distilled NH<sub>3</sub>(*I*) for varying times, where each individual experiment

is represented by one point in Figure 4.4. Current variation with each experiment was compensated by simply potting the time-integrated current versus charged passed in Coulombs (C). The background Fe–i.e. any Fe dissolved in solution from passive processes due to Fe in the glass, supporting electrolyte, or from the electrode during preparation–was constant with time. This constant background was therefore subtracted from every point when calculating the dissolution efficiency.



**Figure 4.4:** Current efficiencies for the dissolution of an Fe disk electrode in distilled  $NH_3(I)$  as a function of the net charge passed at the working electrode during the experiment. Potentials of 1.2, 1.4, or 1.6 V versus NHE were applied for varying amounts of time and the current was integrated to obtain the total charge passed. For all points, 0.1M  $NH_4NO_3$  was used as the supporting electrolyte to avoid the presence of fluorine from the  $PF_6^-$  anion.

At the lowest potential of 1.2 V-the potential corresponding to the wave onset from Figure 4.2-the initial current efficiency for Fe dissolution is approximately 100 %. The calculated current efficiency was actually larger than 100 % for the experiment with the smallest amount of charge passed. This could be due to the relatively large error in collecting and measuring such a small quantity of dissolved Fe (2.5 x  $10^{-7}$  moles), an underestimate in the amount of expected Fe as a result of Fe<sup>2+</sup> instead of Fe<sup>3+</sup> dissolution, and/or the dissolution of stray Fe<sup>0</sup> or surface FeO<sub>x</sub> particles as a result of the rapid, aggressive changes in electrode surface morphology. The current efficiency for Fe dissolution seems to level-off at about 20 percent on approximately the same time-scale as the steady-state current formation shown in Figure 4.3. At the higher potential of 1.4 V, there is no initial spike in dissolution efficiency. Instead it quickly levels off to values less than 5 percent. Essentially the same behavior was seen at 1.6 V. These results are in agreement with the suggestion by Ahrens et al. that there are other chemical processes competing with Fe<sup>3+</sup> dissolution.<sup>16</sup> At lower overpotentials, e.g. 1.2 V versus NHE, nearly all of the anodic current initially goes toward  $Fe^{3+}$ dissolution. However, as time passes, other chemical processes compete with dissolution and lower its efficiency. As the potential increases further-past 1.2 V versus NHE-the rate of the other chemical processes dominates the rate of dissolution, resulting in only a very small fraction of current going toward Fe<sup>3+</sup> dissolution.

If at steady-state only this small fraction of the anodic current is going toward dissolution of  $Fe^{3+}$ , the remaining current must be involved in electrode surface modification and/or oxidation of the NH<sub>3</sub>(*I*) solvent to N<sub>2</sub>. Bubbles rapidly evolved from a

large Fe anode at 1.4 V versus NHE, suggesting N<sub>2</sub> evolution. GC analysis of the headspace in the electrochemical cell during a similar reaction indicates an N<sub>2</sub>:H<sub>2</sub> ratio of 1:7 at the beginning of the experiment, which approached 1:4 at the end (Figure 4.5). This ratio suggests that while H<sub>2</sub> evolution is always the primary reaction occurring at the Pt cathode, another process competes with N<sub>2</sub> evolution at the anode-otherwise the evolution ratio would be closer to the theoretical value of 1:3 for pure  $NH_3(I)$  electrolysis. These results agree with the findings of the ICP experiments in Figure 4.4, and since a potential slightly lower than 1.4 V versus NHE was used, the imperfect ratio of evolved gasses is expected. Unfortunately, it is difficult by this method to precisely relate the measured  $N_2$  to an evolution efficiency at the anode as the solubility of  $N_2$  in the  $NH_3(I)$ solvent depends upon the exact temperature of the reaction vessel, and because the exact pressure in the headspace of the cell was not measured and will fluctuate with the temperature of the solvent as well. However, if we assume that all of the evolved N<sub>2</sub> is present in the headspace of the flask, and compare the moles of N2 measured to the coulombs of charge passed at the electrode, we can calculate that there is about a 20% anodic faradaic efficiency initially, which increases to over 71% by the end of the experiment.

Since a large concentration of  $\text{Fe}^{3+}$  (presumably in the form of  $[\text{Fe}(\text{NH}_3)_6]^{3+}$ ) is dissolved in solution after steady-state has been reached—as was observed by the appearance of a yellow color—it is conceivable that the dissolved Fe acts as a catalyst for oxidation to N<sub>2</sub>. This would explain the increase in current as the Fe dissolves, as



**Figure 4.5:**  $N_2$  and  $H_2$  gas measured by GC from the headspace of the electrochemical cell. Measurements were taken every 30 minutes with a potential of 1.35 V versus NHE applied during the intervals. Molar amounts approximately correspond to the gas present in the headspace of the cell. The supporting electrolyte was 0.1 M  $NH_4NO_3$ . (Inset) The  $H_2:N_2$  evolution ratio over the course of the experiment.

well as the decreased overall efficiency for dissolution as the catalyzed N<sub>2</sub> evolution process becomes dominant. In order to test this possibility, NH<sub>3</sub>(*I*) oxidation was measured with a Pt disk electrode while an increasing concentration of Fe<sup>3+</sup> introduced. There was no change in the CVs in response to the continually increasing Fe<sup>3+</sup> concentration, displayed in Figure 4.6. Thus, dissolved Fe<sup>3+</sup> species such as  $[Fe(NH_3)_6]^{3+}$  do not appear to act as a catalyst.



**Figure 4.6:** Anodic current of the Pt disk electrode in distilled  $NH_3(I)$  before and after dissolution of Fe electrode. Five essentially overlapping scans are depicted.

An increase in current density calculated during the initial CVs may simply arise from corrosion increasing the active surface area. The anodic corrosion of Fe in distilled  $NH_3(I)$  does result in pitting, as clearly shown by SEM images in Figure 4.7, rather than uniform surface corrosion. As a result, the active surface area of the anode increases. Since only the geometric surface area is accounted for when calculating current density, the unaccounted increase in actual surface area causes the apparent current density to be inflated. We note, however, that for practical applications a higher surface area electrode such as the one that develops is desired. From CV capacitance measurements taken between anodic sweeps similar to those shown in Figure 4.2, the active surface area of the Fe electrode was found to increase with successive scans



Figure 4.7: SEM images of Fe foil after use as an anode in 0.1 M NH<sub>4</sub>NO<sub>3</sub> in dry NH<sub>3</sub>(*I*).



**Figure 4.8:** The surface area of an Fe disk electrode as a function of the number of wide cathodic scans measured. The surface area was measured from CV capacitance between each of the wide scans.

(Figure 4.8). However, the increase in surface area approached a limit with an area approximately 25% larger than the initial area. This is consistent with the concomitant decrease in dissolution efficiency as well as the  $H_2:N_2$  evolution ratio approaching 3:1.

Another possibility is that modification of the electrode surface consumes some of the current. Ahrens *et al.* proposed the formation of Fe<sub>4</sub>N, which they suggested would inhibit further corrosion, however did not provide direct evidence.<sup>16</sup> Indeed, after extended periods of positive applied potential a black film forms on the Fe electrode surface, which could indicate a change in its composition (Figure 4.9). Since the resulting film was too amorphous for characterization with x-ray diffraction (XRD), and too thin for detection with energy dispersive x-ray spectroscopy (EDS), x-ray photoelectron spectroscopy (XPS) measurements of the modified film were used to determine the composition of the modified electrode. Three peaks are resolved in the Nitrogen 1s region at 406.9 eV, 399.4 eV, and 396.4 eV, shown in Figure 4.10a. The peak at 406.9 (violet) can be assigned to the small amount of residual NO<sub>3</sub><sup>-</sup> from the



**Figure 4.9:** Photos of custom Fe disk electrodes taken before (a) and after (b) electrolysis showing the formation of a black film covering the electrode surface.



**Figure 4.10:** XPS of the Nitrogen 1s region (a), the Fe 2p region (b), and the Oxygen 1s region (c) of an *in situ* modified Fe electrode surface.

electrolyte.<sup>22–24</sup> Since most of the electrolyte was rinsed away with fresh, distilled  $NH_3(I)$ this peak is barely distinguishable from the background. The peak at 399.4 eV (blue) is atoms.23,25,26 surface Fe assigned to an NH<sub>x</sub> species bonded to Unfortunately, it is difficult to determine from these XPS measurements whether this feature is due to bound  $NH_3$  or  $N_2H_4$ , or covalently bound  $-NH_2$ . The peak at 396.4 eV (green) is assigned to FeN<sub>x</sub>-possibly Fe<sub>4</sub>N-due to its close proximity to previous reports of FeN<sub>x</sub>.<sup>27-30</sup> We note that while the peak at 396.4 eV has nearly a full eV lower binding energy than most reports for FeN<sub>x</sub>, it is still in the same region as other metal nitrides.<sup>31</sup>

In the Fe 2p region, there are two peaks comprising the  $2p_{3/2}$  spin state—at 710.6 and 712.2 eV—and two corresponding peaks comprising the  $2p_{1/2}$  spin state—at 724.0 and 725.9 eV. The satellite peaks at 718.9 and 731.6 eV (violet and pink respectively) each were only fit to one peak for simplicity due to the low signal. Since the corresponding  $2p_{3/2}$  and  $2p_{1/2}$  peaks were fit with the positions and heights constrained to fit the appropriate ratio, the use of only one peak to fit each of the satellites should not have affected our interpretation. The lowest-energy peak of 707.7 eV (orange) is assigned to the small amount of exposed atomic Fe<sup>0</sup>. The lower-energy peak pair of 710.6 and 724.0 (dark and light blue) is assigned to Fe<sub>2</sub>O<sub>3</sub> which likely formed upon exposure of the electrode to air. The corresponding Fe<sub>2</sub>O<sub>3</sub> peak in the Oxygen 1s region



**Figure 4.11:** Raman spectrum of *in situ* modified iron anode after exposure to the air on the lab bench overnight.

is found in Figure 4.10(c) at 530.0 eV (blue). This assignment is confirmed by Raman spectroscopy measurements, shown in Figure 4.11.<sup>32</sup> The second peak comprising the Oxygen 1s feature at 530.9 eV (green) is due to adventitious CO which is present in nearly every XPS spectrum. Since there are only two Oxygen states detected, the second pair of peaks in the Fe 2p region–at 712.2 and 725.9 eV (dark and light green)– are assigned to FeN<sub>x</sub>. The Fe-N bond is less polar than the Fe-O bond, consistent with the slightly higher binding energy of these FeN<sub>x</sub> photoelectrons compared to the Fe<sub>2</sub>O<sub>3</sub> photoelectrons assigned above. Thus, the combined XPS results of N and Fe regions



**Figure 4.12:** Steady-state sampled time voltammograms (STVs) of anodic behavior of Pt and *in situ* modified Fe in distilled  $NH_3(I)$ . All points are sampled from 180 seconds into a chronoamperogram at the respective potential and are connected with straight lines.

confirm that the Fe electrode forms  $\text{FeN}_x$  in response to applied bias in NH<sub>3</sub>(*I*). The formation of this nitride film is likely what inhibits further electrode dissolution or pitting. The FeN<sub>x</sub> electrode actually shows strikingly similar anodic performance to a Pt disk electrode at steady-state in distilled NH<sub>3</sub>(*I*) as depicted in Figure 4.12. Sampled time voltammetry (STV) was used to compensate for the slight decrease of the Pt electrode current with time and the drastic increase of the Fe electrode current in the same time.<sup>1</sup> Within the error of the STV method used, the onsets of NH<sub>3</sub>(*I*) oxidation are exactly the same for both Pt and FeN<sub>x</sub>.

### Conclusions

Removing the small amount of water that is present in stock  $NH_3(I)$  strongly affects the electrolysis to  $N_2$  and  $H_2$  on non-noble, Earth-abundant metal anodes like Fe. At very short times in distilled  $NH_3(I)$ , corrosion of the Fe competes with electrolysis, thus lowering current efficiency. However, the surface converts to  $FeN_x$  during the electrolysis of distilled  $NH_3(I)$ , which is far more resistant to further corrosion. While the  $FeN_x$  anode continues to dissolve with applied positive bias, the rate of  $N_2$  evolution increases much faster than the rate of dissolution. Thus, at the high overpotentials used to drive rapid  $NH_3(I)$  electrolysis, the efficiency of corrosion is rather low. Even though the anodic overpotential required for the *in situ* generated, nanostructured  $FeN_x$  surface to reach a 10 mA cm<sup>-2</sup> current density exceeds 1 V, its performance is similar to Pt electrolysis. Our  $FeN_x$  anode results open the door for research to develop Fe and other Earth-abundant electrode materials for  $NH_3$  oxidation, which is the subject of ongoing investigation in our labs.

REFERENCES
#### REFERENCES

- (1) Little, D. J.; Smith, III, M. R.; Hamann, T. W. *Energy Environ. Sci.* **2015**, *8*, 2775–2781.
- (2) Hanada, N.; Hino, S.; Ichikawa, T.; Suzuki, H.; Takai, K.; Kojima, Y. *Chem. Commun. (Camb).* **2010**, *46*, 7775–7777.
- (3) Wang, Y.; Guo, X.; Li, J.; Yang, Y.; Lei, Z.; Zhang, Z. *Open J. Appl. Sci.* **2012**, *2*, 241–247.
- (4) Vitse, F.; Cooper, M.; Botte, G. G. J. Power Sources 2005, 142, 18–26.
- (5) Kapałka, A.; Cally, A.; Neodo, S.; Comninellis, C.; Wächter, M.; Udert, K. M. *Electrochem. commun.* **2010**, *12*, 18–21.
- (6) Heusler, K. E.; Kutzmutz, S. J. Electroanal. Chem. Interfacial Electrochem. **1990**, 285, 93–101.
- (7) Bergstrom, F. W. J. Phys. Chem. **1924**, 29, 160–165.
- (8) Vijh, A. K. J. Electrochem. Soc. 1972, 119, 861.
- (9) Brown, O. R.; Thornton, S. A. J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases **1974**, *70*, 14.
- (10) Jolly, W. L. J. Am. Chem. Soc. 1956, 78, 4849–4849.
- (11) Brown, O. R.; Thornton, S. A. J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases **1974**, *70*, 1269.
- (12) Klocke, D. J.; Hixson, A. N. *Ind. Eng. Chem. Process Des. Dev.* **1972**, *11*, 141–146.
- (13) Asch, L.; Shenoy, G. K.; Friedt, J. M.; Adloff, J. P.; Kleinberger, R. J. Chem. Phys. 1975, 62, 2335.
- (14) Smil, V. Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production; MIT Press, 2001.
- (15) Jones, D. A.; Wilde, B. E. Corrosion 1977, 33, 46–50.

- (16) Ahrens, M.; Schmitt, W.; Heusler, K. E. *Mater. Corros.* **1981**, *32*, 167–173.
- (17) Miles, M. H.; Kellett, P. M. J. Electrochem. Soc. 1968, 115, 1225–1227.
- (18) Ahrens, M.; Heusler, K. E. *Electrochim. Acta* **1982**, *27*, 239–243.
- (19) Goshome, K.; Yamada, T.; Miyaoka, H.; Ichikawa, T.; Kojima, Y. *Int. J. Hydrogen Energy* **2016**, 2–7.
- (20) Gerischer, H.; Mauerer, A. *Electroanal. Chem. Interfacial Electrochem.* **1970**, *25*, 421–433.
- (21) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; 2nd ed.; Wiley and Sons Inc., 2000.
- (22) Folkesson, B. Acta Chem. Scand. 1973, 27, 287–302.
- (23) Hendrickson, D. N.; Hollander, J. M.; Jolly, W. L. *Inorg. Chem.* **1969**, *8*, 2642–2647.
- (24) Aduru, S.; Contarini, S.; Rabalais, J. W. J. Phys. Chem. **1986**, *90*, 1683–1688.
- (25) Campbell, J. H.; Bater, C.; Durrer, W. G.; Craig, J. H. *Thin Solid Films* **1997**, *295*, 8–10.
- (26) Binder, H.; Sellmann, D. Z. Naturforsch **1977**, 33b, 173–179.
- (27) Torres, J.; Perry, C. C.; Bransfield, S. J.; Fairbrother, D. H. *J. Phys. Chem. B* **2003**, *107*, 5558–5567.
- (28) Biwer, B. M.; Bernasek, S. L. *J. Electron Spectros. Relat. Phenomena* **1986**, *40*, 339–351.
- (29) Cocke, D. L. J. Electrochem. Soc. 1989, 136, 3655–3662.
- (30) Wang, X.; Zheng, W. T.; Tian, H. W.; Yu, S. S.; Xu, W.; Meng, S. H.; He, X. D.; Han, J. C.; Sun, C. Q.; Tay, B. K. *Appl. Surf. Sci.* 2003, *220*, 30–39.
- (31) Naumkin, A.; Kraut-Vass, A.; Gaarenstroom, S.; Powell, C. NIST X-ray Photoelectron Spectroscopy Database, 2012, *Version 4.*
- (32) de Faria, D. L. A.; Venâncio Silva, S.; de Oliveira, M. T. J. Raman Spectrosc. 1997, 28, 873–878.

# CHAPTER 5:

EVALUATION OF AMORPHOUS COBALT PHOSPHIDE AS AN EARTH-

ABUNDANT AMMONIUM REDUCTION ELECTROCATALYST

## Introduction

As we previously showed, the reduction of ammonium ( $NH_4^+$ ) on a platinum (Pt) cathode in  $NH_3(I)$  occurs by the reactions shown in equations (5.1) through (5.3).<sup>1</sup> Berkh *et al.* proposed that the  $NH_4^{0*}$  formed in (5.1) is likely stabilized by adsorption to the Pt cathode surface, though they were unable to demonstrate this experimentally.<sup>2</sup> The sum of equations (5.1) through (5.3) is equivalent to (5.4), but the reduction of  $NH_4^+$  directly to the radical species results in a required potential of -0.6 V versus NHE for the reduction process. Thus, in order to allow for the economic viability of on-site  $NH_3(I)$  electrolysis, a new cathode material is needed that will catalyze the hydrogen ( $H_2$ ) evolution reaction in  $NH_3(I)$ , and ideally be comprised of Earth-abundant elements, rather than precious metals like Pt.

$$3NH_4^+ + 3e^- \longrightarrow 3NH_4^{0\bullet}$$
(5.1)

$$3NH_4^{0\bullet} \longrightarrow 3NH_3 + 3H^{\bullet}$$
(5.2)

$$3H^{\bullet} \longrightarrow \frac{3}{2}H_2$$
 (5.3)

Overall: 
$$NH_4^+ + e^- \longrightarrow \frac{1}{2}H_2^- + NH_3^-$$
 (5.4)

There is a large body of research into alternative H<sup>+</sup> reduction materials in aqueous media employing Earth-abundant elements as a replacement for long-used and highly efficient Pt.<sup>3</sup> A very promising candidate from among these is cobalt phosphide (CoP).<sup>4–7</sup> In acidic conditions, CoP has been shown to operate at

overpotentials only slightly larger than Pt.<sup>5</sup> Additionally, it can be easily nanostructured to maximize the active surface area and thus boost performance without modifying the electrode geometry.<sup>6,7</sup>

Palaniappan and coworkers have studied an array of cathode materials for  $NH_3(aq)$  electrolysis, including both noble and transition metals, nanostructured on carbon supports.<sup>8,9</sup> However, in aqueous conditions, water is the species reduced at the cathode, rather than  $NH_4^+$ , and so it is unclear whether these materials will be suitable cathodes in  $NH_3(l)$  as well.<sup>10</sup> In  $NH_3(l)$  conditions, it would be ideal for the cathode surface to have a slightly larger proton affinity than  $NH_3$  so as to extract and reduce  $H^+$  to  $H_2$  directly without forming  $NH_4^{0*}$ . Free phosphine (PH<sub>3</sub>) has a similar proton affinity to  $NH_3$ ,<sup>11</sup> so it is reasonable to hypothesize that exposed phosphide sites in a material like amorphous CoP could accept  $H^+$  from  $NH_4^+$  and serve as an efficient reduction platform.

Saadi *et al.* were able to electrodeposit amorphous CoP–with a significant fraction of amorphous cobalt oxide contaminant–onto copper (Cu) disk substrates as catalysts for H<sup>+</sup> reduction in acidic conditions.<sup>5</sup> The cobalt oxide was removed *in operando*, leaving approximately 20 µm diameter islands of CoP exposed on the Cu surface as confirmed by scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS). The film performed at the same current density for H<sup>+</sup> reduction as a Pt cathode for over 24 hours with a mere 50 mV additional overpotential.

In this chapter, we apply a similar electrodeposited amorphous cobalt phosphide electrode to the reduction of  $NH_4^+$  in  $NH_3(I)$ , and compare its performance to our Pt disk

results.<sup>1</sup> The reductions of  $NH_4^+$  and  $H^+$  dissolved in DMF are also compared to  $NH_4^+$  reduction in  $NH_3(I)$  for both electrodes. Cobalt phosphide is shown to be an inexpensive, simple to fabricate, Earth-abundant alternative cathode material featuring electrochemical performance similar to Pt and with the potential for morphological engineering for commercial devices.

### Experimental

Copper (Cu) disk electrodes were prepared using Cu wire (Arcor, 24 gauge). After polishing, the electrodes were sonicated in a detergent solution (Sparkleen, Fisherbrand), followed by deionized water, followed by isopropanol for 15 minutes each. The electrodes were then kept in the isopropanol until they were rinsed with deionized water immediately before immersion into the electrodeposition solution.

The CoP<sub>x</sub> film deposition was based on the method from Saadi *et al.*<sup>5</sup> The deposition bath consisted of a 10 mL solution with 0.15 M boric acid (Strem, 99.99%), 0.1 M sodium chloride (CCI, 99%), 1.2 M hypophosphorous acid (Spectrum, reagent), and 0.2 M cobalt chloride hexahydrate (Alfa Aesar, 99.9%). A concentrated solution of sodium hydroxide (Macron, reagent ACS) was then added until the pH of the solution was 5.0. Nitrogen gas was bubbled through the solution for at least 30 minutes prior to deposition to remove any dissolved oxygen. Immediately before electrodeposition, the potential at the prepared Cu disk was cycled at 100 mV s<sup>-1</sup> between -0.36 and -1.16 V versus NHE, (-0.5 and -1.3 V versus a homemade Ag/AgCl reference electrode),<sup>12</sup> in the deposition bath to reduce the copper oxide layer in preparation for electrodeposition.

A pulsed deposition method was used to electrodeposit the  $CoP_x$  film, involving a 1 second -0.96 V versus NHE pulse (-1.1 V versus the Ag/AgCl reference), followed by 3 seconds at open circuit. This was repeated 20 times for a total of 20 seconds deposition time. After all 20 cycles were complete, the electrode was gently rinsed with deionized water, rinsed again with acetone, and then dried under a gentle flow of nitrogen gas.

The electrochemically active surface areas of electrodeposited CoP<sub>x</sub> disks were determined by fitting the charging current from cyclic voltammograms at scan rates between 10 and 1000 mV s<sup>-1</sup> in a solution of 0.1 M NH<sub>4</sub>PF<sub>6</sub> (Fluka, 98%, recrystallized) in *N*,*N*-dimethylformamide (Macron, reagent ACS) as described in Chapter 2. All electrochemical experiments were conducted using a Metrohm  $\mu$ AutolabIII potentiostat and employed the custom Ag/AgCl reference electrode.

## **Results and Discussion**

A total of fifteen  $CoP_x$  electrodes were fabricated by the same pulsed deposition method since inconsistency in the film electrodeposition can result from small differences in the Cu disk substrates. By comparison of the SEM images of the bare Cu disk substrate in Figures 5.1(a) and (b) to those of the  $CoP_x$  film in Figures 5.1(c) and (d), it can be seen that the pulsed deposition method results in  $CoP_x$  films conformal with the Cu substrate morphology. The Co:P ratio of the  $CoP_x$  film was measured by EDS to be approximately  $5 \pm 1$ . Due to the amorphous nature of the film and variation in stoichiometry, we will refer to the material as  $CoP_x$ . The excess Co in the



**Figure 5.1:** SEM images of the Cu disk substrate, (a) and (b), and  $CoP_x$  disk electrode corresponding to the curves shown in Figures 5.3, 5.8, and 5.9, (c) and (d).

electrodeposited  $\text{CoP}_x$  film parallels a report by Saadi *et al.* where there was an excess of amorphous cobalt oxide deposited in addition to the desired CoP electrocatalyst.<sup>5</sup> While the cobalt oxide was removed *in operando* by sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) in the literature report, our CoP<sub>x</sub> was unchanged in the cathodic operating conditions in NH<sub>3</sub>(*l*). The films generated by pulsed deposition are different from those produced on similar Cu disk substrates by simply holding the potential at -1.44 V versus NHE for 20 seconds. As depicted in Figure 5.2, "held depositions" produced CoP<sub>x</sub> microspheres, about 1 µm in diameter, with a similar 5:1 Co:P stoichiometry. These microspheres increased the electrode roughness factor by nearly ten-fold, and the produced a high level of variation in electrode composition. The best of these performed similar to an average electrode formed by pulsed deposition, after normalizing the electrochemically active surface area. Thus, in the interest of experimental consistency, the pulsed deposition method was selected for all further electrochemical studies.



**Figure 5.2:** SEM images of a  $CoP_x$  film deposited on a Cu disk substrate by holding - 1.1 V versus Ag/AgCl rather than application of the pulsed deposition method.

The cathodic performance of  $CoP_x$  films deposited on Cu disks was measured using linear sweep voltammetry in 0.1 M NH<sub>4</sub>NO<sub>3</sub> in NH<sub>3</sub>(*l*). These were compared to similar sweeps with a Pt disk cathode, and representative *J-V* curves are depicted in Figure 5.3. Figure 5.3 shows a CoP<sub>x</sub> cathode with performance close to the average, but Figure 5.4 shows a composite of the *J-V* curves of all fifteen CoP<sub>x</sub>. The onsets of these waves are similar to those previously reported for the reduction of NH<sub>4</sub><sup>+</sup> in NH<sub>3</sub>(*l*), where the large overpotential is likely due to the reduction pathway involving NH<sub>4</sub><sup>0</sup>• as an intermediate.<sup>1</sup>



**Figure 5.3:** Cathodic *J-V* curves in 0.1 M  $NH_4NO_3$  in  $NH_3(I)$  with a Pt disk (black) or  $CoP_x$  disk (blue). Linear sweeps were measured at 100 mV s<sup>-1</sup>, and current densities were calculated using the electrochemically active surface area.



**Figure 5.4:** Composite of *J*-*V* curves in 0.1 M  $NH_4NO_3$  in  $NH_3(I)$  from fifteen  $CoP_x$  electrodes fabricated by the pulsed deposition method.

To verify the cathodic process occurring, -1.85 V versus NHE was applied at a  $CoP_x$  electrode surface in 0.1 M NH<sub>4</sub>NO<sub>3</sub> in NH<sub>3</sub>(*l*) for 150 minutes and the gasses in the headspace were measured using gas chromatography. Figure 5.5 shows the production of H<sub>2</sub> gas from a  $CoP_x$  electrode with approximately 100 % Faradaic efficiency. This shows that H<sub>2</sub> evolution is the only reaction of consequence at a  $CoP_x$  cathode in NH<sub>3</sub>(*l*).

As can be seen in Figure 5.6, the first cathodic scan with a  $CoP_x$  cathode in  $NH_3(I)$  features a large cathodic pre-wave which is likely due to the reduction of surface oxides formed from the storage of the electrode in air. This wave is not present in all subsequent scans confirming the irreversibility of the process. To clearly differentiate



**Figure 5.5:** Comparison of the  $\mu$ moles of H<sub>2</sub> measured in the headspace of the electrochemical cell (red diamonds) with the theoretical maximum amount of H<sub>2</sub> if the Faradaic efficiency for H<sub>2</sub> evolution were 100 % (blue circles).

between this irreversible reduction behavior and the  $NH_4^+$  reduction process, the third successive linear sweep is depicted in Figures 5.3, 5.4, and 5.9.

Linear potential sweeps are shown in place of full cyclic voltammograms (CVs) due to lack of clarity from the large hysteretic behavior with  $CoP_x$  electrodes, which can be seen in Figure 5.7. The cathodic current will steadily decrease, approaching a constant plateau with time at a constant potential, as shown in Figure 5.8, periodically interrupted by sudden jumps in the current density. The same behavior can be produced by externally manually agitating the electrode during or between cathodic



**Figure 5.6:** First and second cathodic cyclic voltammograms of a  $CoP_x$  electrode in 0.1 M NH<sub>4</sub>NO<sub>3</sub> in NH<sub>3</sub>(*I*) showing the large cathodic wave only evident on the first scan of each CoP<sub>x</sub> electrode, indicated by the black arrow.

scans. This phenomenon is attributed to the formation and later displacement of  $H_2$  gas bubbles at the surface of the cathode, similar to the anodic behavior reported for Pt anodes in NH<sub>3</sub>(*I*) at sufficiently positive overpotentials.<sup>1</sup> Thus, a current density of about -70 mA cm<sup>-2</sup> is representative of the steady-state current density in Figure 5.8, rather than -65 mA cm<sup>-2</sup>, as this is approximately what the current density jumps to as bubbles are displaced.

While the overpotential required for 10 mA cm<sup>-2</sup> is approximately the same for the Pt and CoP<sub>x</sub> electrodes, their Tafel behaviors are very different, as shown in Figure 5.9 and Table 5.1. While the onset for  $NH_4^+$  reduction on Pt is 200-300 mV lower than that



**Figure 5.7:** Cyclic voltammogram of a  $CoP_x$  electrode in 0.1 M NH<sub>4</sub>NO<sub>3</sub> in NH<sub>3</sub>(*I*) showing hysteresis due to H<sub>2</sub> bubble formation. The scan direction is indicated by the black arrows.

of  $CoP_x$ , the  $CoP_x$  Tafel slope is more than two-fold steeper. This leads to intersection of *J-V* and Tafel plots at about -1.3 V versus NHE. Consequently, the current density for  $NH_4^+$  reduction on  $CoP_x$  exceeds that of Pt at potentials lower than 1.3 V versus NHE. It is difficult, however, to extract any quantitative kinetic information from the Tafel plots in Figure 5.9 as there are several different slopes in different potential regions, and it is unclear which, if any, are suitable to be fit to a Butler-Volmer-type electron transfer.

The Pt Tafel behavior is unusually poor with respect to typical Pt aqueous H<sup>+</sup> reduction characteristics, where slopes of 50 to 120 mV dec<sup>-1</sup> are common.<sup>6</sup> Again, this is likely due to the alternative  $NH_4^+$  reduction pathway involving the radical



**Figure 5.8:** Chronoamperogram of the same  $CoP_x$  electrode shown in Figure 5.3 measured at -1.67 V versus NHE in 0.1 M NH<sub>4</sub>NO<sub>3</sub> in NH<sub>3</sub>(*I*).

**Table 5.1:** Average electrochemical performance of fifteen similar  $CoP_x$  electrodes compared to a Pt disk in 0.1 M NH<sub>4</sub>NO<sub>3</sub> in NH<sub>3</sub>(*I*).

Electrode	V for 10 mA cm <sup>-2</sup>	mV dec <sup>-1</sup>
Pt	-1.46	298
CoP <sub>x</sub>	$\textbf{-1.48} \pm 0.04$	$130\pm18$

intermediate.<sup>1,2</sup> In our previous work we probed the  $NH_4^+$  reduction more closely using  $NH_4PF_6$  dissolved in DMF. A comparison of  $NH_4^+$  reduction with the same Pt and  $CoP_x$  electrodes as those depicted in Figures 5.3, 5.8, and 5.9 is shown in Figure 5.10. The Pt cathodic onset is approximately the same as previously reported,<sup>1</sup> while the  $CoP_x$  reduction onset is about 300 mV more negative, as observed in  $NH_3(I)$ .



**Figure 5.9:** Cathodic Tafel plots corresponding to the *J*-*V* curves depicted in Figure 5.3 in 0.1 M NH<sub>4</sub>NO<sub>3</sub> in NH<sub>3</sub>(*I*) with a Pt disk (black) or CoP<sub>x</sub> disk (blue). Tafel fits are shown in dashed red lines.

In DMF, however, the Tafel slopes for Pt and  $CoP_x$  are similar to each other: about 160 and 225 ± 10 mV dec<sup>-1</sup> respectively (Figure 5.11). The Tafel behavior of  $CoP_x$  indicates slightly poorer relative NH<sub>4</sub><sup>+</sup> reduction performance in DMF, which could easily be attributed to a solvent effect. For instance, if NH<sub>4</sub><sup>+</sup> reduction intermediates are better stabilized by the NH<sub>3</sub>(*I*) environment than the DMF environment, the kinetic barrier for NH<sub>4</sub><sup>+</sup> reduction would be lower in NH<sub>3</sub>(*I*) resulting in more favorable Tafel behavior. The Pt Tafel behavior in DMF, unlike in NH<sub>3</sub>(*I*), is approximately what is expected for the reduction of NH<sub>4</sub><sup>+</sup>, and is similar to what we previously reported.<sup>1</sup> The onset of -0.6 V



**Figure 5.10:** Cathodic *J-V* curves in 0.1 M  $NH_4PF_6$  in DMF with a Pt disk (black) or  $CoP_x$  disk (blue). Linear sweeps were measured at 100 mV s<sup>-1</sup>, and current densities were calculated using the electrochemically active surface area.

versus NHE corresponds with the potential of the direct reduction of  $NH_4^+$ . This further emphasizes how unexpectedly large the Tafel slope for Pt in Table 5.1 is. It is unclear what the cause of the relatively poor performance of a Pt cathode in  $NH_3(I)$  is with respect to DMF when the species reduced is presumably the same:  $NH_4^+$ . It may be the case that a more "innocent" organic solvent would provide a model system that more accurately reflects the cathodic behavior of both Pt and  $CoP_x$  in  $NH_3(I)$  and would allow for *in situ* spectroscopy experiments to probe key intermediates in the  $NH_4^+$  reduction reaction. This problem, in addition to further investigation of Earth-abundant cathode materials is the subject of continued research in our laboratory.



**Figure 5.11:** Cathodic Tafel plots corresponding to the *J*-*V* curves depicted in Figure 5.10 in 0.1 M  $NH_4PF_6$  in DMF with a Pt disk (black) or  $CoP_x$  disk (blue). Tafel fits are shown in dashed red lines.

## Conclusions

By a slight modification to a previously reported electrodeposition solution and application of a pulsed deposition method, amorphous  $CoP_x$  films were deposited conformally onto Cu disk substrates. These films demonstrated electrochemical performances similar to a Pt disk for the reduction of  $NH_4^+$  in  $NH_3(I)$ , even after accounting for the electrochemically active surface area of the electrodes. Due to the simplicity of the deposition procedure, similar  $CoP_x$  should be simple to deposit onto micro- or nanostructured Cu substrates, such as Cu foam, in order to increase cathode performance without increasing geometric area. While it appears that the direct  $NH_4^+$  reduction pathway involving the unstable Rydberg radical intermediate is not bypassed

through use of  $CoP_x$ , these cathodes are comparable to expensive, noble metal cathodes previously reported.

REFERENCES

#### REFERENCES

- (1) Little, D. J.; Smith, III, M. R.; Hamann, T. W. *Energy Environ. Sci.* **2015**, *8*, 2775–2781.
- (2) Berkh, O.; Shacham-Diamand, Y.; Gileadi, E. *J. Electrochem. Soc.* **2008**, *155*, F223–F229.
- McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F. *J. Am. Chem. Soc.* 2015, *137*, 4347–4357.
- (4) Shi, Y.; Zhang, B. Chem. Soc. Rev. 2016, 45, 1529–1541.
- (5) Saadi, F. H.; Carim, A. I.; Verlage, E.; Hemminger, J. C.; Lewis, N. S.; Soriaga, M. P. J. Phys. Chem. C 2014, 118, 29294–29300.
- (6) Popczun, E. J.; Read, C. G.; Roske, C. W.; Lewis, N. S.; Schaak, R. E. *Angew. Chemie Int. Ed.* **2014**, *53*, 5427–5430.
- (7) Callejas, J. F.; Read, C. G.; Popczun, E. J.; McEnaney, J. M.; Schaak, R. E. *Chem. Mater.* **2015**, *27*, 3769–3774.
- (8) Palaniappan, R.; Botte, G. G. J. Phys. Chem. C 2013, 117, 17429–17441.
- (9) Palaniappan, R.; Ingram, D. C.; Botte, G. G. *J. Electrochem. Soc.* **2014**, *161*, E12–E22.
- (10) Gerischer, H.; Mauerer, A. *Electroanal. Chem. Interfacial Electrochem.* **1970**, *25*, 421–433.
- (11) Hunter, E. P. L.; Lias, S. G. J. Phys. Chem. Ref. Data 1998, 27, 413–656.
- (12) Sawyer, D. T.; Sobkowiak, A.; Roberts, J. L. *Electrochemistry for Chemists*; Second.; John Wiley & Sons, Inc.: New York, 1995.

# CHAPTER 6:

CONCLUSIONS AND FUTURE WORK

## Introduction

As demonstrated in previous chapters, by administration of proper electrolyte conditions, noble metals can be completely replaced by Earth-abundant, first row transition metal-based materials like iron nitride (FeN<sub>x</sub>) and cobalt phosphide (CoP<sub>x</sub>) for the electrolysis of liquid ammonia (NH<sub>3</sub>(*l*)). Figure 6.1 shows that the 2-electrode electrolysis of NH<sub>3</sub>(*l*) can occur with nearly the same efficiency using FeN<sub>x</sub> and CoP<sub>x</sub> as the anode and cathode respectively compared to two platinum (Pt) disk electrodes. This represents a significant shift toward sustainability, scalability, and economic feasibility of electrochemical NH<sub>3</sub> splitting in a NH<sub>3</sub> fuel cycle like that described in Chapter 1.



**Figure 6.1:** The electrolysis of  $NH_3(I)$  with a 0.1 M  $NH_4NO_3$  electrolyte using  $FeN_x$  and  $CoP_x$  as the anode and cathode respectively (Spartan green), compared to two Pt electrodes (red).

However, there is still a large need for catalysis of both half-reactions if there is to be any energetic benefit to using  $NH_3$  as a hydrogen fuel carrier. Here, future research directions are proposed that could reduce the electrolysis overpotential substantially and allow for market implementation.

#### Ammonia Oxidation Catalysis

A clear next step in the investigation of  $NH_3(I)$  oxidation catalysts is to synthesize pure, crystalline iron nitride materials–presumably in a variety of different stoichiometries–and compare their anodic performance to the *in situ* generated FeN<sub>x</sub> presented in Chapter 4. This will allow us to learn more about the  $NH_3$  oxidation pathway on iron nitride and potentially provide insight into better anode design. Additionally, it is worth revisiting the poison species on a Pt electrode and comparing it to the nitride species of FeN<sub>x</sub> to investigate how the presence of a surface nitride decreases the performance of a Pt electrode, but increases performance of an Fe electrode.

However, unless a breakthrough occurs while investigating crystalline nitride materials, it is likely that simply searching through pure, solid state materials may not be the best solution for an efficient  $NH_3(I)$  electrochemical oxidation reaction. The best catalyst we have found in  $NH_3(I)$ –FeN<sub>x</sub> as described in Chapter 4–still converges to approximately the same onset as a Pt surface. Significant gains can be made by simply increasing the active surface area of an anode by nanostructuring, as shown by Dong *et al.*,<sup>1</sup> however when normalizing by the resulting roughness factor, the current is still

approximately the same as on a Pt surface. These observations indicate that an outersphere electron transfer is likely the rate-limiting step of the NH<sub>3</sub>(*l*) oxidation process. This is supported by the observation by Katsounaros *et al.* that in aqueous media NH<sub>3</sub> oxidation proceeds by a rate-limiting electron transfer, instead of the previously proposed proton-coupled electron transfer.<sup>2</sup> This is in agreement with our observation that the rate of the NH<sub>3</sub> oxidation reaction is independent of NH<sub>4</sub><sup>+</sup> concentration.<sup>3</sup> If it is true that an outer-sphere process is rate-limiting under the current conditions, then it is unlikely that a bulk material will be able to efficiently drive the NH<sub>3</sub>(*l*) oxidation reaction unless it contains specific catalytically active sites.

In order to gather more specific knowledge about what type of site would be ideal, there is a large effort from the Smith and Hamann groups at Michigan State University to design homogeneous molecular NH<sub>3</sub> oxidation catalysts. Inspired by molecular catalysts for electrochemical water oxidation employing ligands that can support high oxidation states, they are working toward designing new molecules that can support oxidation of NH<sub>3</sub> to N<sub>2</sub> at relatively modest overpotentials. Other research groups have already been able to demonstrate N-H bond cleavage using molecular molybdenum complexes,<sup>4,5</sup> and work toward a complete catalytic cycle is well underway. Synthesizing variations of functional molecular catalysts may delineate factors that are rate-limiting, which could inform design of next-generation catalysts. Ideally, relevant structures can then be built into heterogeneous electrodes in a commercially viable NH<sub>3</sub>(*I*) electrolyzer.

There are a variety of feasible ways to incorporate catalytic sites from homogeneous molecular catalysts into a heterogeneous electrode platform. The simplest of these involves simply immobilizing the molecular catalyst on an electrode surface through one of its ligands. This has the advantage of eliminating current limitations due to catalyst diffusion, thus minimizing the quantity of catalyst needed in a device. This strategy also only minimally changes the electronics of the catalyst. However, synthesis of molecular catalysts is often time-consuming and expensive which can be a major inhibition to commercial implementation.

Ideally, a bulk material can be fabricated that closely mimics the active site of the molecular catalyst, eliminating the need for molecular synthesis altogether. For example, if the key molety in a molecular catalyst is a pendent amine ligand coordinated to an Fe metal center, this could be potentially mimicked simply by attaching pendent amines to a bulk iron nitride material in the form of a self-assembled monolayer. The monolayer can then serve a similar function to the critical ligand in the molecule and facilitate the oxidation reaction.

## **Ammonium Reduction Catalysis**

While it is useful that electrodeposited  $CoP_x$  may replace Pt as a  $NH_4^+$  reduction catalyst in  $NH_3(I)$  similar to its function in aqueous  $H^+$  reduction, the problem of lowering the cathodic overpotential by avoiding the  $NH_4^{0\bullet}$  still remains to be solved. It is a useful step to move away from expensive, noble metals like Pt, but work still needs to be done

to design  $NH_4^+$  reduction catalysts that will extract  $H^+$  from  $NH_4^+$ , and reduce it directly to  $H_2$ , thus avoiding energetically unfavorable radical species.

Analogous to the next step in NH<sub>3</sub> oxidation, electrodes of pure CoP nanoparticles, or bulk crystalline CoP should be fabricated and compared to the electrodeposited CoP<sub>x</sub>. Additionally, there are a multitude of reported transition metal alloys and phosphide materials that perform similarly in aqueous conditions, but may diverge in NH<sub>3</sub>(l).<sup>6–8</sup> Since Pt and CoP<sub>x</sub> are essentially the only two cathode materials investigated in NH<sub>3</sub>(l), it is impossible to make generalizations about the H<sub>2</sub> evolution reaction in NH<sub>3</sub>(l) at large.

Should all cathode materials investigated converge to similar required overpotentials, it will be necessary to more closely probe the reduction intermediates using *in situ* spectroscopy. Incorporating either Pt–or possibly gold–nanoparticles, it should be possible to conduct Surface Enhanced Raman Spectroscopy (SERS) measurements to identify vibrational modes of intermediate species.<sup>9</sup> The difficult part of this experiment is the design of an *in situ* Raman apparatus that can incorporate an electrochemical cell containing NH<sub>3</sub>(*I*) that would need to be kept cold or pressurized during the experiment without the possibility of leaking into the instrument.

As a parallel approach to studying different cathode materials,  $NH_4^+$  reduction should be studied in an array of alternative solvents in addition to *N*,*N*dimethylformamide (DMF). While  $NH_3$  should be stored and transported in pure liquid form to maximize its benefits over other hydrogen storage media, a commercial electrolyzer does not necessarily need to rely on a  $NH_3(I)$  electrolyte. We showed in

Chapters 3 and 5 that the H<sub>2</sub> evolution reaction occurs at more favorable overpotentials in DMF compared to  $NH_3(I)$ . (In water, H<sub>2</sub> evolution occurs at the optimum 0 V versus RHE, though this is due to the reduction of H<sub>2</sub>O.)<sup>10</sup> A possible route to diminishing the  $NH_4^+$  reduction overpotential, therefore, is to conduct the reaction in a solvent that can destabilize the  $NH_4^+$  ion enough to promote H<sup>+</sup> reduction without the production of Rydberg radical intermediates, while being sufficiently anhydrous to eliminate the anodic poisoning process described in Chapters 3 and 4.

A different pathway toward  $NH_4^+$  reduction catalysis involves a similar approach to the  $NH_3$  oxidation techniques previously discussed. A proton reduction catalyst– inspired by existing proton reduction catalysts that are active in aqueous conditions– could be discovered to efficiently reduce  $NH_4^+$  in  $NH_3(I)$ . Such a catalyst, again, would need to feature a moiety with a greater proton affinity than  $NH_3$  in order to extract  $H^+$ from  $NH_4^+$  and avoid the unwanted radical pathway. This molecular catalyst could then either be immobilized onto an electrode surface, or else an electrode surface could be fabricated to mimic the critical moieties of the catalyst. REFERENCES

### REFERENCES

- (1) Dong, B.-X.; Tian, H.; Wu, Y.-C.; Bu, F.-Y.; Liu, W.-L.; Teng, Y.-L.; Diao, G.-W. *Int. J. Hydrogen Energy* **2016**, *41*, 14507–14518.
- (2) Katsounaros, I.; Chen, T.; Gewirth, A. A.; Markovic, N. M.; Koper, M. T. M. *J. Phys. Chem. Lett.* **2016**, *7*, 387–392.
- (3) Little, D. J.; Smith, III, M. R.; Hamann, T. W. *Energy Environ. Sci.* **2015**, *8*, 2775–2781.
- (4) Bezdek, M. J.; Guo, S.; Chirik, P. J. *Science (80-. ).* **2016**, *354*, 730–733.
- Bhattacharya, P.; Heiden, Z. M.; Wiedner, E. S.; Raugei, S.; Piro, N. A.; Kassel,
   W. S.; Bullock, R. M.; Mock, M. T. *J. Am. Chem. Soc.* 2017, *139*, 2916–2919.
- (6) Callejas, J. F.; Read, C. G.; Roske, C. W.; Lewis, N. S.; Schaak, R. E. Chem. Mater. 2016, 28, 6017–6044.
- (7) Cox, C. R.; Lee, J. Z.; Nocera, D. G.; Buonassisi, T. *Proc. Natl. Acad. Sci.* **2014**, *111*, 14057–14061.
- McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F. *J. Am. Chem. Soc.* 2015, *137*, 4347–4357.
- (9) Le Ru, E. C.; Etchegoin, P. G. *Principles of Surface-Enhanced Raman Spectroscopy*; Elsevier, 2009.
- (10) Palaniappan, R.; Ingram, D. C.; Botte, G. G. J. Electrochem. Soc. 2014, 161, E12–E22.