Electrochemically Induced Urea to Ammonia on Ni Based Catalyst

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ABSTRACT

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**Electrochemically Induced Urea to Ammonia on Ni Based Catalyst**

Director of Dissertation: Gerardine G. Botte

Ammonia is a crucial chemical used in many fields such as the fertilizer, textile, and food industries. Nowadays, ammonia is commonly used as a reducing agent to reduce nitrogen oxide (NOx) to non-harmful nitrogen gas and water which is called the selective catalytic reduction (SCR) process. For the on-site production of ammonia, two traditional methods are urea hydrolysis and urea pyrolysis. However both of them require high temperature and pressure which are not accessible in mobile engines. A novel electrochemically induced urea to ammonia (eU2A) process in alkaline media was introduced and investigated in this investigation. Nickel beads are employed as the working catalyst in a two-electrode eU2A reactor using 7.0 M KOH as the supporting electrolyte at 70 °C. The ammonia generation rate per effective volume of catalyst in the eU2A process is ~28 times higher than the thermal hydrolysis of urea (THU). The eU2A operates at low temperature and pressure which is suitable for SCR process in mobile engines and saves energy. The eU2A process is a promising technique that finds applications on the SCR process for the removal of nitride oxide from combustion systems (e.g., diesel vehicles and power plants).

In addition, the mechanism of eU2A in the alkaline medium using nickel electrodes was investigated in a classical three-electrode reactor with a mercury/mercury oxide reference electrode. In this investigation, the intermediates and products in the bulk
solution were monitored by Fourier Transform Infrared spectroscopy, and the intermediates and products on the catalyst surface in eU2A process were analyzed by in-situ Raman spectroscopy. Urea electrolysis and THU (in the bulk solution) take place in parallel with the eU2A process in the eU2A reactor. It was found that the ammonia production rate depends strongly on the amount of nickel oxyhydroxide and the concentration of OH⁻ ions. In addition, the redox couple of Ni²⁺ and Ni³⁺ ions played important roles in ammonia generation in the eU2A process. Based on these observations and analyses, an eU2A mechanism is proposed in this dissertation.

The catalytic effect of Ni based working electrode could also be found when using K₂CO₃ as the supporting electrolyte during the eU2A process. However, Ni electrodes were found to corrode when the supporting electrolyte was changed to K₂CO₃. To deal with this problem, a novel graphene-coated Ni electrode was developed to improve its ammonia corrosion resistance while unexpectedly enhancing the ammonia generation rate in the eU2A process. The development of a corrosion resistant electrode is crucial for the eU2A reactions since the concentration of ammonia is inevitably high on the surface of the electrode in the heterogeneous ammonia generating process, leading to severe corrosion of the electrode and the loss of generated ammonia as well. In this research, the graphene was derived from raw coal by using the chemical vapor deposition method and then self-lifted onto a Ni electrode to form a protective layer for corrosion prevention. Transmission electron microscopy showed that the synthesized graphene had few layers and in-situ Raman spectroscopy indicated that the coating of graphene was stable during the eU2A process. As a result, the ammonia corrosion of the Ni electrode was
dramatically reduced by ~ 20 times with the graphene coating method. More importantly, a higher ammonia generation rate (~ 2 times) was achieved using the graphene-coated Ni working electrode compared to a bare Ni electrode in the eU2A process.
DEDICATION

Dedicated to my family
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>3</td>
</tr>
<tr>
<td>Dedication</td>
<td>6</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>7</td>
</tr>
<tr>
<td>List of Tables</td>
<td>13</td>
</tr>
<tr>
<td>List of Figures</td>
<td>15</td>
</tr>
<tr>
<td>Chapter 1: Introduction</td>
<td>20</td>
</tr>
<tr>
<td>1.1 Project Significance</td>
<td>20</td>
</tr>
<tr>
<td>1.2 Research Objectives</td>
<td>24</td>
</tr>
<tr>
<td>Chapter 2: Literature Review</td>
<td>28</td>
</tr>
<tr>
<td>2.1 Ammonia</td>
<td>28</td>
</tr>
<tr>
<td>2.2 Urea to Ammonia</td>
<td>28</td>
</tr>
<tr>
<td>2.3 Methods for Urea to Ammonia Conversion</td>
<td>29</td>
</tr>
<tr>
<td>2.3.1 Urea Hydrolysis to Ammonia</td>
<td>29</td>
</tr>
<tr>
<td>2.3.2 Urea to Ammonia by Non-Thermal Plasma</td>
<td>30</td>
</tr>
<tr>
<td>2.4 The Advantages of eU2A</td>
<td>30</td>
</tr>
<tr>
<td>2.4.1 The Effect of Water Vapor in SCR</td>
<td>31</td>
</tr>
<tr>
<td>2.4.2 The Effect of Hydrogen in SCR</td>
<td>32</td>
</tr>
<tr>
<td>2.5 The Mechanism of Converting Urea to Ammonia</td>
<td>33</td>
</tr>
<tr>
<td>2.5.1 Urea Hydrolysis</td>
<td>33</td>
</tr>
<tr>
<td>2.5.2 Catalysis of Urea to Ammonia Using Urease</td>
<td>35</td>
</tr>
<tr>
<td>2.5.3 Electro-Catalytic Dissociation of Urea</td>
<td>36</td>
</tr>
<tr>
<td>2.6 Ammonia Corrosion of Ni in eU2A</td>
<td>37</td>
</tr>
<tr>
<td>2.7 The Anti-Corrosion Graphene Coating</td>
<td>38</td>
</tr>
<tr>
<td>Chapter 3: Experimental Methodology</td>
<td>40</td>
</tr>
<tr>
<td>3.1 The Two-Electrode eU2A Reactor</td>
<td>40</td>
</tr>
<tr>
<td>3.2 The Three-Electrode eU2A Reactor</td>
<td>43</td>
</tr>
<tr>
<td>3.3 Ammonia Determination Using an Ion Selective Electrode</td>
<td>44</td>
</tr>
<tr>
<td>3.4 UV-Visible Spectroscopy for Urea Determination</td>
<td>48</td>
</tr>
<tr>
<td>3.5 Gas Chromatograph (GC)</td>
<td>50</td>
</tr>
<tr>
<td>3.6 Fourier Transform Infrared Spectroscopy (FTIR)</td>
<td>51</td>
</tr>
</tbody>
</table>
Table 5.1 Electrochemical performance for urea electrolysis at different applied potentials during 3 hours of operation of the eU2A process using 5.0 M urea in the presence of 5.0 M KOH. Ideal gas law was assumed for the estimation of the moles of the gases produced (refer to Appendix A4.2 for details) ........................................................ 83

Table 5.2 FTIR bands assignment of 5.0 M Urea in the presence of 5.0 M KOH solution during eU2A and THU ...................................................................................................... 84

Table 5.3 Raman bands assignment of 5.0 M urea in the presence of 5.0 M KOH solution during eU2A and THU ...................................................................................................... 88

Table A1.1 Ammonia generation in the 24-hour eU2A (1.65 V, 70 °C) experiment in the two-electrode reactor using 7.0 M KOH supporting electrolyte ........................................ 126

Table A1.2 Ammonia generation in the 24-hour THU (70 °C) experiment in the two-electrode reactor using 7.0 M KOH supporting electrolyte ........................................ 127

Table A1.3 Ammonia generation in the 3-hour eU2A (70 °C) experiments in the three-electrode reactor using 1.0, 2.5, and 7.0 M KOH supporting electrolyte ....................... 127

Table A1.4 Ammonia generation in the 3-hour eU2A (70 °C) experiments in the three-electrode reactor using 5.0 M KOH supporting electrolyte at different applied potential ......................................................................................................................................... 128

Table A1.5 Ammonia generation in the 3-hour THU (70 °C) experiments in the three-electrode reactor using different concentrations of KOH supporting electrolyte ........ 128

Table A1.6 Ammonia generation in the 24-hour eU2A (0.75 V vs. Hg/HgO, 70 °C) and THU (70 °C) experiments in the three-electrode reactor using 2.5 M K2CO3 supporting electrolyte ..................................................................................................................... 129

Table A1.7 Ammonia generation in the 3-hour eU2A (0.965 V vs. Hg/HgO, 70 °C) and THU (70 °C) experiments in the three-electrode reactor using 3.0 M KHCO3 supporting electrolyte ..................................................................................................................... 129

Table A1.8 Ammonia generation in the 12-hour eU2A (0.85 V vs. Hg/HgO, 70 °C) experiments in the three-electrode reactor in the K2CO3/KHCO3/NH3/H2O equilibrium system ..................................................................................................................... 130

Table A1.9 Ammonia generation in the 12-hour THU (70 °C) experiment in the three-electrode reactor in the K2CO3/KHCO3/NH3/H2O equilibrium system ..................................................................................................................... 131

Table A2.1 The concentration of residual urea in the 24-hour eU2A (1.65 V, 70 °C) and THU (70 °C) experiments in the two-electrode reactor using 7.0 M KOH supporting electrolyte ..................................................................................................................... 132

Table A4.1 Composition of gas sample in the 24-hour eU2A (1.65 V, 70 °C) experiments in the two-electrode reactor ........................................................................ 136
Table A4.2 Composition of gas sample normalized with air in the 24-hour eU2A (1.65 V, 70 °C) experiments in the two-electrode reactor ............................................................ 136
Table A4.3 Material balance of urea and ammonia in the 24-hours eU2A and THU experiments (1.65 V, 70 °C) in the two-electrode reactor ......................................................... 137
Table A4.4 The composition of gas gaseous products at different applied potentials during in 3 hours of operation of the eU2A process using 5.0 M urea in the presence of 5.0 M KOH ..................................................................................................................... 138
Table A4.5 The composition of gas gaseous products at different applied potentials during in 3 hours of operation of the eU2A process using 5.0 M urea in the presence of 5.0 M KOH ..................................................................................................................... 138
Table A4.6 The amount of generated gaseous products at different applied potentials during in 3 hours of operation of the eU2A process using 5.0 M urea in the presence of 5.0 M KOH ..................................................................................................................... 139
Table A4.7 Comparison of nitrogen production between theoretical and actual value amount at different applied potentials during in 3 hours of operation of the eU2A process using 5.0 M urea in the presence of 5.0 M KOH ..................................................................................................................... 139
Table A5.1 The forward reaction rate constants at different reaction conditions........ 140
LIST OF FIGURES

Figure 1.1. Schematic picture of urea SCR in a mobile engine ........................................... 23
Figure 1.2. Schematic picture of ammonia SCR in a mobile engine ............................... 23
Figure 1.3. Proposed urea SCR utilizing the eU2A technique in a mobile engine ......... 24
Figure 2.1. Comparison of NH3 SCR and urea SCR. It can be seen that the working windows of NH3 SCR are broader [16]. ................................................................. 29
Figure 2.2. Reaction rates as a function of temperature on a commercial U2A™ reactor based on a 40% urea solution feed [6]. ................................................................. 30
Figure 2.3. Conversion of NO versus H2O concentration in the feed. ● 190 °C, ▲ 210 °C, ▼ 230 °C, ■ 250 °C. Feed: 10% O2, 1000 ppm NO, 1000 ppm NH3, 0-7.5% H2O, balance N2. Flow rate: 500 mL min⁻¹ at normal temperature and pressure (NTP) [33]. .. 31
Figure 2.4. Conversion of NO versus temperature for dry and wet feed. ● 0% H2O, ▲ 2.5% H2O, ▼ 5% H2O, ■ 7.5% H2O. Feed: 10% O2, 1000 ppm NO, 1000 ppm NH3, 0-7.5% H2O, balance N2. Flow rate: 500 mL min⁻¹ (NTP) [33]. ................................................... 32
Figure 2.5. NO conversion to N2 (○) and N2O (●) vs. time of 50 ppm SO2 addition in H2-NH3-SCR at 200 °C (GHSV =70,000 h⁻¹) [39]. ................................................................. 33
Figure 2.6. Hydrolysis of urea as a function of pH at 66 °C [44]. .................................. 34
Figure 2.7. Proposed mechanism of urease for urea to ammonia [45]. ............................ 36
Figure 2.8. Distribution–pH diagram for 0.01 M Ni2⁺ in 1.0 M (NH4)2SO4 solution [52]. ........................................................................................................................................... 38
Figure 2.9: Mother of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite. The image is reproduced from Geim and Novoselov [21]. .................................................................................................................. 39
Figure 3.1. Design of the two-electrode eU2A reactor. (a) The features of the reactor vessel and working electrode. (b) Photograph of the cathode, anode, and reactor vessel from top and side view ................................................................................................................................. 42
Figure 3.2. The two-electrode eU2A reactor ................................................................. 43
Figure 3.3. The three-electrode eU2A reactor. The reference electrode was supported by a homemade Luggin capillary. ................................................................. 44
Figure 3.4: Schematic picture of the ammonia gas-sensing probe [55].......................... 45
Figure 3.5. UV-vis spectra of standard urea solutions from 0.008 M to 0.040 M. The linear relationship between the absorbance and urea concentration was obtained at 420 nm as shown in the inset figure ................................................................................................................................. 49
Figure 3.6. Typical gas chromatogram for a collected gas sample ............................... 50
Figure 3.7. KBr pellet-pressing die. .................................................................................. 51

Figure 3.8. (a) Schematic configuration of the in-situ Raman eU2A cell. (b) Photograph of the in-situ Raman eU2A cell. The working electrode (WE) and counter electrode (CE) are both Ni foil, and the reference electrode (RE) is Hg/HgO. ........................................ 52

Figure 3.9. The CVD setup for graphene growth on copper foil. The setup consists of a high-temperature furnace, gas delivery system with flow controllers, and exhaust system with a vacuum pump [61]. ................................................................................................ 54

Figure 3.10. Temperature profile of CVD growth of graphene on Cu foil. The synthesis procedure has five steps: I) Evacuate to 100 mTorr and purge with 100 sccm Hydrogen; II) Ramp furnace to 1050 °C; III) Anneal the copper; IV) Move the quartz boat with the coal inside the heat zone of the furnace; V) Fast cooling by moving the quartz boat out of heat zone of the furnace. .................................................................................................. 55

Figure 3.11. Schematic of the CVD setup for producing graphene from raw coal which consists of a quartz tube furnace connected to a vacuum pump and hydrogen gas cylinder. Magnets are attached to the two quartz boats that are used as support for the copper foil and coal. ..................................................................................................................................................... 55

Figure 3.12. (a) Flow chart of making a graphene-coated Ni electrode; (b) PMMA-graphene self-lifted onto Ni foil; (c) Photograph of graphene-coated Ni working electrode. ........................................................................................................................................... 57

Figure 3.13. Flow chart for transferring graphene on the TEM grid and silicon wafer for TEM and AFM analyses. ................................................................................................................. 58

Figure 3.14. Nonlinear calibration of the Ni ion with standard Ni$^{2+}$ solutions with concentrations from 2 mg L$^{-1}$ to 12 mg L$^{-1}$. ...................................................................................................................... 60

Figure 4.1. (a) Schematic representation of the eU2A process; (b) Schematic of the eU2A reactor (I and II are sample ports); (c) Schematic of the gas collection system for the gas analysis (III is the sample port for collecting gas for GC analysis). ................................................. 63

Figure 4.2. Ammonia generation in the eU2A process at (a) different temperatures (a) and (b) different applied potentials using DEF in the presence of 7.0 M KOH in 90 minutes experiment; (c) Ammonia generation and (d) Residual urea in the eU2A (70 °C, 1.65 V) process and its comparison with the THU (70 °C) in a period of 24 hours using DEF in the presence of 7.0 M KOH. ................................................................................................................. 66

Figure 5.1. Schematic representation of reaction vessel. Both the working electrode and counter electrode are Ni foil, while the reference electrode is Hg/HgO. Temperature was set at 70 °C. Sample ports allowed collecting gases and liquid. ................................................................................................................. 74

Figure 5.2. Electrochemical cell for in-situ Raman spectroscopy. The eU2A reaction of 5.0 M urea in the presence of 5.0 M KOH at 0.462 V was conducted in the cell at 70 °C. Raman spectra of intermediate species and products were obtained with the laser focused onto the working electrode surface through a silica window. ............................................................................. 77

Figure 5.3. Performance of eU2A at different potentials and KOH concentrations. (a) CVs of Ni electrodes in 1.0, 2.5, 5.0, and 7.0 M KOH at 70 °C. (b) Experimental results
of ammonia generation of eU2A and THU using 5.0 M urea in the presence of 1.0, 2.5, 5.0, and 7.0 M KOH at 70 °C. (c) Comparison of the ammonia generation from eU2A reaction at 1.0, 2.5, 5.0, and 7.0 M KOH. A proportional correlation was observed between the peak current in the CVs at different concentrations of KOH and the ammonia generation rate, which indicates that the formation of NiOOH in eU2A has a positive effect on the catalytic conversion of urea to ammonia.

Figure 5.4. Comparison of the eU2A and the THU processes at 70 °C. (a) Effect of applied potential at 5.0 M urea and 5.0 M KOH. (b) CVs of Ni electrodes in 5.0 M KOH in the presence and absence of 5.0 M urea overlapped with additional ammonia generation rate (at 0.425 V, 0.462 V and 0.485 V vs. Hg/HgO). During urea electrolysis, Ni$^{3+}$ is reduced to Ni$^{2+}$ while urea is oxidized to N$_2$. At higher applied potentials Ni$^{3+}$ is reduced to Ni$^{2+}$, indicating a positive correlation between additional ammonia generation rate and regenerated Ni$^{2+}$ ions.

Figure 5.5. FTIR spectra of 5.0 M KOH in the presence and absence of 5.0 M urea during eU2A (a) (0.462 V vs. Hg/HgO) and THU (b). The peak shift at 2170 cm$^{-1}$ indicates CNO$^-$ exists at the bulk solution for both the eU2A and THU. The peak that appears at 1438 cm$^{-1}$ is assigned to NH$_4^+$ indicating the generation of ammonia during both the eU2A and THU.

Figure 5.6. Raman spectra of 5.0 M KOH in the presence of 5.0 M urea during eU2A at 0.462 V vs. Hg/HgO and (d-e) during THU. The absence of the CNO$^-$ peak at 2170 cm$^{-1}$ in the eU2A and the presence of it in the THU indicate that CNO$^-$ is not an intermediate of the reaction during the eU2A process.

Figure 5.7. Proposed eU2A mechanism. One Ni ion (Ni$^{3+}$) binds and activates urea, while the second Ni ion (Ni$^{2+}$, generated during urea electrolysis [12]) binds a hydroxyl group from the water. The hydroxyl group is activated for attack on the urea carbon to eliminate ammonia with the help of Lewis acid Ni$^{2+}$ and Ni$^{3+}$. The intermediate then collapses and forms NH$_3$ and CO$_2$ eventually.

Figure 6.1. Flow chart for transferring graphene on the TEM grid and silicon wafer for TEM and AFM analysis.

Figure 6.2. Schematic of the three-neck eU2A reactor. The working electrodes are Ni foil and graphene-coated Ni and the counter electrode is Pt foil, while the reference electrode is Hg/HgO. Temperature was set at 70 °C. The sample port allowed collecting liquid samples and determining pH of the electrolyte in the reactor.

Figure 6.3. (a) TEM image of large area and continuous coal derived graphene film; Inset: SAED with six diffraction spots demonstrating the crystalline nature of the coal derived graphene film. (b, c) High magnification TEM image with the edge of the coal derived graphene film exhibiting bi-layers to few layers of the film.

Figure 6.4. (a) AFM image of the CVD synthsized graphene film on silicon wafer. The wrinkles and overlapping of the graphene film were shown as brighter spots on the image. (b) Height profile of different line scans of the graphene film. ~5-10 nm thickness of the film was exhibited by the line scans which shown that the graphene film is few-layered.
Figure 6.5. Raman spectra of graphene-coated Ni before (curve I) and after (curve II) 24 hours’ eU2A experiment and bare Ni foil (curve III). ................................................................. 103

Figure 6.6. (a) Normalized -by active geometric area of the electrodes- cyclic voltammograms of 2.5 M K$_2$CO$_3$ in the (a) absence and (b) presence of 5.0 M urea at 70 °C using the Ni foil and graphene-coated Ni electrodes, at a scan rate of 10 mV s$^{-1}$. ......................................................................................................................................... 104

Figure 6.7. (a) Concentration of generated ammonia in the electrolyte during the eU2A (70°C, 0.750 V vs. Hg/HgO) process using the Ni foil (6.0 cm$^2$) and graphene-coated Ni (2.0 cm$^2$) and its comparison with the THU (70 °C) process in a period of 24 hours using 5.0 M urea in the presence of 2.5 M K$_2$CO$_3$. (b) Normalized concentration (per cm$^2$ of the working electrode) of generated ammonia on the electrode surface during eU2A (70 °C, 0.750 V vs. Hg/HgO) process using the Ni foil and graphene-coated Ni. Ammonia generation increased in the eU2A compared to the THU process and the generated ammonia per surface area is higher using the graphene-coated Ni than using the Ni foil. ......................................................................................................................................... 105

Figure 6.8. (a) Normalized concentration of Ni ion (per cm$^2$ of the working electrode) in the electrolyte in the 24-hours eU2A experiments using the Ni foil and graphene-coated Ni working electrodes. (b) pH change during eU2A reactions using the Ni foil and graphene-coated Ni. The pH value of the electrolyte is time dependent; pH value is reduced in eU2A process due to the transformation of K$_2$CO$_3$ to KHCO$_3$ by the generated CO$_2$ from eU2A reaction. With the help of graphene coating, the normalized Ni loss per surface area was reduced by ~ 20 times. ................................................................................................................. 107

Figure A1.1. The concentration of ammonia in the eU2A and THU experiments in the three-electrode reactor using K$_2$CO$_3$/KHCO$_3$/NH$_3$/H$_2$O equilibrium supporting electrolyte. ......................................................................................................................................... 131

Figure A3.1. Gas sampling from the two-electrode eU2A reactor......................... 133
Figure A3.2. Gas sampling from the three-electrode eU2A reactor...................... 134
Figure A6.1. The three-electrode eU2A reactor using a three-neck flask. The reference electrode was supported by a homemade Luggin capillary. ................................. 141
Figure A7.1. (a) The electrochemical cell for in-situ Raman spectroscopy; (b) the schematic arrangement of the working electrode and counter electrode. ......................... 142
Figure A8.1. (a) Additional ammonia generation rate of eU2A using 7.0 KOH with the Ni beads and Ni foil as the working electrode. (b) Normalized additional ammonia generation rate (per cm$^2$) of eU2A using 7.0 KOH with the Ni beads and Ni foil as the working electrode................................................................. 144
Figure A8.2. Normalized additional ammonia generation rate (per cm$^2$) in the 24-hour eU2A experiments using 2.5 M K$_2$CO$_3$ as the supporting electrolyte with the Ni foil and graphene-coated Ni as the working electrode. ................................. 145
Figure A8.3. Normalized additional ammonia generation rate (per cm²) of eU2A using different supporting electrolytes with the Ni foil and graphene-coated Ni as the working electrode................................................................. 146

Figure A8.4. Equilibrium pressure of carbon dioxide over (a) 30 percent and (b) 40 percent equivalent potassium carbonate solution [6]................................................................. 147

Figure A8.5: Ammonia generation in the eU2A and THU experiments for 5.0 M urea in the K₂CO₃/KHCO₃/NH₃/H₂O equilibrium system at 70 °C. ......................................................... 148

Figure A8.6: Normalized additional ammonia generation rate in the eU2A experiments using different supporting electrolytes with the Ni foil and graphene-coated Ni as the working electrode............................................................................................................ 149

Figure A8.7. Concentration of the Ni ions in the reagent solution in the 12-hour eU2A (0.85 V vs. Hg/HgO, 70 °C) experiments with the Ni foil and graphene-coated Ni as the working electrodes and the 12-hour THU (70 °C) experiment for 5.0 M urea in the K₂CO₃/KHCO₃/NH₃/H₂O equilibrium system. .............................................................. 150

Figure A9.1. The reagent solution turned to blue indicating the corrosion of the Ni electrode. The solution changes from transparent to bluish color after the 24-hour eU2A (0.750 V vs. Hg/HgO, 70 °C) experiment for 5.0 M urea in the presence of 2.5 M K₂CO₃. ......................................................................................................................................... 151

Figure A9.2: Concentration of the Ni ions in the reagent solution in the 24-hour eU2A experiments (0.75 V vs. Hg/HgO, 70 °C) with the Ni foil and graphene-coated Ni working electrodes using 5.0 M urea in the presence of 2.5 M K₂CO₃.............................................................. 152

Figure A10.1. Copper melting in the Mable agent. ........................................................ 153

Figure A10.2. Graphene being cleaned in DI water. .................................................. 153

Figure A11.1. SEMs of the graphene-coated Ni with magnification of (a) 50, (b) 500, (c) 3000, and (d) 5000. The area highlighted with a green rectangle corresponds to the higher magnification on the next image pointed out by a green arrow................................................................. 154

Figure A12.1. Solubility of ammonia in water [7].......................................................... 155

Figure A12.2. Equilibrium ratios for ammonia-water up to the critical point of ammonia [9]......................................................................................................................... 156

Figure A12.3. Schematic diagram for the migration of ammonia in the eU2A system. 156
CHAPTER 1: INTRODUCTION

1.1 Project Significance

Emissions containing nitrogen oxides (NOx) have a significant impact on the health of living beings and the environment. Nitrogen dioxide (NO$_2$), in particular, is a major air pollutant mostly emitted from mobile engines in trucks and buses and from furnaces in industrial plants. Additionally, NO$_2$ also reacts in the atmosphere, in the presence of sunlight, to form ozone (in the ambient air) and acid rain [1]. Gas emission from mobile engines in trucks and buses generally was regulated by the Environmental Protection Agency (EPA), and the NOx emission standard has become more and more stringent over the years. After 1998, the regulations were expanded to non-mobile combustion systems, such as furnaces in power plants and industrial plants. An effective method to remove NOx from gas emission is the selective catalytic reduction (SCR) process, and this process uses reducing agents to turn NOx to non-harmful substances, such as N$_2$ and H$_2$O [1]. Typically, anhydrous or aqueous ammonia is used as a reducing agent in the SCR process [2]. The chemical reactions for converting NOx to non-harmful substances are listed below [3, 4]:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$
$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \quad (2)$$
$$3NO_2 + 4NH_3 \rightarrow 3.5N_2 + 6H_2O \quad (3)$$

However, ammonia is a toxic and corrosive substance, which makes the handling of ammonia in activities such as storage and transportation dangerous and costly for many of its applications [2]. Therefore, the on-site generation of ammonia from urea has
gained substantial attention in the research and industrial communities. Commercial urea to ammonia (U2A) conversion systems have already been developed and applied in power plants [5-7], but these U2A techniques employ high temperature and pressure which makes them difficult to adapt for mobile engine systems. Thus a simple technique is required to convert urea to ammonia under moderate operation conditions, which has become the key point in this investigation of the on-site generation of ammonia.

The urea to ammonia conversion reaction can be promoted using catalysts such as urease [8], or a number of oxides, such as alumina, silica, and palladium complex [9, 10]. A nickel (Ni) based electrochemical catalyst was developed and patented by Botte to oxidize urea to produce nitrogen (N₂), hydrogen (H₂) and ammonia (NH₃) [11]. In certain experimental conditions, urea conversion to ammonia can be promoted and becomes predominant when the reaction temperature increases to 70 °C [11]. A prototype reactor for electrochemically induced urea to ammonia (eU2A) has been developed at the Center for Electrochemical Engineering Research (CEER), Ohio University, to evaluate the conversion of urea to ammonia via an electrochemical approach. Yet, the eU2A mechanism needs to be further understood. Theoretical calculations of the urea oxidation mechanism on nickel oxyhydroxide (NiOOH) in an alkaline medium (urea electrolysis) at room temperature using the molecular modeling approach have been attempted [12] at CEER. However the reaction mechanism for the predominant conversion of urea to ammonia through electrochemical approach at higher temperature has not been thoroughly investigated. Therefore the major objective of this study is to understand the reaction mechanism for the eU2A process. This mechanism will be developed by
monitoring the intermediates and products associated with the conversion of urea to ammonia on the Ni based catalyst in alkaline media.

Compared with commercial SCR techniques used in power plants, the SCR techniques applied in mobile engines have some drawbacks. One of the major drawbacks is that the reaction temperature needed for the SCR process may not be attained in certain conditions. One of the solutions to overcome the drawbacks of the commercial SCR used for mobile engines is employing urea SCR as shown in Figure 1.1. In urea SCR, the urea solution is injected to an SCR chamber, where the decomposition of urea over the catalyst surface leads to the formation of ammonia and to the reduction of the NOx present in the chamber. The commercially available urea solution is called diesel exhaust fluid (DEF) and it contains 32.5% urea. However under low-load driving conditions, urea SCR is trapped with curtailed dosing problems due to the low exhaust temperature [13]. The incomplete decomposition of urea in curtailed dosing contaminates the SCR catalyst. The regeneration of the SCR catalyst requires heating and deep cleaning with high pressurized air, which increases the operation cost. In addition, the overall NOx conversion effectiveness is reduced for urea SCR because of the insufficient ammonia offered from the urea at this temperature [13]. Additionally, high-quality DEF is needed to prevent any damage to the SCR catalyst if there is contamination in DEF (e.g., due to the presence of minerals in water used for making the DEF solution) [14]. Furthermore, it is anticipated that the exhaust temperature will further be reduced in the future to increase the efficiency of mobile engines. Therefore, any techniques, such as eU2A, that enable
urea to ammonia conversion at lower temperatures will easily fit into future regulation frameworks.

Figure 1.1. Schematic picture of urea SCR in a mobile engine.

The alternate approach to solve the temperature issue in commercial SCR is direct ammonia SCR, as shown in Figure 1.2. This technique does not have curtailed dosing problems and the NOx conversion rate is higher than in urea SCR at low temperatures [15]. However, the installation of pressurized ammonia tanks in vehicles can be dangerous. The ammonia SCR technique is often unattractive because of the cost related to its safety systems and the potential danger associated with the harmful leakage of ammonia.

Figure 1.2. Schematic picture of ammonia SCR in a mobile engine.

The eU2A process using the Ni based catalyst is the solution offered in this investigation, as it combines both advantages of urea SCR and NH₃ SCR. In this
approach or technique, the urea to ammonia conversion takes place in a separated eU2A reactor, and the catalytic reduction of NOx is confined to the chamber. The generated ammonia from the eU2A reaction is then used for direct NH₃ SCR.

This technique enables direct NH₃ dosing for the SCR process, and thereby has the full benefit of the NH₃ SCR and safe urea storage [15, 16].

![Figure 1.3](image)

**Figure 1.3.** Proposed urea SCR utilizing the eU2A technique in a mobile engine.

### 1.2 Research Objectives

As proposed above, the eU2A process is a suitable technique for the on-site generation of ammonia which can be fed into the SCR process in mobile engines. Therefore, the overall objectives of this dissertation are to prove the feasibility of the eU2A process, discern the factors that affect ammonia generation in the eU2A process and develop a fundamental understanding of the process. Additionally, the corrosion of Ni due to the ammonia formed in the eU2A process using K₂CO₃ as the supporting electrolyte will be addressed.

The investigation starts with a two-electrode eU2A system that does not use a reference electrode, which is more practical and convenient in real-life application. By comparing the ammonia generation rate between the eU2A and the thermal hydrolysis of
urea to ammonia (THU) processes under different operation conditions, including different temperatures, different applied potentials, and different supporting electrolytes, the advantages of the eU2A process can be revealed.

This research work is the initial phase of investigation in this field since few works have been done to study the electrochemically induced process for urea conversion to ammonia and no clear mechanism has been established to define the process. The potential mechanisms involved in the eU2A process will be investigated using a three-electrode system by introducing a mercury/mercury oxide (Hg/HgO) reference electrode. By monitoring and identifying the intermediates, products, and by-products, both in the bulk solution and on the surface of the working electrode, a clear understanding of the reaction steps during the eU2A process can be derived.

The generation of CO₂ during the eU2A process gradually changes the initial supporting electrolyte, KOH, to K₂CO₃. Therefore, the eU2A process was also studied with K₂CO₃ as the supporting electrolyte. However, the ammonia was found to cause corrosion of the Ni electrode when the supporting electrolyte was changed to K₂CO₃. Ni is corrosion resistant to a diluted ammonium hydroxide solution, but a rapid attack on Ni appears when the ammonium hydroxide concentration is higher than 1% [17]. Since the eU2A process involves a heterogeneous reaction with ammonia generation on the Ni working electrode surface, the localized ammonia concentration on the Ni electrode surface is high. In addition, as shown in the literature review, when K₂CO₃ is used as the supporting electrolyte, the solution pH falls into a region where Ni reacts with ammonia to form a soluble Ni-ammonia complex. Therefore Ni working electrode is vulnerable in
the eU2A process. To overcome this problem, coating the Ni electrode surface with graphene is proposed in this dissertation as a corrosion prevention method.

Graphene has many intrinsic properties such as incomparably high electron mobility, excellent thermal and mechanical properties, a large specific surface area, and exceptional chemical stability [18-21]. Graphene coating has been proven as an effective method for protecting metal surfaces from corrosion [18, 22]. In addition, a graphene-Ni nanocomposite was shown to be promising catalyst for urea electrolysis [23]. It was also observed that with a graphene-covered surface, the peak current for NiOOH (the proposed working catalyst in eU2A) formation is higher than when using bare Ni foil. Therefore, a graphene coating on the Ni electrode is expected to not only protect Ni from ammonia corrosion but also increase the ammonia generation rate.

Within this context, the specific objectives of this study are as follows:

1. To ascertain that the eU2A process is feasible for the on-site production of ammonia and to confirm the advantages of eU2A over THU by comparing the ammonia generation rate under different operation conditions.

2. To investigate the factors that correlate with ammonia generation in the eU2A process to get a better understanding and to propose a mechanism for the eU2A process based on the observations in this investigation.

3. To prove that the corrosion of the Ni working electrode due to ammonia can be prevented or reduced by a graphene coating and to compare the ammonia generation rate with and without the graphene coating. This objective requires successful graphene synthesis and graphene coating on the Ni electrode.
To achieve the above mentioned objectives, the present work includes the use of
electrochemical techniques, such as cyclic voltammetry (CV) and chronoamperometry;
and analytical techniques, including ultraviolet and visible (UV-visible) spectroscopy,
gas chromatography with a TCD detector, Fourier transform infrared spectroscopy
(FTIR), Raman spectroscopy, transmission electron microscopy (TEM), atomic force
microscopy (AFM), and atomic absorption spectroscopy (AAS) with a Ni hollow cathode
lamp.
CHAPTER 2: LITERATURE REVIEW

2.1 Ammonia

Ammonia is an important chemical utilized in various fields such as the fertilizer [24], and food industries [25]. Ammonia is a proven hydrogen resource in the fuel cell industry [26]. In mobile engines and industrial furnaces, it is often used as an effective reducing agent for in the SCR process to control NOx emissions. A large-scale process to synthesize ammonia was invented by Haber from elemental hydrogen and nitrogen gas at high temperature (~ 500 °C) and high pressure (~ 150-200 atm) using an iron catalyst [27].

Exposure to high concentrations of ammonia is harmful to human health. The Occupational Safety and Health Administration (OSHA) classifies anhydrous ammonia as a highly hazardous chemical. The short-time (15 minutes) exposure limit is 35 ppm, or 27 mg m\(^{-3}\) under the Process Safety Management Standard [6, 28]. As a result, the transportation, storage, and handling of ammonia has strict safety and environmental regulatory requirement which makes the utilization of ammonia costly [29].

2.2 Urea to Ammonia

Urea is stable under ambient temperature and pressure and its nontoxic property presents no hazardous effect to the environment. No leakage and explosion problems are associated with urea that affect ammonia utilization, which allows it to be shipped in bulk and stored for a long period of time before being converted to ammonia. Therefore, urea has become a favorable ammonia source.
The commercial method of urea hydrolysis to ammonia that are practiced in power plants, such as U2A™ by Wahlco, requires 150 °C and 5-6 atm, which is not suitable for the deNOx SCR process in mobile engines since the operation conditions cannot be satisfied [6]. In the case of mobile engines, urea is converted to ammonia using the heat of the exhaust, and the produced ammonia takes part in the NOx reduction reaction across the SCR catalyst. However, in lean combustion, such as in low-load urban driving, curtailed urea dosing facilitates the process [13, 30]. In contrast, direct NH₃ SCR broadens the working range, thus allowing the emission of NOx from low-load urban driving to meet the emission standard (Figure 2.1) [16].

![Figure 2.1. Comparison of NH₃ SCR and urea SCR. It can be seen that the working windows of NH₃ SCR are broader [16].](image)

2.3 Methods for Urea to Ammonia Conversion

2.3.1 Urea Hydrolysis to Ammonia

Urea hydrolysis is the traditional and predominant method of producing ammonia from urea for the SCR process. Urea can naturally be decomposed to ammonia and
carbon dioxide at a low rate at room temperature. At temperatures less than 239 °F (115 °C) the urea hydrolysis reaction does not occur at a significant rate and “it would give rated ammonia production at around 305 °F (152 °C)” [6] as shown in Figure 2.2.

![Figure 2.2](image)

Figure 2.2. Reaction rates as a function of temperature on a commercial U2A™ reactor based on a 40% urea solution feed [6].

2.3.2 Urea to Ammonia by Non-Thermal Plasma

Iitsuka et al. and Prieto et al. investigated a non-thermal plasma method to produce ammonia from urea at 120 °C [31, 32]. However, the conversion rate was not explored due to the poor mass balance and uncertainty about the mechanism of urea to ammonia re-forming in the discharge plasma. Besides, this process requires high voltage (15 kV) and high frequency (5 kHz), according to the literature [32], and they are not applicable in mobile engines since the conditions are inaccessible.

2.4 The Advantages of eU2A

The urea to ammonia conversion and NOx reduction process are decoupled by utilizing the eU2A technique for ammonia generation as shown in Figure 1.3. Thus,
direct NH₃ SCR and safer use can both be employed. In addition, the direct supply of ammonia gas without water and the byproduct of hydrogen from eU2A can provide more benefits for the urea SCR.

2.4.1 The Effect of Water Vapor in SCR

In the urea SCR system, the injection of a urea solution increases the partial pressure of water vapor inside the reactor, causing catalyst deactivation and affecting the NOx conversion rate. As shown in Figure 2.3, the NOx conversion rate drastically decreased when the water concentration was increased in the SCR chamber. It was also observed that the working temperature range of NO reduction was narrowed down with the presence of water vapor in the SCR chamber as shown in Figure 2.4 [33].

![Figure 2.3](image)

Figure 2.3. Conversion of NO versus H₂O concentration in the feed. ● 190 °C, ▲ 210 °C, ▼ 230 °C, ■ 250 °C. Feed: 10% O₂, 1000 ppm NO, 1000 ppm NH₃, 0-7.5% H₂O, balance N₂. Flow rate: 500 mL min⁻¹ at normal temperature and pressure (NTP) [33].
32

Figure 2.4. Conversion of NO versus temperature for dry and wet feed. ● 0% H2O, ▲ 2.5% H2O, ▼ 5% H2O, ■ 7.5% H2O. Feed: 10% O2, 1000 ppm NO, 1000 ppm NH3, 0-7.5% H2O, balance N2. Flow rate: 500 mL min⁻¹ (NTP) [33].

In the eU2A reactor, the 70 °C-80 °C operating temperature is lower than the water vapor point in ambient conditions. Therefore, water vapor is limited in the flue gas. Additionally, the eU2A reactor is loaded outside the SCR system and it is easier to remove water vapor from the NH3 reservoir using water absorption methods.

2.4.2 The Effect of Hydrogen in SCR

Urea electrolysis is a parallel reaction in the eU2A process, which means a small amount of hydrogen gas is produced in the process and this production of hydrogen has no harmful effect on the SCR process. H2 SCR has received much attention because it is efficient and nontoxic, and forms less N2O at low temperatures [34-36]. The H2 SCR can operate at low temperatures of above 55 °C as it was first claimed by Fu and Chuang [37]. As a result, H2 SCR has the advantage of working for low-load lean combustion conditions when the exhaust temperature is low. A recent investigation indicated that it can convert 75% of NO over a Pt/SiO2 catalyst at 90 °C [38]. Moreover, by adding H2, a
great improvement in the NOx conversion rate was achieved in NH$_3$ SCR and urea SCR [39-41]. The addition of H$_2$ also prevents N$_2$O formation over a wide temperature range. It was also found that the catalyst Ag/Al$_2$O$_3$ showed higher SO$_2$ tolerance with the addition of H$_2$ to the reducing agent [39] as shown in Figure 2.5. Therefore, the H$_2$ generated in the eU2A process provides an additional advantage to the eU2A technique.

![Figure 2.5. NO conversion to N$_2$ (○) and N$_2$O (●) vs. time of 50 ppm SO$_2$ addition in H$_2$-NH$_3$-SCR at 200 °C (GHSV = 70,000 h$^{-1}$) [39].](image)

2.5 The Mechanism of Converting Urea to Ammonia

2.5.1 Urea Hydrolysis

In the urea SCR system for mobile engines, the urea hydrolysis of urea to ammonia using a urea water solution (UWS) follows two stages. In the first stage, UWS dehydrates, as depicted in Eq. 4, and the solid urea decomposes to ammonia and isocynic acid (HCNO), as shown in Eq. 5 [42].

\[
CO(NH$_2$)$_2$(aq) \rightarrow CO(NH$_2$)$_2$(s) \tag{4}
\]

\[
CO(NH$_2$)$_2$(s) \rightarrow NH$_3$(g) + HCNO(g) \tag{5}
\]
In the second stage, as shown in Eq. 6, HCNO is further decomposed to ammonia and carbon dioxide depending on the nature of the catalyst. Generally, HCNO decomposition occurs on the SCR catalyst, occupying the working surface area of the catalyst only for the SCR process and thus reducing the conversion rate of NOx. Therefore, some techniques have added an upstream catalyst just for HCNO decomposition [43]. Warner conducted a detailed analysis of urea hydrolysis at different pH values [44]. In alkaline solutions, the following reactions were proposed:

\[
CO(NH_2)_2(aq) \rightarrow NH_4^+ + CNO^- \quad (7)
\]

\[
NH_4^+ \rightarrow NH_3 + H^+ \quad (8)
\]

\[
H_3O^+ + CNO^- \rightarrow NH_3 + CO_2 \quad (9)
\]

Figure 2.6. Hydrolysis of urea as a function of pH at 66 °C [44].

When the pH value is above 12, reactions (7) and (9) could be considered irreversible, thus both reactions follow first-order reactions [44]. For different pH values,
Warner also did a series of experiments to quantify the reaction rate constant for the hydrolysis of urea to ammonia as shown in Figure 2.6. The researcher observed that when the pH is higher than 12, the alkalinity becomes rate controlling [44].

2.5.2 Catalysis of Urea to Ammonia Using Urease

Urea to ammonia can be catalytically improved using urease as a catalyst, by which the process of eU2A can be better understood. Ureases are a Ni-dependent enzyme family, and jack bean urease is shown to be a very proficient, stable, and highly specific enzyme [8, 45]. Figure 2.7 depicts a proposed mechanism for the catalytic conversion of urea to ammonia using urease. One Ni ion (Ni-1) binds and activates the urea molecule, with one resonance structure stabilized by a nearby carboxylate ion, while the second Ni ion (Ni-2) binds with a hydroxide ion. The latter molecule is activated for attack on the urea carbon by a protein residue acting as a general base. The collapse of the tetrahedral intermediate eliminates ammonia with the help of an active site thiol present in the urease molecule, which is proposed to act as a general acid [45].
2.5.3 Electro-Catalytic Dissociation of Urea

Though several studies have investigated the feasibility of various feasible catalysts for the urea hydrolysis process [43, 46], currently the work related to urea to ammonia conversion in alkaline medium through an electrochemical approach is limited. Hence, the oxidation mechanism of other organic compounds, such as methanol and ethanol, on Ni based catalysts [47-49] and the research work on urea catalytic hydrolysis and electrolysis [12] are used as references for the mechanism investigation of the eU2A process.

Daramola et al. [50] studied the dissociation rates of urea in the presence of NiOOH using Density Functional Theory (DFT) methods and reported the desorption of CO$_2$ from urea as the rate-limiting step. According to the authors, the mechanism could be the indirect dissociation of urea to ammonia and cyanate ion through NiOOH (Ni$^{3+}$) owing to the formation of Ni(OH)$_2$ (Ni$^{2+}$):
The reaction of a cyanate ion with a hydroxide ion is proposed, but not explored in their study. Or, it could be the direct decomposition of urea to ammonia and carbon dioxide, as indicated in Eq. 12 [51].

\[
NiOOH \cdot OH^- + CO(NH_2)_2 \rightarrow [Ni(OH)_2 OH \cdot NHCONH_2]_{ads} \tag{10}
\]

\[
[Ni(OH)_2 OH \cdot NHCONH_2]_{ads} \rightarrow [Ni(OH)_2 OH \cdot NCO]_{ads} + NH_3 \tag{11}
\]

2.6 Ammonia Corrosion of Ni in eU2A

During the eU2A process, the reagent in the reactor has a high ammonia concentration, especially on the surface of the working electrode, since the eU2A reaction is heterogeneous. Because there is Ni-ammonia complex (Eq. 13, n = 1-6) [2] formation, corrosion becomes an issue in the eU2A process. Figure 2.8 shows the form of a Ni\(^{2+}\) ion in different pH regions for 0.01M Ni\(^{2+}\) in 1.0 M (NH\(_4\))\(_2\)SO\(_4\) solution. Between pH 8 and 12, a series of Ni-ammonia complexes have an increasing number of incorporated ammonia ligands, and six ligands are allowed at the maximum for accommodation by the Ni ion [52]. For the pH region beyond 12, the stable form is Ni(OH)\(_2\), which means when using KOH in the eU2A reaction, Ni will stick on the electrode surface in the form of Ni(OH)\(_2\). However, when the pH value of the solution is lower than 12, the soluble Ni-ammonia complex forms to cause a loss of Ni.
In an eU2A reaction using 1.0-7.0 M KOH as the supporting electrolyte, the pH value of the reagent solution is higher than 13, and the corrosion of Ni is subtle [53]. However when using 2.5 M K₂CO₃ as the supporting electrolyte at 70°C, the pH value of the reagent is ~ 11. In addition, ~ 70% of K₂CO₃ will eventually be converted to KHCO₃ at an equilibrium state when CO₂ is consistently generated during eU2A [54], and the pH value of the electrolyte will be further reduced. According to Figure 2.8, Ni²⁺ will be in the form of a Ni-ammonia complex ([Ni(NH₃)ₙ]²⁺). The formation of the complex not only causes the corrosion of the Ni catalyst but also reduces the generation of ammonia by consuming ammonia as ligands to form the Ni-ammonia complex.

2.7 The Anti-Corrosion Graphene Coating

Graphene is the name given to a flat monolayer composed of sp² hybridized carbon atoms that are tightly packed. Geim and Novoselov won the Nobel Prize in 2010 for their discovery of 2D graphene material. Graphene can be “wrapped up into 0D
buckyballs, rolled into 1D nanotubes or stacked into 3D graphite” [21], as represented in Figure 2.9. The structure and excellent properties of graphene were well demonstrated by Geim and Novoselov [21]. As an anti-corrosion coating method, the graphene coating can protect a metal surface, but not alter the intrinsic properties of the protected metal [18]. Therefore graphene is proposed to protect Ni in the ammonia-concentrated environment in the eU2A experiments.

Figure 2.9: Mother of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite. The image is reproduced from Geim and Novoselov [21].
CHAPTER 3: EXPERIMENTAL METHODOLOGY

3.1 The Two-Electrode eU2A Reactor

The eU2A reactor vessel was assembled with a lid, a bottom and a hollow cylinder. All three parts were machined at the Center for Electrochemical Engineering Research (CEER) from Teflon rods (Virgin Electrical Grade Teflon rods with 75 mm diameter from McMaster-Carr). The size of each part and the dimensions of the fittings on the lid are shown in Figure 3.1a. The O-ring seal was made of Fluorosilicone (Paker), which has good chemical resistance to ammonium hydroxide. Compression fittings were used to connect the thermocouple, gas outlet, sample port, and electrodes’ current collectors, as shown in Figure 3.1b. The reactor is a two-electrode system. The anode was built by filling a Ni mesh (DEXMET Corporation, 7 Ni 7-077) cylinder-type basket with 2,000 Ni beads (purity 99%, surface area of 0.32 cm², New England Miniature Balls), and a Ni rod (diameter 6.35 mm and purity 99.5%) was used as the anode current collector as shown in Figure 3.1a. The anode was the working electrode in the reactor with a volume of 47 cm³, which was measured by water displacement. The cathode consisted of a round Ni mesh (bottom diameter: 6.0 cm; height: 9 cm) (DEXMET Corporation, 7 Ni 7-077) and the picture of the cathode is shown in Figure 3.1b. The cathode mesh was placed concentrically around the anode (the distance between the electrodes was 7.5 mm). A Ni wire (diameter 1.0 mm, purity 99.5%, Alfa Aesar) was spot-welded into the mesh of the cathode and used as cathode current collector (see “cathode” in Figure 3.1b). A silicone strip heater (ZORO tools, SHS80411) was pasted around the reactor vessel as a heating element controlled by a temperature controller.
(Econo Temperature controller 12125-14) equipped with a type “K” thermocouple (OMEGA Engineering Inc.). The uncertainty of the temperature was ± 1 °C. The heater was covered by fiberglass (Frost King) and insulation tape (Polyken). After assembling the reactor, a two-electrode eU2A experimental system was set up as shown in Figure 3.2.

The reagent -250 mL DEF in the presence of 7 M KOH- was made by dissolving KOH (containing 10~15% of water, Fisher Scientific) into DEF (32.5% of urea, Old World Industries, LLC). The ammonia gas was trapped in a 1.0 L 1.0 M sulfuric acid solution made from the dilution of concentrated sulfuric acid (purity 98.0%, Fisher Scientific). Between each of the two experiments, the cathode and anode were rinsed with 0.01 M HCl and followed by sonication in deionized water (DI) for 1 hour using a sonicator (Zenith Ultrasonics, G2-40) at 40kHz. Finally, the cathode and anode were rinsed with DI water and then allowed to dry naturally. In the eU2A experiments, voltage was applied once the reagent reached the desired operating temperature. The applied cell voltage was controlled by an Arbin BT2000 potentiostat. The ammonia that was generated and the urea that was consumed during the heating cycle of the eU2A process were quantified and subtracted from the final results for material balance and the ammonia generation rate. The thermal hydrolysis process (THU) took place in the same reactor without applying a cell voltage between the electrodes.
Figure 3.1. Design of the two-electrode EU2A reactor. (a) The features of the reactor vessel and working electrode. (b) Photograph of the cathode, anode, and reactor vessel from top and side view.
3.2 The Three-Electrode eU2A Reactor

To understand the mechanism of the eU2A process, the experiments were performed in a three-electrode eU2A reactor system. The body of the three-electrode eU2A reactor was a 100-mL three neck flask, the working electrode was a Ni foil (2.0 x 3.0 cm, purify > 99%, Alfa Aesar), and the counter electrode was also a Ni foil (2.0 x 3.0 cm, purify > 99%, Alfa Aesar). Hg/HgO was introduced into the reactor as the reference electrode supported by a Luggin capillary, as shown in Figure 3.3. Ni wire (diameter 1.0 mm, purity 99.5%, Alfa Aesar) was spot-welded to the working and counter electrode as the current collector. A heating mantle (Gals-Col®) was used to heat the electrolyte which was controlled by a temperature controller (Econo Temperature controller 12125-14) equipped with a type “K” thermocouple (OMEGA Engineering Inc.).

To investigate the corrosion behaviors of the Ni working electrodes in the eU2A experiments, the counter electrode was changed to a platinum foil (1.0 cm x 1.0 cm,
purity > 99%, Alfa Aesar). The corrosion of the working electrodes was compared between the graphene-coated Ni (1.0 cm x 2.0 cm; its preparation is discussed in Section 3.9) and bare Ni foil (2.0 x 3.0 cm, purity > 99%, Alfa Aesar). Pt wires (diameter 0.5 mm, purity 99.5%, Alfa Aesar) were spot-welded separately to the working and counter electrodes as the current collectors.

Figure 3.3. The three-electrode eU2A reactor. The reference electrode was supported by a homemade Luggin capillary.

3.3 Ammonia Determination Using an Ion Selective Electrode

The concentration of ammonia in solutions was determined by using an ammonia selective electrode (ISE) (Orion 710A+, Thermo Electron Corporation), which consisted of an ISE meter and an ammonia gas-sensing probe (schematically shown in Figure 3.4). By adding the adjusting solution (Orion 951210, Thermo Electron Corporation) to the sample, the ammonium ion in the solution was transformed to ammonia gas (Eq. 14)
which diffused into the inner body of the gas-sensing probe through a hydrophobic but porous membrane [55].

\[
NH_4^+ + OH^- \rightleftharpoons NH_3 \uparrow + H_2O \tag{14}
\]

The changes in pH value inside the probe was recorded and analyzed by the ISE meter to determine the concentration of ammonia in the testing samples.

![Schematic picture of the ammonia gas-sensing probe](image)

Figure 3.4: Schematic picture of the ammonia gas-sensing probe [55].

The ammonia generated in the experiments consisted of two parts: the dissolved ammonia in the electrolyte in the reactor and the emitted ammonia trapped in the acid trap. For the eU2A reaction using KOH as the supporting electrolyte in the two-electrode reactor, the ammonia in both the reactor and the trap was measured while for the other experiments, the ammonia was measured only in the reactor unless otherwise specified, assuming the generated ammonia would be completely dissolved in the reactor.

At each sample point, a certain amount of the reagent solution was collected from the reactor using a long needle syringe and diluted to 100 mL. The concentration of
ammonia in the diluted samples (in ppm, 1 ppm = 5.87×10⁻⁵ M for ammonia) was measured using the ammonia ISE. The concentrations of ammonia in the reactor and trap were determined by Eq. 15 and Eq. 16. Then the total generated ammonia was the sum of ammonia in the reactor and the trap as shown in Eq. 17.

\[
C_{NH_3,r} = C_{NH_3, sample, r} \times \frac{V_f}{V_{i,r}} \times 5.87 \times 10^{-5}
\]  
(15)

\[
C_{NH_3,t} = C_{NH_3, sample, t} \times \frac{V_f}{V_{i,t}} \times 5.87 \times 10^{-5}
\]  
(16)

\[
n_{NH_3} = C_{NH_3, r} \cdot V_r + C_{NH_3, t} \cdot V_t
\]  
(17)

where,

- \(C_{NH_3, sample, r}\), the measured concentration of ammonia in the diluted sample in the reactor, in ppm;
- \(C_{NH_3, r}\), the measured concentration of ammonia in the diluted sample in the reactor, in M;
- \(C_{NH_3, sample, t}\), the measured concentration of ammonia in the diluted sample in the trap, in ppm;
- \(C_{NH_3, t}\), the measured concentration of ammonia in the diluted sample in the trap, in M;
- \(n_{NH_3}\), the total amount of ammonia generated in the experiments, in mol;
- \(V_f\), the volume of the diluted sample, in mL, \(V_f = 100\) mL;
- \(V_{i,r}\), the volume of the solution sampled out from the reactor, in mL;
- \(V_{i,t}\), the volume of the solution sampled out from the trap, in mL;
In the eU2A process, to exclude the effect of THU in the bulk solution, the term “additional ammonia” was created to demonstrate the concentration difference between the ammonia generated in the eU2A and THU experiments (Eq. 19), which quantifies the amount of ammonia generated on the surface of the working electrode in the eU2A reactor. The additional ammonia generation rate was calculated using Eq. 20 and Eq. 21. The normalized additional ammonia generation rate per area was calculated using Eq. 22.

\[ C_{i, \text{add.}} = C_{i, \text{eU2A}} - C_{i, \text{THU}} \quad (i = 1, 2, 3, \ldots, n) \]  

\[ r_i = \frac{dC_{i, \text{add.}}}{dt} = \frac{C_{i+1, \text{add.}} - C_{i, \text{add.}}}{\Delta t_i} \quad (i = 1, 2, 3, \ldots, n) \]  

\[ r = \frac{\sum_{i=1}^{n} r_i}{N} \]  

\[ r_A = \frac{r}{A} \]  

where,

- \( C_{i, \text{add.}} \), the additional ammonia generated on the surface of the working electrode, in M;
- \( C_{i, \text{eU2A}} \), the concentration of the ammonia generated during the eU2A experiments, in M;
- \( C_{i, \text{THU}} \), the concentration of the ammonia generated during the THU experiments, in M;
- \( i \), the sample point;
- \( r_i \), the additional ammonia generation rate between the two adjacent sampling points, in M min\(^{-1}\) or M h\(^{-1}\);
- \( r \), the additional ammonia generation rate, in M min\(^{-1}\) or M h\(^{-1}\);
- \( r_A \), the normalized additional ammonia generation rate, in M min\(^{-1}\) cm\(^{-2}\) or M h\(^{-1}\) cm\(^{-2}\).
\( \Delta t \), time intervals between two adjacent sampling points, in min or h;

\( N \), the total numbers of the sampling points;

\( A \), the geometric surface area of the working electrode used in the eU2A process, in cm\(^2\);

### 3.4 UV-Visible Spectroscopy for Urea Determination

UV-visible spectroscopy was performed with a Hewlett Packard Spectrophotometer HP 8452A to determine the amount of urea converted during the experiments. A coloring agent [56] was used to color the urea-containing sample solutions. The agent was prepared by mixing 2 g of p-dimethylaminobenzaldehyde (p-dye, Fisher Scientific), 100 mL of ethyl alcohol (95\%, Denatured with isopropyl alcohol (IPA) and methanol, Fisher Scientific), and 10 mL of hydrochloric acid (12.1 N, Fisher Scientific). As shown in Figure 3.5, the standard solutions, 0.008, 0.016, 0.024, 0.032, and 0.040 M, were prepared by dilution from 1 M of urea solution made of urea powder (purity > 99\%, Fisher Scientific) to calibrate the UV-visible spectroscopy. As demonstrated in Figure 3.5, the broad maximum absorbance region (420 nm to 435 nm) presented by the urea-containing solutions and p-dye can be used to quantify the concentration of the urea. At 420 nm, the standard solutions had the maximum absorbance, and the concentration of urea, \( C_{\text{urea}} \), in was proportional to the absorbance, \( A_{\lambda} \), \( C_{\text{urea}} = 0.0916A_{\lambda} + 0.00231, \; R^2 = 0.9996 \). As a result, the urea concentrations for the samples could be obtained based on the absorbance at 420 nm using this linear equation.
The testing samples were prepared as follows: 0.4 mL from the 50 mL diluted testing samples were transferred to UV-visible cuvettes and mixed with 1.6 mL coloring agent and 2.0 mL DI water to make 4.0 mL colored samples. The UV spectra of the samples were then obtained with the UV-visible spectrophotometer. Based on the linear equation in Figure 3.5(inset) and the absorbance of each sample at 420 nm, the concentrations of the diluted samples were determined. The concentration of residual urea in the reactor was then calculated using Eq. 23.

\[
C_{area, r} = C_{area \ sample, r} \times \frac{V_f}{V_i}
\]

where,

- \(C_{area, r}\), the additional ammonia generated on the surface of the working electrode, in M;
- \(C_{area \ sample, r}\), the concentration of generated ammonia during the eU2A experiments, in M;
- \(V_f\), the volume of the diluted sample, in mL;
- \(V_i\), the volume of the solution sampled out from the reactor, in mL;

Figure 3.5. UV-vis spectra of standard urea solutions from 0.008 M to 0.040 M. The linear relationship between the absorbance and urea concentration was obtained at 420 nm as shown in the inset figure.
3.5 Gas Chromatograph (GC)

The components of the gaseous products, which were collected from the gas collection column as shown in Appendix A3, were determined by a gas chromatograph (GC) (Agilent Technologies 7890 B). The GC, running helium as a carrier gas, was equipped with a Molsieve 13X column and a thermal conductivity detector to separate N₂, O₂, and H₂ simultaneously. The percentage of each gas component was determined by calibration with the peak area of standard gases using the GC. After excluding the contamination of air in the collected gas, the amount of generated N₂ and H₂ could be approximately calculated using the ideal gas law. The presence of ammonia in the gas phase was not expected since the emitted ammonia was trapped in the DI water in the column. Similarly, any CO₂ produced was absorbed by the KOH solution to form K₂CO₃ in the reactor. A typical chromatogram for the sampling gas is presented in Figure 3.6.

Figure 3.6. Typical gas chromatogram for a collected gas sample.
3.6 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was conducted on a Bruker Vertex 80 Instrument Spectrum One Fourier Transform Spectrometer using the KBr pellet-pressing method. A small amount of ground KBr was transferred to the pellet-making die and sufficient pressure was applied (Figure 3.7). After 2 minutes, the die was disassembled to obtain a KBr pellet. In each measurement, a 20 μL testing sample was dropped on the pellet before an FTIR scan. The FTIR spectra for the samples were then collected in the wave numbers of 68-4451 cm⁻¹ region. The single-beam FTIR spectrum of the KBr pellet was acquired as the background before each measurement.

![Figure 3.7. KBr pellet-pressing die.](image)

3.7 In-situ Raman Spectroscopy

The in-situ measurements can give insight to the reaction pathway involved in an electrochemical reaction. This technique is applied to obtain information in relation to the intermediates and products formed during the electrochemical induction of urea to ammonia on a Ni catalyst. The Raman spectra were recorded at certain temperatures using a Bruker Senterra Raman spectrometer and microscope equipped with a 10X
objective lens, 20 mW power and 532 nm laser excitation wavelength. The electrochemical process was conducted using a Solartron 1281 multiplexer potentiostat in a conventional three-electrode cell setup with Ni foil as the working and counter electrode, and with Hg/HgO as the reference electrode. The assembly of the electrochemical cell is shown in Figure 3.8 and its dimensions are shown in Appendix Figure A7.1. For the experiments, the Raman spectra were recorded using the spectrometer with the lens focusing onto the working electrode surface through a silica window embedded in the cell.

Figure 3.8. (a) Schematic configuration of the *in-situ* Raman eU2A cell. (b) Photograph of the *in-situ* Raman eU2A cell. The working electrode (WE) and counter electrode (CE) are both Ni foil, and the reference electrode (RE) is Hg/HgO.
3.8 Chemical Vapor Deposition of Graphene

Chemical vapor deposition (CVD) is a conventional method used to deposit thin films on substrates, generally metal foil, through chemical reactions from vapor species [57]. Large-area graphene films with high quality can be synthesized by the CVD technique [58, 59]. A CVD system incorporates a gas delivery and removal system, a higher-temperature reactor (furnace), and a metal substrate for thin film growth [57]. In the gas delivery and removal system, flow controllers connected to the inlet of the furnace are employed to control the flow rate of the reactive gases. Both precursor gases and gases as reducing agents are provided for the reaction in the reactor to proceed. The non-reacted gaseous species are vented out through the exhaust [57]. The CVD system is operated at atmospheric pressure or low pressure depending on the need of the reaction, and if low pressure is needed, then one or more vacuum pumps are used [57].

Figure 3.9 exhibits a CVD system with a high-temperature furnace and gas delivery system for this investigation. The plentiful availability of inexpensive coal resource makes it a low-cost carbon source to produce nanostructures [60]. Therefore in this work, coal was utilized as the carbon source for growing graphene. Vijapur [61] determined the optimization parameters for CVD graphene production from Wyodak Coal. The graphene used for the surface coating on the Ni electrode in this investigation was made following Vijapur’s investigation.
Figure 3.9. The CVD setup for graphene growth on copper foil. The setup consists of a high-temperature furnace, gas delivery system with flow controllers, and exhaust system with a vacuum pump [61].

The temperature profile for the CVD graphene synthesis process and the description of each step are shown in Figure 3.10. The CVD setup for producing graphene from raw coal is shown schematically in Figure 3.11 with the dimensions of the quartz tube and quartz boated reported. The two quartz boats used in the process was first rinsed with acetone. After rinsing with acetone, copper was positioned on the end of one of the two quartz boats while 10 mg of Wyoming coal (< 44 µm, sieved, Wyodak coal seam) was put on the other end of the other boat, as shown in Figure 3.11. The pressure in the CVD quartz tube was built to 100 mTorr using the vacuum pump. After that, hydrogen gas (purity, 99.999%, Praxair) was flowed into the tube at a rate of 100 sccm. The pressure in the tube was maintained at ~2-5 Torr. In 40 minutes, the furnace was heated to and maintained at 1050 °C during the entire graphene synthesis process.

When the temperature of the furnace reached 1050 °C, the copper foil was moved inside the heating zone by an external magnet, as shown in Figure 3.11 and annealed for 15 minutes; then, the quartz boat with coal was moved next to the copper foil for
graphene growth. After another 30 minutes, a graphene film was grown on the surface of the copper. Both of the two quartz boats were moved out of the heating zone by the external magnet. When the synthesis process was finished, the furnace was cooled down to room temperature and turned off afterwards. The graphene/copper stack was taken out of the tube after turning off the vacuum pump and the gas flow to the system.

Figure 3.10. Temperature profile of CVD growth of graphene on Cu foil. The synthesis procedure has five steps: I) Evacuate to 100 mTorr and purge with 100 sccm Hydrogen; II) Ramp furnace to 1050 °C; III) Anneal the copper; IV) Move the quartz boat with the coal inside the heat zone of the furnace; V) Fast cooling by moving the quartz boat out of heat zone of the furnace.

Figure 3.11. Schematic of the CVD setup for producing graphene from raw coal which consists of a quartz tube furnace connected to a vacuum pump and hydrogen gas cylinder. Magnets are attached to the two quartz boats that are used as support for the copper foil and coal.
3.9 Preparation of a Graphene-Coated Ni Working Electrode

The Ni foil (2.0 cm x 3.0 cm, purity > 99%, Alfa Aesar) used for making the graphene-coated Ni working electrode was first polished with sand paper (600 grit, Gator Finishing) and then sandblasted with alumina powder (27.5 micron, Crystal Mark, Inc.) for 2 minutes. Figure 3.12a displays the flow chart of the making of graphene-coated Ni. The graphene-coated copper foil was taken out of the quartz tube and then spin-coated with a supportive layer of poly(methyl methacrylate) (PMMA), a polymer. After dissolving the copper substrate in the Marbles reagent (10 g CuSO₄, 50 mL HCl, 50 mL DI water) [62], the PMMA/graphene stack was transferred to DI water and left for 3 hours to clean the graphene surface. The PMMA/graphene stack was self-lifted onto the Ni foil afterwards, as shown in Figure 1b. The PMMA was then removed by rinsing the PMMA/graphene stack on the Ni electrode with acetone to complete the preparation of the graphene-coated Ni. After drying the graphene-coated Ni for 30 minutes at 70 °C in the oven, the graphene edges were sealed by Teflon tape, as shown in Figure 3.12c and the dimension of the exposed area of the graphene-coated Ni was 1.0 cm x 2.0 cm.
3.10 Physical Characterization of CVD Graphene

Transmission electron microscopy (TEM) was used to investigate the crystal structure and surface morphology of the graphene films. The TEM images and the selected area electron diffraction (SAED) of the CVD graphene film were obtained using a JEOL JEM 2100F transmission electron microscope. The atomic force microscopy (AFM) images of graphene were obtained using an Agilent 5500 AFM/STM microscope in AC mode with NSC 15/AIBS probes (resonant frequency of 325 kHz) from MikroMasch USA under ambient conditions. The flow chart for preparing the graphene sample for the TEM and AFM analyses is shown in Figure 3.13. After dissolving the copper substrates in the Marbles reagent, the floating CVD graphene film was rinsed with
DI water to remove contamination and to clean the surface before transferring it onto a lacey carbon TEM grid (300 mesh, copper) for the TEM analysis and onto a silicon wafer for the AFM analysis.

![Flow chart for transferring graphene on the TEM grid and silicon wafer for TEM and AFM analyses.](image)

Figure 3.13. Flow chart for transferring graphene on the TEM grid and silicon wafer for TEM and AFM analyses.

3.11 Scanning Electron Microscopy (SEM)

The surface morphology of the graphene-coated Ni electrode was obtained by scanning electron microscopy (SEM) using a JEOL JSM-6390 scanning electron microscope (15kV, 14 mm working distance). The SEM images were obtained before masking the edge of the graphene on a Ni substrate for the eU2A experiments.

3.12 Atomic Absorption Spectroscopy (AAS)

A flame atomic absorption spectrometer (AAAnalyst 400, PerkinElmer, Inc) equipped with a hollow cathode lamp for the Ni element was used as a determination method for testing the concentration of Ni ions in the reagent solution during the
experiments. Absorbance measurements were made at the Ni sensitive line at 232.0 nm. The flame gases were air/acetylene. The lamp current was 20 mA, the air flow rate was maintained at 10 L min⁻¹, and the acetylene flow rate was set at 2.5 L min⁻¹. The Ni ion standard solution with concentrations ranging from 2 mg L⁻¹ to 12 mg L⁻¹ was prepared by dilution from 1000 mg L⁻¹ of Ni reference standard solution (FLSN70-500, ±1%, Fisher Scientific). The nonlinear regression curve of absorbance for 2 to 12 ppm standard Ni ion solutions is shown in Figure 3.14. Samples from the reactor were collected and diluted to the range of 2 mg L⁻¹ to 12 mg L⁻¹. The concentrations of Ni ions in the testing samples were given by the instrument after calibration with the standard solutions, and the concentration of Ni ions in the electrolyte was then calculated by following Eq. 24. Because the geometric areas of the working electrodes (graphene-coated Ni and bare Ni) were different, the normalized concentration of Ni ions in the electrolyte was calculated using Eq. 25.

\[
C_{Ni \, ion} = \frac{C_{Ni \, ion, \, sample} \times V_f}{V_i} \tag{24}
\]

\[
\bar{C}_{Ni \, ion} = \frac{C_{Ni \, ion}}{A} \tag{25}
\]

where,

\(C_{Ni \, ion}\), the concentration of Ni ion in the bulk solution, in mg L⁻¹;

\(\bar{C}_{Ni \, ion}\), the normalized concentration of Ni ion in the bulk solution, in mg L⁻¹;

\(C_{Ni \, ion, \, sample}\), the concentration of Ni ion in the diluted solution, in mg L⁻¹;

\(V_f\), the volume of the diluted sample, in mL;
$V_i$, the volume of the solution sampled out from the reactor, in mL;

$A$, the area of the working electrode, in cm$^2$;

Figure 3.14. Nonlinear calibration of the Ni ion with standard Ni$^{2+}$ solutions with concentrations from 2 mg L$^{-1}$ to 12 mg L$^{-1}$. 

![Nonlinear calibration of Ni ion](image)
CHAPTER 4: ELECTROCHEMICALLY INDUCED CONVERSION OF UREA TO AMMONIA

The contents of this chapter have been published in *ECS Electrochem. Lett.*, a peer-reviewed journal: Lu, F.; Botte, G. G., Electrochemically Induced Conversion of Urea to Ammonia. *ECS Electrochem. Lett.* 2015, 4 (10), E5-E7 [63].

4.1 Introduction

Ammonia is an important chemical used in many fields such as the fertilizer industry [64], and food industry [25]. One popular application of ammonia is to control nitrogen oxide (NOx) emissions, and this technology is known as selective catalytic reduction (SCR). SCR systems are typically found on large utility boilers, industrial boilers, and municipal solid waste boilers. The technology has been verified to reduce NOx by 70-95%. Recent applications include diesel engines, such as those found on large ships, diesel locomotives, gas turbines, power plants, and even automobiles [65-67]. However, ammonia is considered a hazardous chemical [2]. Therefore, instead of using ammonia, most SCR systems use urea (nontoxic). Urea can be thermally hydrolyzed into ammonia on demand as shown in Eq. 26 [68].

\[ CO\left(\text{NH}_2\right)_{\alpha} + H_2O \rightarrow 2\text{NH}_3 + CO_2 \]  \hspace{1cm} (26)

Thermal conversion of urea to ammonia processes used in power plants -such as urea pyrolysis (540 °C) [7] and urea hydrolysis (150 °C, 5-6 atm) [6]- are not suitable for mobile engines since the reaction conditions are inaccessible. Current thermal hydrolysis of urea (THU) processes employed in diesel engine vehicles doses urea by injecting urea-
water solutions (this mixture is known as diesel effluent fluid, DEF, 32.5% urea in deionized water) make use of the exhaust temperature to convert urea to ammonia. However, in low-load urban driving, the exhaust temperature goes from 300 °C to 130 °C and even lower. The overall NOx conversion effectiveness in the system is low due to the curtailed urea dosing caused by insufficient conversion of urea [13]. In addition, the quality of the DEF needs to be high since the SCR catalyst can be damaged if there is contamination in DEF (e.g., due to minerals in water used for making DEF [14]).

In this dissertation, we demonstrate a new technology that allows the electrochemical conversion of urea to ammonia, the eU2A process [69, 70]. This process allows the production of ammonia on demand by applying a cell voltage as depicted in Figure 4.1a [69, 70]. This technology enabled the decoupling of the ammonia production from the exhaust system in diesel engine vehicle SCR applications, as well as portable urea to ammonia reactors.

4.2 Experimental Methods

The two-electrode eU2A reactor was built at the Center for Electrochemical Engineering Research (CEER) and is schematically presented in Figure 4.1b. A heat jacket with a controller (Econo Temperature controller 12125-14) was used to heat and maintain the temperature of the reagent in the reactor. The eU2A process was performed in a two-electrode system and the cell voltage was controlled by an Arbin BT2000 potentiostat. The anode (working electrode) of the reactor was made by Ni beads and a Ni mesh was used as cathode (see Section 3.1). Part of the ammonia produced was dissolved
in the solution in the reactor, while the rest in vapor phase was captured in a glass vessel containing 1.0 l of 1.0 M sulfuric acid solution (Figure 4.1b). An ammonia ion selective electrode (ISE) (Orion 710A+, Thermo Electron Corporation) was used to measure the concentration of ammonia in both the reactor and the acid trap (Section 3.3).

Figure 4.1. (a) Schematic representation of the eU2A process; (b) Schematic of the eU2A reactor (I and II are sample ports); (c) Schematic of the gas collection system for the gas analysis (III is the sample port for collecting gas for GC analysis).
The ammonia production rate in the eU2A process was measured at different applied voltages and temperatures. The eU2A process was compared with the thermal hydrolysis of urea (THU) in the same reactor (without applying a cell voltage). The volume of solution in the reactor was kept constant in all the experiments (250 mL). And these experiments were performed with DEF solution containing 7.0 M KOH. The concentration of urea was measured by UV-vis spectroscopy using a Hewlett Packard Spectrophotometer HP 8452A (Section 3.4). The gases other than ammonia and CO₂ generated in the eU2A process were collected (schematically exhibited in Figure 4.1c) and analyzed by gas chromatography (GC) -SRI 8610C Gas Chromatograph equipped with a Mole Sieve 5A column and a thermal conductivity detector. Argon gas was used as the carrier gas.

4.3 Results and Discussion

The effect of temperature in the eU2A process at constant voltage (1.65 V) is shown in Figure 4.2a. The ammonia production rate is a function of temperature as expected since the working electrode volume was only 18.8% of the volume of the reactor (see Section 3.1). The maximum operating temperature was set at 70 °C to limit the evaporation of water from the reactor. Figure 4.2b shows the experimental results of the eU2A conducted at different voltages ranging from 1.35 V to 1.65 V. At short times, the effect of cell voltage in the moles of ammonia generated is negligible. After 45 minutes, there is a clear difference between 1.65 V and other voltages. At this voltage,
there is some N\textsubscript{2} evolution from the working electrode due to urea electrolysis according
to Eq. 27 \[71\].

\[ CO(NH\textsubscript{2})_{\text{(aq)}} + 6OH^- \rightarrow N\textsubscript{2} + CO\textsubscript{2} + 5H\textsubscript{2}O + 6e^- \] (27)

The N\textsubscript{2} gas evolving may refresh the electrode surface making the catalyst
available for urea conversion while at other applied voltages, the effect is negligible. This
enhancement may also be due to inherent mixing caused by the gas evolution. Therefore,
1.65 V was chosen as the applied voltage for the long time (24 hours) experiments of the
eU2A process.

Figure 4.2c shows a comparison of the ammonia generated at 70 °C during 24-
hour experiments in the eU2A process (at 1.65 V) and the THU process. A dramatic
increase in the ammonia generation is observed in the eU2A when compared with the
THU. In a period of 24 hours, 1.609 moles of ammonia were generated in the eU2A
process, while 0.256 moles were generated in the THU process. The rate of ammonia
generation per effective volume (volume of the catalyst, 47 cm\textsuperscript{3}) for the eU2A process is
20.39 g h\textsuperscript{-1} L\textsuperscript{-1} after subtracting the ammonia generated from the thermal contribution,
0.256 moles. The rate for the THU process is 0.73 g h\textsuperscript{-1} L\textsuperscript{-1} per effective volume (volume
of the reagent, 250 mL). That is, the effective rate of ammonia generation of the eU2A
process is \sim 28 times higher than that of the THU process. Accordingly, the concentration
of urea decreases more rapidly in the eU2A process compared with THU as shown in
Figure 4.2d.
Our results demonstrate that the hydrolysis of urea can be electrochemically induced using an inexpensive transition metal, Ni. In basic solution, $\text{Ni}^{2+}$ is oxidized to $\text{Ni}^{3+}$ forming Ni oxyhydroxide according to Eq. 28. It is proposed that the NiOOH serves as a catalyst for the hydrolysis of urea according to Eq. 29 (see Section 3.2). At the cathode of the reactor, hydrogen evolves according to Eq. 30.

$$\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (28)$$

$$\text{CO(NH}_2)\text{(aq)} + \text{H}_2\text{O} \xrightarrow{\text{NiOOH}} 2\text{NH}_3 + \text{CO}_2 \quad (29)$$
The eU2A process can compete with the urea electrolysis in alkaline media (Eq. 27) to produce nitrogen [12, 71, 72]. It has recently been proved by in-situ electrochemical x-ray diffraction that NiOOH reacts quickly with urea [73]. The hydrolysis of urea (Eq. 24) could be favored by operating the electrochemical cell at voltages that enable the formation of NiOOH with minimum direct oxidation of urea to nitrogen (with the applied potential close to the peak potential for NiOOH formation while far less than urea oxidation peak, see Section 3.2) and the formation of NiOOH catalyst can also be enhanced by adding slight amounts of Rh into the Ni catalyst [74].

Warner postulated that urea hydrolysis -THU summarized by reaction (1)- consists of two steps. The first step is the decomposition of urea to ammonia and isocyanic ion (Eq. 31) which is irreversible at pH less than 5 and greater than 12 [44]. The second step is the hydrolysis of isocyanic ion to produce ammonia and CO$_2$ (Eq. 32) [44].

\[
2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{30}
\]

\[
CO(NH_2)_2 \rightleftharpoons NH_3 + H^+ + CNO^- \tag{31}
\]

\[
H^+ + CNO^- + H_2O \rightarrow NH_3 + CO_2 \tag{32}
\]

In acid solution, reaction (32) is too fast, and no isocyanic ion has been reported. In alkaline medium, reaction (32) is slow and the presence of isocyanic ion is favored [44]. When the pH increases, the rate constant of the first step increases remarkably while the one of the second step decreases (e.g., using 4.04 M NaOH as the supporting solution, the rate constant of the first step is about 5 times the rate constant of the second [44]). As a consequence, in alkaline solution, the stoichiometric ratio of produced ammonia and
decomposed urea is less than 2 -e.g., 1.38 at pH of 12.78 and 100°C [44]. After the 24-hour experiments, the ratio of produced ammonia and decomposed urea in the THU was 1.19, much lower than the ratio in the eU2A, which was 1.96 (the subtle loss of urea in urea electrolysis is included, Appendix A4). The oxidation state of Ni in NiOOH is $\text{Ni}^{3+}$, which is considered a hard acid (Lewis acid) [75]. Therefore, it is hypothesized that the NiOOH layer catalyst formed in the eU2A process provides acid sites that promote the reaction in the second step (Eq. 32) minimizing the formation of isocyanic ions.

No CO$_2$ and ammonia gases were detected in the gas chromatograph (Section 3.5), since CO$_2$ was absorbed in the reactor by the KOH and ammonia was trapped in both the reactor and the acid trap. H$_2$, O$_2$, and N$_2$ were observed in the gas sample and the volumetric ratio H$_2$: O$_2$: N$_2$ was 61.9%: 7.2%: 30.9% (Appendix Table A4.2). It is hypothesized that air was present in the dead volume of the system -such as headspace and connecting hoses- when the reactor was assembled. However, there was extra N$_2$ in the gas, which indicates that the urea electrolysis (Eq. 27) occurs in parallel to the eU2A reactions (Eqs. 28 and 29). The production of H$_2$ could offer additional advantages to the eU2A since it could assist the NH$_3$ SCR by reducing the reaction temperature and increasing the activity of the catalyst in the SCR reactor [39].

The average current in the eU2A process, during the 24-hours experiments, is 0.364 A, therefore, the consumed electrical energy in ammonia production for electrochemical process is 0.63 Wh g$^{-1}$. The electrical energy is low, because, it is only needed to produce the catalyst (NiOOH), which requires one electron transferred.
Previous research has established that no rapid urea hydrolysis reaction takes place at temperatures lower than 140 °C [5]. The concentration change of urea in the reactor was used to estimate the overall reaction rate constants, $k$, for Eq. 26 and Eq. 29 in the presence of KOH assuming it was first-order reaction [44]. In the THU process, $k = 0.00039 \text{ min}^{-1}$, which is in agreement with the results as reported in the literature [44]. On the other hand, in the eU2A process, $k = 0.00140 \text{ min}^{-1}$, which is ~ 30% of that of the urea hydrolysis process [5] at 140 °C and 100 kg cm$^{-2}$ (Appendix Table 5.1). That is, the eU2A process enables significant ammonia production at lower operating pressure and temperature (atmospheric pressure, 70 °C) comparing to the urea hydrolysis (100 kg cm$^{-2}$, 140 °C). These findings could lead to significant energy savings as well as less expensive reactors (the eU2A process could avoid the use of high pressure vessels).

4.4 Conclusion

A new electrochemical process for the conversion of urea to ammonia, the eU2A process, was demonstrated. It enables the optimum conversion of urea to ammonia due to the hypothesis that it limits the formation of isocyanic ions in alkaline media. The process enables remarkable ammonia generation rate at lower operation temperature and pressure. The new process could offer several advantages for SCR systems in vehicles. It could enable the decoupling of the ammonia generation from the exhaust system, preventing curtailed urea dosing while reducing the amount of water (steam) from the SCR reactor/catalyst -which is considered one of the reasons for lowering the conversion of
NO [33]. The hydrogen produced could potentially lead to mileage extender in vehicles and a better optimization of the SCR reactor.

Since the eU2A is an electrochemically induced process, electrodes with larger surface areas—such as finer Ni beads, Ni foams, and Ni nanocomposites, among others—could also be utilized to enable higher ammonia generation rates and better packing. Moreover, the use of flow reactors could enable better exposure of the catalyst surface to the reagent solution, which would result in higher ammonia generation rates in the eU2A process.
CHAPTER 5: UNDERSTANDING THE ELECTROCHEMICALLY INDUCED
CONVERSION OF UREA TO AMMONIA USING NI BASED CATALYSTS

The contents of this chapter have been published in *Electrochimica Acta*, a peer-reviewed journal: Lu, F.; Botte, G. G., Understanding the electrochemically induced conversion of urea to ammonia using Ni based Catalysts. *Electrochimica Acta* 2017, 246, 564-571 [76].

5.1 Introduction

The Environmental Protection Agency (EPA) regulation of nitrogen oxides (NOx) emissions is of significant concern these days [2]. To meet the stricter regulations, selective catalytic reduction of NOx using ammonia as reducing agent, is proved to be an effective method to eliminate NOx [77]. However, handling ammonia is difficult in most cases since it is toxic and corrosive, thus its transportation and storage becomes costly [28]. Therefore, on-site generation of ammonia from urea has gained attention. Commercial urea to ammonia (U2A) systems have been implemented in power plants [5-7]. However, the U2A process used in power plants requires high temperature and pressure, which creates limitations in mobile engines, especially during start up of the engine. Urea to ammonia reaction could be promoted using catalysts such as urease [8] or a number of oxides such as alumina, silica, and Palladium complexes [9, 10]. However, these catalysts have limitation including activity and operating temperature. To address these concerns, Botte proposed an electrochemical process to convert urea to nitrogen (N₂), hydrogen (H₂) and ammonia (NH₃) using Ni based electrodes in alkaline media [11].
At certain operating conditions, the conversion of urea to ammonia – electrochemically induced urea to ammonia, eU2A- dominates the process and minimum N₂ is produced [11].

In previous studies, we have demonstrated that eU2A is enabled by applying a cell voltage on a Ni cathode and Ni anode at 1.65 V [63]. At relatively low temperature, 70°C, urea was hydrolyzed to ammonia in alkaline media due to the applied electrochemical potential at higher rates than the thermal hydrolysis of urea at the same conditions. It was proposed that the eU2A takes place according to the following reactions at the anode (Eqs. 33 and 34) and cathode (Eq. 35):

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (33)
\]

\[
\text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} \underbrace{\text{NiOOH}}_{\text{Ni}^{3+}} \rightarrow 2\text{NH}_3 + \text{CO}_2 \quad (34)
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \quad (35)
\]

It was hypothesized that Ni(OH)₂ (Ni²⁺) undergoes oxidation to its active form NiOOH (Ni³⁺) which catalyzes the decomposition of urea as per Eq. 33 and Eq. 34. Therefore at 70 °C, the urea to ammonia reaction was induced in the presence of electrochemically produced NiOOH catalyst. Daramola et al. [50] studied the dissociation rates of urea in the presence of NiOOH using density functional theory (DFT) methods. The authors proposed a possible mechanism for the dissociation of urea, in which the urea adsorbs on the catalyst surface and through the H donation on the NiOOH catalyst surface could lead to the production of ammonia leaving CNO⁻ still adsorbed on the catalyst surface [50]. However, the mechanism of the urea decomposition to ammonia via
the electrochemical process is still unclear; in particular, the formation of CNO⁻ has not been investigated experimentally.

Cyclic voltammetry (CV) was used to analyze the oxidation and reduction processes. Constant potential eU2A experiments were conducted and compared with thermal hydrolysis of urea (THU) process. In-situ Raman spectroscopy was used to monitor the intermediates and products during the reaction on the catalyst surface. Ex-situ Fourier Transform Infrared (FTIR) was conducted to identify the intermediates and products in the bulk solution during the reaction. By comparing time-dependent Raman and FTIR spectra for both the eU2A and THU experiments, a possible pathway for the eU2A is proposed.

5.2 Experimental Methods
5.2.1 Reagents and Experimental Setup

Urea (purity 99.8%) and KOH (purity > 85%) used in the experiments were supplied by Fisher Scientific. Ultra-pure water (Alfa Aesar, HPLC grade) was used throughout, unless otherwise specified. As shown in Figure 5.1, the electrochemical tests were carried out in a three neck flask using a Solartron 1281 Multiplexer Potentiostat with Ni foil (2.0 cm x 3.0 cm, purity > 99%, Alfa Aesar) as the working electrode, Ni foil (2.0 cm x 3.0 cm, purity > 99%, Alfa Aesar) as the counter electrode, and Hg/HgO as the reference electrode (Koslow Scientific). Both the working and counter electrodes were polished with sandpaper (600 and 320 grits, Gator Finishing) to remove any impurities and oxides that could have formed during manipulation (for example, during spot
welding of the current collectors) followed by sonication in DI water for 10 min. Ni wires (diameter 1.0 mm, purity 99.5%, Alfa Aesar) were used as current collectors. The current collectors were spot welded on the nickel foils using Miller® resistance spot welder (SSW-2020ATT) operating at 9 A for 1 second. The reference electrode was supported using a Luggin capillary filled with the supporting electrolyte (KOH at the concentration according to each experiment).

A total of 125 mL of reactant solution was used for each experiment. The solution was heated to 70 °C using a heat jacket with a temperature controller (Econo Temperature controller 12125-14). All the experiments were conducted at 70 °C unless specified differently which follows the previous investigation by Lu and Botte [63]. The fifth pseudo-steady state voltammograms are reported. All the voltammograms in this study were performed between 0.20 V and 0.65 V vs. Hg/HgO at a scan rate of 10 mV s⁻¹.

Figure 5.1. Schematic representation of reaction vessel. Both the working electrode and counter electrode are Ni foil, while the reference electrode is Hg/HgO. Temperature was set at 70 °C. Sample ports allowed collecting gases and liquid.
Constant potential experiments were performed to determine the ammonia production rate as a function of time in the eU2A process. In such experiments, a sample of 0.5 mL solution was collected from the reactor every 30 minutes. The concentration of ammonia was measured using an ammonia ion selective electrode as described in Section 3.3. Experiments were also performed at constant temperature without an applied potential, the THU mode. The gases other than ammonia and CO$_2$ generated during the experiments were trapped in a gas collection column and analyzed by gas chromatograph (Agilent Technologies 7890 B) equipped with a Molsieve 13X column and a thermal conductivity detector as described in Section 3.5.

5.2.2 Ex-situ FTIR

*Ex-situ* Fourier transform infrared spectroscopy (FTIR) for both the eU2A and THU were conducted using a Bruker Vertex 80 Instrument Spectrum One Fourier Transform Spectrometer. Sampling was performed every one hour by placing 20μl electrolyte from the bulk solution onto a disposable KBr pellet. FTIR spectra were then collected in the wave numbers of 68-4451 cm$^{-1}$ and the single-beam spectrum of the KBr pellet was acquired before each measurement to compensate as the background.

5.2.3 In-situ Raman Spectroscopy

An *in-situ* electrochemical cell was built to identify the intermediate of the reactions on the catalyst surface during the eU2A process, a schematic of the cell is shown in Figure 5.2 and its dimensions are shown in Appendix A7. The electrochemical
tests were carried out using a Solartron 1252A potentiostat in a three-electrode cell setup with Ni foil (1.0 cm x 1.0 cm, purity > 99%, Alfa Aesar) as the working electrode, and Ni foil (0.5 cm x 2.0 cm, purity > 99%, Alfa Aesar) as the counter electrode, and Hg/HgO as the reference electrode (Koslow Scientific). Both the working and counter electrodes were polished with sandpaper (600 and 320 grits, Gator Finishing) to remove any impurities and oxides that could have formed during manipulation (for example, during spot welding of the current collectors) followed by sonication in DI water for 10 min. Ni wires (diameter 1.0 mm, purity 99.5%, Alfa Aesar) were used as current collectors. The current collectors were spot welded on the nickel foils using Miller® resistance spot welder (SSW-2020ATT) operating at 9 A for 1 second. The cell was filled with 5.0 M urea in the presence of 5.0 M KOH for both eU2A (at 0.462 V vs. Hg/HgO) and THU experiments. Raman spectra were recorded for the experiments using a Bruker Senterra Raman spectrometer with the lens focusing onto the working electrode surface. The Raman spectrometer was equipped with a microscope that has a 10x objective lens, and used 532 nm wavelength laser excitation that had 20 mW power.
Figure 5.2: Electrochemical cell for in-situ Raman spectroscopy. The eU2A reaction of 5.0 M urea in the presence of 5.0 M KOH at 0.462 V was conducted in the cell at 70 °C. Raman spectra of intermediate species and products were obtained with the laser focused onto the working electrode surface through a silica window.

5.3 Results and Discussion

5.3.1 Comparison Between the eU2A and THU process

The CVs of Ni electrode at different concentrations of KOH at 70°C are shown in Figure 5.3a. As hypothesized in our previous publication [63], NiOOH works as the catalyst to hydrolyze urea to ammonia. At the peak potential of the CV using different concentrations of KOH, the amount of NiOOH was assumed to reach the maximum, thus constant potential eU2A experiments were conducted at the peak potentials according to the concentration of KOH in the electrolyte. Because thermal hydrolysis of urea can take place simultaneously during the eU2A experiments, the concept of additional generated ammonia is introduced and defined as the difference in the concentration of ammonia between eU2A and THU. The concentrations of ammonia in the reactor vessel during eU2A (\(C_{i, eU2A}\)) and THU (\(C_{i, THU}\)) are shown in Figure 5.3b. The amount of additional ammonia generation is calculated using Eq. 37 and the rate of the additional ammonia generation rate is calculated using Eqs. 36, 38 and 39.
\[ C_{i, \text{add.}} = C_{i, \text{eU2A}} - C_{i, \text{THU}} \quad (i = 1, 2, 3, ..., n) \]  
(36)

\[ n_{i, \text{add.}} = (C_{i, \text{eU2A}} - C_{i, \text{THU}}) \times V_r \quad (i = 1, 2, 3, ..., n) \]  
(37)

\[ r_i = \frac{dC_{i, \text{add.}}}{dt} = \frac{C_{i+1, \text{add.}} - C_{i, \text{add.}}}{\Delta t_i} \quad (i = 1, 2, 3, ..., n) \]  
(38)

\[ r = \frac{\sum_{i=1}^{N} r_i}{N} \]  
(39)

where,

- \( C_{i, \text{add.}} \), the concentration of additional generated ammonia in the eU2A process, in M;
- \( C_{i, \text{eU2A}} \), the concentration of ammonia generated in the reactor during eU2A experiments, in M;
- \( C_{i, \text{THU}} \), the concentration of ammonia generated in the reactor during THU experiments, in M;
- \( i \), sample point;
- \( n_{i, \text{add.}} \), the amount of additional ammonia generated during eU2A -excluding the contribution of the THU, in mol;
- \( V_r \), the volume of electrolyte in the reactor, in L; \( V_r = 0.125 \text{ L} \) for the three-electrode reactor;
- \( r_i \), the additional ammonia generation rate between two adjacent sampling points, in M min\(^{-1}\);
- \( r \), the additional ammonia generation rate in eU2A process, in M min\(^{-1}\);
- \( \Delta t_i \), time intervals between two adjacent sampling points, in min;
\( N \), total numbers of the sampling points;

As shown in Figure 5.3c, there is a proportional correlation between additional ammonia generation rate and peak current at each KOH concentration, which indicates that the eU2A reaction is strongly dependent on the formation of NiOOH. There is also an anomaly, at 7.0 M KOH the peak current is lower than 2.5 M KOH; however, the additional ammonia generation rate is higher. This phenomenon indicates that besides the amount of NiOOH, the presence of OH\(^-\) could also increase the additional ammonia generation rate.
Figure 5.3. Performance of eU2A at different potentials and KOH concentrations. (a) CVs of Ni electrodes in 1.0, 2.5, 5.0, and 7.0 M KOH at 70 °C. (b) Experimental results of ammonia generation of eU2A and THU using 5.0 M urea in the presence of 1.0, 2.5, 5.0, and 7.0 M KOH at 70 °C. (c) Comparison of the ammonia generation from eU2A reaction at 1.0, 2.5, 5.0, and 7.0 M KOH. A proportional correlation was observed between the peak current in the CVs at different concentrations of KOH and the ammonia generation rate, which indicates that the formation of NiOOH in eU2A has a positive effect on the catalytic conversion of urea to ammonia.
5.3.2 Effect of Applied Potential on the eU2A Process

Figure 5.4a shows the experimental results of the eU2A for 5.0 M urea in the presence of 5.0 M KOH conducted at 0.425 V, 0.462 V and 0.485 V vs. Hg/HgO reference electrode. The corresponding additional ammonia generation rate for each applied potential is plotted in Figure 5.4b. As shown in the CVs in Figure 5.4b, the onset potential for urea electrolysis (0.380 V vs. Hg/HgO at 5.0 M urea_5.0 M KOH) is lower than that for Ni^{2+} oxidation to Ni^{3+} (0.402 V vs. Hg/HgO at 5.0 M KOH), which indicates that the electrolysis of urea takes place in parallel to the eU2A process. This conclusion is also proven by the results shown in Table 5.1 (a detailed analysis of the Faradaic efficiency and the GC results are described in Appendix A4.2). At all three applied potentials, N_{2} formation from urea electrolysis was observed, which takes place according to the following reaction [12]:

$$CO(NH_2)_2 + 6OH^- \rightarrow N_2 + 5H_2O + CO_2 + 6e^-$$

(40)
Figure 5.4. Comparison of the eU2A and the THU processes at 70 °C. (a) Effect of applied potential at 5.0 M urea and 5.0 M KOH. (b) CVs of Ni electrodes in 5.0 M KOH in the presence and absence of 5.0 M urea overlapped with additional ammonia generation rate (at 0.425 V, 0.462 V and 0.485 V vs. Hg/HgO). During urea electrolysis, Ni$^{3+}$ is reduced to Ni$^{2+}$ while urea is oxidized to N$_2$. At higher applied potentials Ni$^{3+}$ is reduced to Ni$^{2+}$, indicating a positive correlation between additional ammonia generation rate and regenerated Ni$^{2+}$ ions.
Table 5.1

Electrochemical performance for urea electrolysis at different applied potentials during 3 hours of operation of the eU2A process using 5.0 M urea in the presence of 5.0 M KOH. Ideal gas law was assumed for the estimation of the moles of the gases produced (refer to Appendix A4.2 for details).

<table>
<thead>
<tr>
<th>Applied Potential, V vs. Hg/HgO</th>
<th>Average Current Density*, A cm⁻²</th>
<th>Produced N₂, mol</th>
<th>Faradaic Efficiency for Urea Electrolysis, %</th>
<th>Additional Generated Ammonia, mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.425</td>
<td>7.75×10⁻⁴</td>
<td>3.76×10⁻⁵</td>
<td>43.4</td>
<td>1.26×10⁻²</td>
</tr>
<tr>
<td>0.462</td>
<td>1.69×10⁻³</td>
<td>9.44×10⁻⁵</td>
<td>49.8</td>
<td>3.86×10⁻²</td>
</tr>
<tr>
<td>0.485</td>
<td>2.22×10⁻³</td>
<td>1.64×10⁻⁴</td>
<td>65.9</td>
<td>5.89×10⁻²</td>
</tr>
</tbody>
</table>

* Geometric area of working electrode is 6.0 cm²

The Faradaic efficiency for urea electrolysis are 43.4%, 49.8%, and 65.9%, for 0.425 V, 0.462 V and 0.485 V vs. Hg/HgO reference electrode, respectively. This indicates that 56.6%, 50.2%, and 34.1% of the charge passed is used for reaction 33 at the different applied potentials. Higher Faradaic efficiency for urea electrolysis was obtained at higher applied potential. According to the mechanism of urea electrolysis, urea is electrolyzed to N₂ while Ni³⁺ is reduced to Ni²⁺ in the process [12]. Therefore, less Ni³⁺ (more Ni²⁺) is available in the eU2A process at 0.485 V, but higher additional ammonia generation is found at this potential, which suggests that Ni²⁺ also plays an important role in the catalytic dissociation of urea.

5.3.3 Ex-situ FTIR Analysis

Figure 5.5 demonstrates the time-dependent FTIR spectra of 5.0 M urea in the presence of 5.0 M KOH during 3 hours experiments in both eU2A (0.462 V vs. Hg/HgO)
and the THU process. The assignment of each peak is shown in Table 5.2. Frequencies related to urea (at 1167 cm\(^{-1}\), 1452 cm\(^{-1}\), 1626 cm\(^{-1}\), and 1673 cm\(^{-1}\)) \cite{78, 79} and ammonia (at 1438 cm\(^{-1}\)) -- indicating its generation - can be observed \cite{80}. Another important peak is the frequency at 2170 cm\(^{-1}\) which is assigned to CNO\(^-\) \cite{81}, The CNO\(^-\) peak is observed in both the THU and eU2A; but since there is thermal hydrolysis of urea in the bulk solution in eU2A experiments, it cannot be concluded that CNO\(^-\) is an intermediate during the eU2A process. Raman spectroscopy at the surface of the electrode was used to investigate this topic further; this is discussed in in Section 5.3.4.

Table 5.2

<table>
<thead>
<tr>
<th>Wavenumber, cm(^{-1})</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1167</td>
<td>NH(_2) in urea</td>
<td>\cite{78}</td>
</tr>
<tr>
<td>1438</td>
<td>NH(_4^+)</td>
<td>\cite{80}</td>
</tr>
<tr>
<td>1452</td>
<td>C-N in Urea</td>
<td>\cite{79}</td>
</tr>
<tr>
<td>1626</td>
<td>N-H in Urea</td>
<td>\cite{79}</td>
</tr>
<tr>
<td>1673</td>
<td>C=O in Urea</td>
<td>\cite{79}</td>
</tr>
<tr>
<td>2170</td>
<td>CNO(^-)</td>
<td>\cite{81}</td>
</tr>
</tbody>
</table>
Figure 5.5. FTIR spectra of 5.0 M KOH in the presence and absence of 5.0 M urea during eU2A (a) (0.462 V vs. Hg/HgO) and THU (b). The peak shift at 2170 cm$^{-1}$ indicates CNO$^-$ exists at the bulk solution for both the eU2A and THU. The peak that appears at 1438 cm$^{-1}$ is assigned to NH$_4^+$ indicating the generation of ammonia during both the eU2A and THU.

5.3.4 *In-situ Raman Spectroscopy Analysis*

The Raman spectra of the electrolyte in eU2A and THU are shown in Figure 5.6 and the peak assignment is listed on Table 5.3. The strong band at the beginning in 1001 cm$^{-1}$ is assigned to N-C-N stretching, resulting from the symmetric vibration mode $v_4$(A1) of urea [82, 83]. During the experiments, the peak at 1070 cm$^{-1}$ -assigned to the carbonate group- shifted to stronger [84], indicating the gradual formation of CO$_2$ -which is then
captured by the KOH forming potassium carbonated in the process. The peak shift at 3318 cm\(^{-1}\) is due to the formation of \(\text{NH}_4^+\) group [85] that demonstrates the generation of ammonia in the eU2A process. An additional peak appears at 3612 cm\(^{-1}\), which is assigned to \(\text{Ni}^{2+}\) due to simultaneous oxidation of the Ni foil to \(\text{Ni}^{2+}\) when Ni diffuses in the KOH solution [86]. One would have expected to see the disappearing of this peak when \(\text{Ni}^{2+}\) oxides to \(\text{Ni}^{3+}\) during the electrochemical conversion of urea [87]. However, the existence of the \(\text{Ni}^{2+}\) peak in the Raman spectra of the eU2A indicates that some of the \(\text{Ni}^{3+}\) was reduced to \(\text{Ni}^{2+}\) due to the urea electrolysis reaction [12]. The broad band above 3000 cm\(^{-1}\) is OH vibration in water, which also has three additional peaks at 3230 cm\(^{-1}\), 3380 cm\(^{-1}\), and 3480 cm\(^{-1}\); these three peaks overlapped with this broad band belongs to urea [88].

The only obvious difference between the eU2A and the THU is the peak shift at 2170 cm\(^{-1}\) for THU, which is assigned to the -CN antisymmetric vibration in CNO\(^-\) [89]. This indicates that in the eU2A process, either CNO\(^-\) could not adsorb on the catalyst surface or that it decomposes rapidly on the catalyst surface. However, it is not possible to be the former reason, because after 12 h of elapse time CNO\(^-\) is still observed on the surface in the THU mode. Therefore, it can be concluded that CNO\(^-\) is the intermediate of urea to ammonia in the THU reaction -confirmed via FTIR and Raman- but it is not an intermediate for the eU2A process. This last is driven by a surface reaction enabled by the applied potential.
Figure 5.6. Raman spectra of 5.0 M KOH in the presence of 5.0 M urea (a-c) during eU2A at 0.462 V vs. Hg/HgO and (d-e) during THU. The absence of the CNO\(^{-}\) peak at 2170 cm\(^{-1}\) in the eU2A and the presence of it in the THU indicate that CNO\(^{-}\) is not an intermediate of the reaction during the eU2A process.
Table 5.3

Raman bands assignment of 5.0 M urea in the presence of 5.0 M KOH solution during eU2A and THU

<table>
<thead>
<tr>
<th>Wavenumber, cm⁻¹</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1001</td>
<td>ν4(A1) of urea</td>
<td>[82, 83]</td>
</tr>
<tr>
<td>1070</td>
<td>ν1(A1) of carbonate</td>
<td>[84]</td>
</tr>
<tr>
<td>1165</td>
<td>ν3(A1) of urea</td>
<td>[82]</td>
</tr>
<tr>
<td>1602</td>
<td>ν2(A1) of urea</td>
<td>[82]</td>
</tr>
<tr>
<td>1676</td>
<td>ν1(A1) of urea</td>
<td>[82]</td>
</tr>
<tr>
<td>2170</td>
<td>Anti-symmetric of CNO⁻</td>
<td>[89]</td>
</tr>
<tr>
<td>3318</td>
<td>NH₄⁺</td>
<td>[85]</td>
</tr>
<tr>
<td>3000-3750</td>
<td>O-H in water</td>
<td>[88]</td>
</tr>
<tr>
<td>3230</td>
<td>Urea overlapped O-H</td>
<td>[88]</td>
</tr>
<tr>
<td>3380</td>
<td>Urea overlapped O-H</td>
<td>[88]</td>
</tr>
<tr>
<td>3480</td>
<td>Urea overlapped O-H</td>
<td>[88]</td>
</tr>
<tr>
<td>3612</td>
<td>Ni²⁺</td>
<td>[86]</td>
</tr>
</tbody>
</table>

5.3.5 Mechanistic Consideration

The mechanism of urea to ammonia in the eU2A process is complicated since there are three parallel reactions that occur at the same time: (1) thermal hydrolysis of urea to ammonia in alkaline solution at the bulk; (2) urea electrolysis to N₂, CO₂, and H₂ at the surface of the electrode; and (3) the electrochemically induced urea to ammonia in alkaline solution at the surface of the electrode. This work aims to provide a better understanding of the eU2A mechanism, therefore, all three reactions should be considered. Two possible mechanisms can be considered on the basis of the available literature [50, 51]. The first mechanism is based on the indirect catalytic reactions as proposed in Eqs. 41-43. After oxidizing Ni(OH)₂ to NiOOH (Eq. 33), both OH⁻ and urea are adsorbed on the NiOOH surface, and then urea experiences a deformation to give one molecule of ammonia, leaving CNO⁻ and hydroxide adsorbed on the Ni(OH)₂ surface [50]. The CNO⁻ is further hydrolyzed to ammonia and CO₂.
It has been reported that once CNO\(^-\) is formed, it is hard to desorb \[12\], thus the CNO\(^-\) should have been found by Raman spectroscopy on the surface of the catalyst. However, this is not in agreement with the eU2A experiments (as described in Section 3.4), which challenges the proposed steps (Eqs. 41-44) of the first mechanism. The hydrolysis of CNO\(^-\) was not discussed in Daramola et al.’s investigation \[50\], but it has been demonstrated by other researchers that CNO\(^-\) will further be hydrolyzed to ammonia and CO\(_2\) as shown in Eq. 44 \[44, 90\].

Another reason for not considering this mechanism is that for every one mole of additional ammonia released in Eq. 40, one mole of NiOOH is consumed. Considering 3 hours of the eU2A experiment of 5.0 M urea in the presence of 5.0 M KOH at 0.462 V vs. Hg/HgO as an example, the average current density is 1.69×10\(^{-3}\) A cm\(^{-2}\) (Table 5.1). According to Faraday’s law and the current efficiency of 50.2% for reaction 1, the amount of NiOOH that can be used is 5.71×10\(^{-4}\) mol based on Eq. 45. Therefore, the amount of ammonia generated in eU2A should be less than 1.14×10\(^{-3}\) mol (if 100% of CNO\(^-\) is hydrolyzed to ammonia). Since the additional generated ammonia is 3.86×10\(^{-2}\) mol (Table 5.1), this mechanism does not represent the experimental findings.
\[ \eta_{\text{NiOOH}} = \eta_{\text{NiOOH}} \frac{It}{ZF} \]  

where,

\( F \), Faraday’s constant, \( F = 96485 \text{ } \text{C} \text{ mol}^{-1} \);

\( I \), Average current, in A;

\( \eta_{\text{NiOOH}} \), faradaic efficiency for NiOOH formation, in %;

\( n_{\text{NiOOH}} \), Moles of available NiOOH, in mol;

\( t \), Time, in s;

\( z \), Electrochemical equivalent, \( z = 1 \) according to Eq. 33;

Another potential mechanism could be the direct decomposition of urea as shown in Eqs. 46 and 47 [51]. Urea adsorbs onto the Ni\(^{3+}\) surface and then decomposes to products such as ammonia and CO\(_2\). The second potential mechanism is still facing obstacles. For example, the maximum amount of Ni\(^{3+}\) is formed at peak potential 0.462 V vs. Hg/HgO, refer to CV of Ni electrodes in 5.0 M KOH (Figure 5.4b). According to the second proposed mechanism, the maximum additional ammonia generation rate should be reached at 0.462 V vs. Hg/HgO, but higher generation rates are obtained at 0.485 V vs. Hg/HgO which contradicts the second mechanism. During urea electrolysis, Ni\(^{3+}\) is reduced to Ni\(^{2+}\) while urea is oxidized to N\(_2\). The higher applied potential implies that more Ni\(^{3+}\) could be reduced to Ni\(^{2+}\) [72]. Therefore, the positive correlation between additional ammonia generation rate and applied potential indicates that Ni\(^{2+}\) regenerated in the urea electrolysis also promotes the ammonia generation in the eU2A process.

\[ \text{NiOOH} + \text{CO(NH}_2\text{)}_2 \rightarrow [\text{NiOOH} \cdot \text{CO(NH}_2\text{)}_2]_{\text{ads}} \]  

(46)
However, the higher applied potential generates more H₂ (Table 5.1) gas, even though H₂ has been reported to provide a positive effect for NH₃ SCR [39], the effect of the ratio between H₂ and NH₃ for the SCR reaction has not been investigated. It will be important in the future to couple the optimization of the eU2A process (applied potential) with the performance of the NH₃ SCR, as it is possible that higher applied potentials would benefit the efficiency of the SCR system due to the cogeneration of H₂.

Finally, a mechanism similar to the catalytic hydrolysis of urea to ammonia using urease [8, 91] can be adapted [50, 51]. The extended mechanism is schematically represented in Figure 5.7. A value of the applied potential is not provided in the schematic, as it will be affected by the concentration of electrolyte as well as the electrocatalyst composition and morphology. During the eU2A process, urea electrolysis is inevitable and some NiOOH molecules are first reduced to Ni(OH)₂ [72]. Then Ni³⁺ and Ni²⁺ work as a pair (steps I, II, and III in Figure 5.7), which is similar to the proposed mechanism of urease hydrolysis [8, 45]. Urea is adsorbed on the Ni³⁺ site while OH from the water is adsorbed on the Ni²⁺ site leaving reactive H (step IV in Figure 5.7), by OH attacking, bridging and recombination with H, one ammonia molecule is released, leaving carbamic acid on the surface (step V in Figure 5.7). Since CNO⁻ was not found in the Raman spectroscopy, there could be two hypotheses for steps V to step VI which need to be investigated in the future: one is carbamic acid decomposes to ammonia and CO₂ directly or it decomposes to HCNO and the latter molecule is hydrolyzed to ammonia and
CO₂ rapidly on the catalyst surface with the positive influence of the hard Lewis acid on the Ni⁺³/Ni²⁺ surface [75, 92, 93].

Figure 5.7. Proposed eU2A mechanism. One Ni ion (Ni⁺³) binds and activates urea, while the second Ni ion (Ni²⁺, generated during urea electrolysis [12]) binds a hydroxyl group from the water. The hydroxyl group is activated for attack on the urea carbon to eliminate ammonia with the help of Lewis acid Ni²⁺ and Ni⁺³. The intermediate then collapses and forms NH₃ and CO₂ eventually.

5.4 Conclusion

The mechanism of electrochemically induced urea to ammonia was investigated. It was demonstrated that CNO⁻ is not an intermediate of the reaction for the eU2A process. Through experiments at different concentrations of supporting KOH and different applied potentials, the catalytic effect of Ni⁺³ and Ni²⁺ was elucidated. By applying a constant potential, Ni⁺³ is formed on the working electrode surface. Pairing with Ni²⁺, which comes from urea electrolysis, urea decomposes to ammonia and carbamic acid, the latter is finally decomposed to ammonia and CO₂. Further studies are still needed to demonstrate this hypothesis. For instance, there could be other steps in
which carbamic acid decomposes to \( H_2O \) and HCNO, the latter could be further hydrolyzed to \( NH_3 \) and \( CO_2 \). In addition, the localized pH during the eU2A reaction could play a significant role; therefore, it is recommended to monitor the localized pH in future work to provide a comprehensive understanding of the eU2A process. The mechanism could also be studied via Density Functional Theory methods.
CHAPTER 6: AMMONIA GENERATION VIA A GRAPHENE-COATED NICKEL CATAYLST

The contents of this chapter have been published in Coatings, a peer-reviewed journal: Lu, F.; Botte, G. G., Ammonia Generation via a Graphene-Coated Nickel Catalyst. Coatings 2017, 7 (6), 72 [94].

6.1 Introduction

Ammonia is a commonly used reducing agent for selective catalytic reduction of NOx in combustion engines and power generation. Due to safety and environmental concerns, there has been an increased utilization of urea-derived ammonia production [95] based on the chemical hydrolysis of urea at high temperature. To improve the efficiency of the conversion of urea to ammonia at lower temperatures, Botte proposed a new method that implements nickel based electrodes with the aid of an electric field to convert urea to ammonia [96]. The method is known as the electrochemically induced conversion of urea to ammonia (eU2A, see Eq. 48) and it has been demonstrated to be an effective on-site method for ammonia generation from urea [96, 97]:

\[
CO(NH_2)_2 \xrightarrow{\text{NiOOH at 70 °C}} 2NH_3 + CO_2
\]  

(48)

For example, in the eU2A process, by applying a constant potential at 70 °C, urea is converted to ammonia at a higher rate than homogeneous urea hydrolysis at ambient pressure and low temperature [97]. However, the supporting electrolyte, potassium hydroxide (KOH) [97], is neutralized to K_2CO_3 by CO_2 released from urea in the eU2A process. During the reaction, the electrolyte in the eU2A reactor became bluish due to the
corrosion of the Ni electrode from the formation of the Ni-ammonia complex ion. In addition, part of the ammonia produced reacts with the Ni ions in the electrolyte to form the complex, which caused the decrease of the ammonia evolution/production in the eU2A process with time.

Graphene is a single atomic monolayer of graphite with excellent thermal and mechanical properties such as incomparable high electron mobility, large specific surface area and exceptional chemical stability [19-21]. Coating with graphene has been proved to be an effective anti-corrosion method for protecting the metals’ surface without altering the intrinsic properties of the protected metals [18, 22]. Prasai et al. found that multi-layer graphene-coated Ni corroded 20 times less than bare Ni [98]. Furthermore, it has already been proven that graphene-Ni nanocomposites are promising catalysts for urea electrolysis [23, 99]. Reactions such as hydrogen production from water can be induced through the interface of graphene/Ni [100]. Graphene has improved the corrosion resistance of stainless steel [22]. Thus, the use of graphene coating to protect a Ni electrode in the eU2A process using K₂CO₃ as supporting electrolyte was conceived as a method to reduce the ammonia corrosion of Ni from the electrode, to reduce the consumption of ammonia ligands, and to avoid the need of replacing the electrolyte in the eU2A process. In addition, according to cyclic voltammograms (CV) experiments, the peak current of NiOOH (the effective working catalyst for the eU2A process) using graphene-coated Ni electrodes is higher than bare Ni, thus it enables higher additional ammonia generation rate on the electrode [99].
In this dissertation, a graphene coating method was developed for protecting Ni working electrodes from ammonia corrosion. The graphene film was made by chemical vapor deposition (CVD) and self-lifted on Ni foil. The graphene-coated Ni was used as the working electrode for the eU2A reactions using K$_2$CO$_3$ as the supporting electrolyte. The investigation demonstrates that the corrosion rate of graphene-coated Ni electrode, in terms of weight loss of Ni per surface area, is dramatically reduced when compared to a bare Ni electrode. In addition, this Ni catalyst with anti-corrosive graphene coating gives a much higher normalized ammonia generation rate (per geometric area of the electrode) than a bare Ni foil electrode.

6.2 Experimental Methods

6.2.1 Preparation of the Graphene-Coated Ni Electrode

The Ni foils (purity > 99%, Alfa Aesar, 2.0 cm x 3.0 cm) used for making all the electrodes were first polished with sand paper (600 grit, Gator Finishing) and then sandblasted with alumina powder (27.5 micron, Crystal Mark, Inc.) for 2 min. The pretreated Ni foils were spot-wired to Ni wires (diameter 1.0 mm, purity 99.5%, Alfa Aesar) for collecting the current. Low sulfur sub-bituminous coal (Wyodak coal seam) was used as a solid carbon source for growing the graphene film on copper substrate using the CVD method [61] (refer to Section 3.8 for details).

The flow chart of the process for making the graphene-coated Ni is shown in Figure 3.12a. Once the graphene film was synthesized on a copper substrate, a supportive layer of Poly(methyl methacrylate) (PMMA) was spin-coated onto the graphene. After
dissolving the copper substrate in the Marbles reagent (10 g CuSO₄, 50 mL HCl, 50 mL DI water) [62], the PMMA/graphene stack was transferred to DI water for 3 hours for surface cleaning and then self-lifted onto a pretreated Ni foil as shown in Figure 3.12b. The PMMA was then removed by rinsing the PMMA/graphene stack on the pretreated Ni electrode with acetone to complete the making of the graphene-coated Ni. After drying for 30 minutes at 70 °C in the oven (Model 30GC Lab Oven, Quincy Lab), the edges of the graphene were sealed with Teflon tape to prevent the interference of the uncoated nickel in the evaluation of the catalyst as shown in Figure 3.12c, therefore, the exposed area (active area) of the graphene-coated Ni was 1.0 cm x 2.0 cm.

6.2.2 Physical Characterization of Graphene

Transmission Electron Microscopy (TEM) images and selected area electron diffraction (SAED) of the CVD graphene film were obtained using a transmission electron microscope (JEOL JEM 2100F). The atomic force microscopy (AFM) images were obtained using an Agilent 5500 AFM/STM microscope in AC mode with NSC 15/AlBS probes (resonant frequency of 325 kHz) from MikroMasch USA under ambient conditions. The flow chart for preparing the graphene sample for TEM and AFM analysis is shown in Figure 6.1. After dissolving the copper substrates in the Marbles reagent, the floating CVD graphene film was rinsed with DI water to remove contamination and to clean the surface before transferring it onto a lacy carbon TEM grid (300 mesh, Copper) for TEM analysis and a silicon wafer for AFM analysis.
Figure 6.1. Flow chart for transferring graphene on the TEM grid and silicon wafer for TEM and AFM analysis.

Raman spectra of the graphene-coated Ni and Ni foil were recorded using a Bruker Senterra Raman spectrometer (equipped with a microscope with a 10x objective lens; Bruker Corporation) at 532 nm wavelength laser excitation (20 mW power).

6.2.3 Cyclic Voltammetry and Urea to Ammonia

Urea (purity 99.8%) and K$_2$CO$_3$ (purity 99.0%) used in the experiments were purchased from Fisher Scientific. Deionized water prepared by EVOQUA deionization system was used throughout the experiments unless otherwise specified. As shown schematically in Figure 6.2, the electrochemical tests were carried out in a three neck flask (100 mL) using a Solartron 1281 Multiplexer Potentiostat (Solartron Analytical) with the graphene-Ni as the working electrode (WE), Pt foil (1.0 cm x 2.0 cm, purity > 99.0%, Alfa Aesar) as the counter electrode (CE), and Hg/HgO as the reference electrode (RE). The reference electrode was supported using a Luggin capillary filled with 2.5 M
K₂CO₃. For comparison purposes, pretreated bare Ni foil was also used as a working electrode.

Figure 6.2. Schematic of the three-neck eU2A reactor. The working electrodes are Ni foil and graphene-coated Ni and the counter electrode is Pt foil, while the reference electrode is Hg/HgO. Temperature was set at 70 °C. The sample port allowed collecting liquid samples and determining pH of the electrolyte in the reactor.

Solutions of 125 mL of 2.5 M K₂CO₃ in the presence and absence of 5.0 M urea were used for the experiments. All the experiments were performed at 70°C -heating was provided using a heat mantle (Glas-Col®, Glas Col, LLC.) with a temperature controller (Econo Temperature controller 12125-14, VWR International, LLC.). In all cases, the fifth pseudo-steady state cyclic voltammograms (CVs) between 0.5 V and 1.0 V vs. Hg/HgO, at a scan rate of 10 mV s⁻¹, are reported. The eU2A experiments were performed at a constant potential vs. the reference electrode for a period of 24 hours. The applied potential used corresponds with the oxidation peak of the CVs in the absence of urea. In addition, experiments were performed without applying a potential to determine
the amount of ammonia produced in the bulk solution due to the thermal hydrolysis of urea (THU) [63]. An ammonia ion selective electrode (ISE) (Orion 710A+, Thermo Electron Corporation) was used to measure the concentration of ammonia in the reactor (Section 3.3). The pH change of the solution was monitored using a pH meter (OAKTON Acorn pH 5 meter).

6.2.4 Quantification of Corrosion

The corrosion of Ni was quantified as the concentration of Ni ions in the solution. Atomic absorption spectroscopy (AAS) was employed to measure the concentration of Ni ions in the solution (Appendix A9).

6.3 Results

6.3.1 Physical Characterization

The nature of the graphene film is shown by TEM in Figure 6.3. The image (Figure 6.3a) represents a continuous graphene film over a large area on the TEM grid with wrinkles and overlapping which were introduced due to the transfer process. The SAED image (inset in Figure 6.3a) reveals the six diffraction spots depicting the hexagonal diffraction pattern and the crystalline structure of the coal derived graphene films. Two or more layers of graphene are shown (Figures 6.3b and 6.3c) on the edge of the film.
Figure 6.3. (a) TEM image of large area and continuous coal derived graphene film; Inset: SAED with six diffraction spots demonstrating the crystalline nature of the coal derived graphene film. (b, c) High magnification TEM image with the edge of the coal derived graphene film exhibiting bi-layers to few layers of the film.

The AFM image (Figure 6.4a) shows the continuous graphene film on silicon substrate. Line scans were performed on the various regions of graphene films to determine the thickness, as depicted in the AFM image (Figure 6.4a). The corresponding height profiles (Figure 6.4b) show that the thickness is ~ 5-15 nm across the line scans suggesting the formation of few layer graphene films. The brighter areas (with greater thickness) in the AFM image are caused by the back-folding and/or overlapping which can be clearly observed in TEM analysis.
Figure 6.4. (a) AFM image of the CVD synthesized graphene film on silicon wafer. The wrinkles and overlapping of the graphene film were shown as brighter spots on the image. (b) Height profile of different line scans of the graphene film. ~5-10 nm thickness of the film was exhibited by the line scans which shown that the graphene film is few-layered.

The Raman spectra of the graphene on the surface of the Ni electrode were obtained before and after the eU2A experiments (Figure 6.5, curves I and II). In both cases, the Raman spectra exhibited a D band at 1360 cm$^{-1}$, a zone-boundary phonon mode in first-order Raman spectra attributed to the defects in the graphene films [61]; a G band at 1585 cm$^{-1}$, assigned to the tangential vibrations of sp$^2$ bonded carbon atoms [61]; and a 2D band at 2700 cm$^{-1}$, a boundary phonon mode in second order Raman spectra associated with graphene [61]. The ratio of the intensity of the 2D band to the G band (I$_{2D}$/I$_{G}$) is approximately 1, indicating that the coated graphene is bi-layered to few-layered graphene [62, 101-103] films, which is in agreement with the TEM and AFM analysis. The consistency of the Raman spectra of the coated graphene before and after the experiments implies that the graphene coating is stable during the eU2A process. In
contrast, no D, G, and 2D bands are found in the Raman spectrum of the bare Ni electrode (Figure 6.5 curve III).

Figure 6.5. Raman spectra of graphene-coated Ni before (curve I) and after (curve II) 24 hours’ eU2A experiment and bare Ni foil (curve III).

6.3.2 Cyclic Voltammetry

The normalized (by active geometric area of the electrodes) cyclic voltammograms (CVs) of 2.5 M $\text{K}_2\text{CO}_3$ in the absence and presence of 5.0 M urea at 70°C using the Ni foil and graphene-coated Ni, at a scan rate of 10 mV s$^{-1}$, are shown in Figure 6.6. The CVs illustrates an anodic and cathodic peak in relation to the NiOOH/Ni(OH)$_2$ redox couple (Eq. 49) for both working electrodes.

$$\text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (49)$$

In the forward scan of the CVs in Figure 6.6a, an anodic peak is observed at 0.750 V vs. Hg/HgO corresponding to the oxidation of Ni(OH)$_2$ to NiOOH. In the reverse scan,
a cathodic peak is seen at 0.645 V vs. Hg/HgO due to the reduction of NiOOH to Ni(OH)₂. The CVs also demonstrate that the redox current of NiOOH is enhanced after graphene coating. That is, in the same geometric area, the graphene-coated Ni enables more active sites of NiOOH for the eU2A reaction. When adding 5.0 M urea, the anodic current density increased, indicating that urea starts to be electrolyzed to N₂ as proposed by Vedharathinam and Botte [12]. The disappearance of the cathodic peak (see Figure 6.6b) means that in the eU2A process, NiOOH is consumed, thus no cathodic current could be observed.

![Figure 6.6](image)

Figure 6.6. (a) Normalized -by active geometric area of the electrodes- cyclic voltammograms of 2.5 M K₂CO₃ in the (a) absence and (b) presence of 5.0 M urea at 70 °C using the Ni foil and graphene-coated Ni electrodes, at a scan rate of 10 mV s⁻¹.

### 6.3.3 Generation of Ammonia in the eU2A and THU Process

The generated ammonia during 24 hours eU2A (0.750 V vs. Hg/HgO) using graphene-coated Ni and bare Ni working electrodes and THU experiment is shown in Figure 6.7a.
Figure 6.7. (a) Concentration of generated ammonia in the electrolyte during the eU2A (70°C, 0.750 V vs. Hg/HgO) process using the Ni foil (6.0 cm$^2$) and graphene-coated Ni (2.0 cm$^2$) and its comparison with the THU (70 °C) process in a period of 24 hours using 5.0 M urea in the presence of 2.5 M K$_2$CO$_3$. (b) Normalized concentration (per cm$^2$ of the working electrode) of generated ammonia on the electrode surface during eU2A (70 °C, 0.750 V vs. Hg/HgO) process using the Ni foil and graphene-coated Ni. Ammonia generation increased in the eU2A compared to the THU process and the generated ammonia per surface area is higher using the graphene-coated Ni than using the Ni foil.

The generated ammonia on the electrode surface in the eU2A experiments is the total ammonia produced excluding the ammonia produced in the bulk solution (THU) as calculated in Eq. 50. The normalized generated ammonia per surface area of the electrode is then calculated according to Eq. 51 and the results are shown in Figure 6.7b.

\[
C_{i,\text{add}} = C_{eU2A,i} - C_{THU,i} \quad (i = 1, 2, 3, \ldots, n) \tag{50}
\]

\[
\bar{C}_{i,\text{add}} = \frac{C_{i,\text{add}}}{A} \tag{51}
\]

where,

\( C_{THU,i} \), the concentration of ammonia at sample point \( i \) in the THU experiment, in M;

\( C_{eU2A,i} \), the concentration of ammonia at sample point \( i \) in the eU2A experiment, in M;

\( i \), number of the sample point;
$C_{i, \text{add}}$, the additional ammonia generated on the surface of the working electrode, in M;

$A$, geometric area of the working electrode, in cm$^2$;

$\bar{C}_{i, \text{add}}$, the normalized additional ammonia generated on the surface of the working electrode, in M cm$^{-2}$;

In the eU2A process, 0.0181 M cm$^{-2}$ ammonia is produced on the Ni foil electrode and 0.0402 M cm$^{-2}$ on the graphene-coated Ni electrode (Figure 6.7b). That is, the generated ammonia rate -per active area of the electrode- in the eU2A process using the graphene-coated Ni is more than 2 times higher than using the bare Ni foil. The graphene coating enhanced the eU2A reaction, which facilitated a higher ammonia generation rate. The enhancement possibly comes from the intrinsic properties of graphene and/or from a change in the electric-double layer, however, such mechanism was not explored in this dissertation.

6.3.4 Ammonia Corrosion on the Graphene-Coated Ni Electrode

During the eU2A experiment, ammonia is generated on the surface of the Ni electrode and it would cause corrosion of the electrode to form $[\text{Ni(NH}_3\text{)}_n]^{2+}$ complex [52, 104]. The electrolyte in the eU2A experiment using the Ni foil as the working electrode became bluish while in contrast the electrolyte was colorless when using the graphene-coated Ni. This indicates that graphene coating helped reducing the corrosion of Ni in the eU2A process. The change of the concentration of Ni ion during the experiments was measured by AAS and the results are shown in Appendix Figure A9.2, then the
normalized concentration of Ni ions are calculated using Eq. 25 and the results are shown
in Figure 6.8a.

As shown in Figure 6.8a, the gradient of the normalized concentration of Ni ion
increased due to the generation of ammonia in the electrolyte, which causes severe
corrosion. The pH value of the electrolyte during the eU2A experiments decreased as a
function of time (as shown in Figure 6.8b). A series of Ni-ammonia complexes
([Ni(NH₃)ₙ]²⁺) have been reported in the pH region from 8 to 12, where the number n
increases when the pH increases [105]. The pH value of the electrolyte decreased from
11.4 to 10.4 (Figure 6.8b) due to the conversion of K₂CO₃ to KHCO₃ by the generated
CO₂ from the eU2A reaction (Eq. 48). The pH value in the eU2A experiment using the
graphene-coated Ni electrode is slightly lower due to the enhanced urea to ammonia
conversion rate, which generates more CO₂ (see Equation 1). In this pH range, the number of incorporated ammonia ligands for the Ni-ammonia complexes is 5 or 6 [105], therefore large amount of ammonia is lost due to the complexation on the bare Ni working electrode. In addition, the eU2A process is a heterogeneous reaction and the ammonia generated from the electrode surface causes the localized concentration of ammonia to be higher at the surface of the electrode than at the bulk solution. This explains why the bare Ni electrode was easily attacked in the region near the surface of the electrode. In contrast, the protective graphene layer could be explained by two hypothesized mechanisms: (1) blocking the ammonia from touching the Ni ion thus reducing the corrosion rate dramatically as shown in Figure 6.8a and (2) creating a localized high concentration of OH⁻ ions on the surface of the Ni as reported by Botte [99]. It is most likely that there is small amount of Ni lost from the graphene-coated Ni due to the structure defects of the graphene film, which exposes the bare Ni surface to the electrolyte. Therefore, it is expected that graphene films with fewer defects would be more favorable for anti-corrosion coating of the electrodes in the eU2A process.

6.4 Discussion and Conclusion

Ni is corrosion-resistant in many applications including diluted ammonium hydroxide solution, but the rapid attack on Ni still occurs especially when the concentration of ammonia is higher than 1% (or 0.588 M) [106]. Even though the generated ammonia is less than 0.588 M in the bulk (Figure 6.7a), because the generation comes from the surface of the electrode, the localized ammonia would be higher than 1 %,
which will initiate the corrosion of Ni. When the Ni electrode works in the eU2A process in 1.0 - 7.0 M KOH supporting solution as described in previous investigation [97], the pH of the solution is higher than 13, therefore, no nickel-ammonia complex can be formed. However, as the supporting electrolyte is converted to K₂CO₃, ~ 70% of it will be transformed to KHCO₃ at equilibrium state with the continuously released CO₂ from the urea hydrolysis [107], making the pH of the electrolyte fall into a region where Ni-ammonia complexes ([Ni(NH₃)ₙ]²⁺, n = 2 - 6) form on the surface of the Ni electrode [105]. The complexes are soluble in the electrolyte dragging Ni from the surface of the working electrode, which propagates ammonia corrosion.

Graphene coating effectively inhibits the complexation-dragging process and therefore becomes a promising anti-corrosion method for protecting the Ni electrode from ammonia corrosion in the eU2A process. The CVD synthesized graphene was successfully transferred onto the Ni working electrode with the help of PMMA, which ensured its continuous integrity and homogeneity (the coverage and homogeneity can be seen in scanning electron microscopy (SEM) images in Appendix A11). The coating of graphene is bi-layered to few-layered as demonstrated by the TEM analysis and the Raman spectra. It was proved by Raman spectra that the coating of graphene on the Ni electrode is longstanding during the eU2A reaction. However, some defects were noticed on the surface of the graphene, therefore it is hypothesized that better corrosion resistance could be achieved if the Ni electrode was coated with defect-free graphene.

Surprisingly, the graphene coating did not inhibit the eU2A reaction; instead a higher ammonia generation rate was achieved using the graphene-coated Ni electrode. In
24 hours of eU2A reaction, the loss of Ni was reduced by 9.09 mg L\(^{-1}\) cm\(^{-2}\) or 0.155 mM cm\(^{-2}\) (Figure 6.8a) after graphene coating, therefore, it is estimated that the produced ammonia could be at best increased by 0.930 mM cm\(^{-2}\) -assuming the number of incorporated ammonia ligands is 6. However, the generated ammonia increased by 0.0221 M cm\(^{-2}\) (Figure 6.7b). This means that the increased ammonia generation not only comes from the corrosion minimization, but also from a mechanism by which the graphene coating enhanced the catalytic effect of Ni on the eU2A reaction. It is recommended to investigate the performance of graphene-coated Ni electrodes with the direct CVD growth of graphene on Ni foil since it has its own peculiarities [108, 109] and provides a more firmed attachment which can help with the elucidation of the mechanism. Also, the effect of monolayer and defect free graphene-coated Ni electrodes should be investigated in the future. Furthermore, the OH\(^{-}\) concentration in the reactor is crucial for eU2A reactions thus the ammonia generation rate is decaying due to the reducing pH. However the reaction rate will become stable after the equilibrium of K\(_2\)CO\(_3\)/KHCO\(_3\)/NH\(_3\)/H\(_2\)O is reached. With this consideration, long time experiment will be conducted in the future.
CHAPTER 7: CONCLUSION AND FUTURE WORK

7.1 Conclusions

7.1.1 Feasibility of the eU2A Technique

This dissertation revealed a novel method to convert urea to ammonia, which is referred to as eU2A using a Ni based catalyst. The eU2A process was proven to be an effective method to produce ammonia on-site. At the moderated operation condition at 70 °C and ambient pressure, a remarkable ammonia generation rate was achieved using the eU2A process. Under different operating conditions throughout the dissertation, eU2A demonstrated greater ammonia generation rates compared to the THU process. In the two-electrode eU2A reactor with Ni beads as the active catalyst (with the highest surface area of the Ni electrodes tested), more than 6 times of ammonia was generated in the eU2A process (1.609 mol) compared to the THU process (0.256 mol) in 24 hours. Moreover, since urea is converted to ammonia in the eU2A process through an electrochemical approach, the ammonia generation can further be increased by enlarging the active surface area of the Ni working electrode.

The decoupling of ammonia generation in the eU2A and NH3 SCR process in the exhaust system avoids curtailed urea dosing when the exhaust temperature is low. In addition, the accumulation of water (steam) could be prevented in the SCR chamber because ammonia is generated in the eU2A reactor outside the SCR chamber; thus, the efficiency of NOx reduction could be improved by using dry ammonia feed [33]. Another advantage that the eU2A process offers is the production of H2 gas along with ammonia, which could potentially increase the NOx reduction rate in the NH3 SCR system.
Therefore, the SCR reactor could be optimized when equipped with an eU2A reactor. Furthermore, the ammonia generation rate can be adjusted by changing the cell voltage which is beneficial for quick response to meet the demand of ammonia for a SCR reaction.

7.1.2 Fundamental Study of the Mechanism of eU2A

Three parallel reactions were found to occur in the eU2A reactor: (1) urea hydrolysis to ammonia with the help of heat and the alkalinity in the bulk solution; (2) urea electrolysis to N\textsubscript{2}, H\textsubscript{2} and CO\textsubscript{2} on the surface of the electrode; and (3) eU2A in the alkaline solution on the surface of the electrode. The alkalinity is crucial for ammonia generation, as it not only affects urea hydrolysis but also the eU2A process. When the pH of the reagent solution is increased, the ammonia generation rate increases (see the comparison in Appendix Figure A8.3), except when using 7.0 M KOH as the supporting electrolyte, which indicates that OH\textsuperscript{-} ions positively contribute to the ammonia generation from the urea. The eU2A process uses the Ni based catalyst, when a positive potential is applied on the Ni working electrode, Ni\textsuperscript{2+} (Ni(OH)\textsubscript{2}) oxidizes to Ni\textsuperscript{3+} (NiOOH) and Ni\textsuperscript{3+} reduces to Ni\textsuperscript{2+} through urea electrolysis. Both Ni\textsuperscript{2+} and Ni\textsuperscript{3+} had positive correlation with the ammonia generation rate in this study.

A mechanism of eU2A is proposed based on these facts: (1) Ni\textsuperscript{2+}, Ni\textsuperscript{3+}, and OH\textsuperscript{-} ions have a positive effect on ammonia generation in the eU2A process; (2) the eU2A reaction happens in parallel to urea electrolysis and THU; and (3) CNO\textsuperscript{-} is found not to be an intermediate in the eU2A process through \textit{in-situ} Raman. The proposed mechanism
is as follows: In alkaline media, after applying a constant potential on Ni working electrode, Ni$^{3+}$ is formed on the working electrode surface. Pairing with Ni$^{2+}$, which comes from the urea electrolysis in the meantime, urea decomposes to ammonia and carbamic acid, and the latter molecule decomposes to ammonia and CO$_2$.

7.1.3 Graphene Coating on Ni Electrode for the eU2A Process

Ni is corrosion-resistant in diluted ammonium hydroxide solutions. However, because eU2A is a heterogeneous reaction, the generation of ammonia at the electrode surface increases the localized ammonia concentration, which initiates the corrosion of the Ni electrode. When the pH of the reagent solution falls into the region of 8 to 12, Ni$^{2+}$ reacts with excess NH$_3$ to form [Ni(NH$_3$)$_n$]$^{2+}$, and these complex ions are soluble, thus dragging Ni away from the electrode surface and propagating the ammonia corrosion of the Ni electrode in the eU2A process. It is possible that pH of the reagent solution in the eU2A process reduced to the region of 8 to 12 because the generated CO$_2$ neutralizes the initially added KOH supporting electrolyte to form K$_2$CO$_3$. In this dissertation, the concentration of Ni ions in the bulk solution was used to quantify the corrosion of Ni and more than 10 mg L$^{-1}$ cm$^{-2}$ of Ni was corroded when using 2.5 M K$_2$CO$_3$ as the supporting electrolyte in the eU2A process. Therefore prevent the corrosion of the Ni electrodes is important in the eU2A process.

The graphene coating was found to be an effective method to inhibit the Ni ammonia complexation and to reduce the ammonia corrosion of Ni. After applying the graphene coating, the corrosion of Ni was reduced ~ 20 times (< 0.5 mg L$^{-1}$ cm$^{-2}$) when
compared to the bare Ni electrode in the eU2A process using 5.0 M urea in the presence of 2.5 M K₂CO₃. In this study, the multi-layered graphene was successfully synthesized from Wyodak Coal through the CVD method. The coal used for making the graphene is abundant, and using coal as the carbon source for making graphene is relatively cheap. Additionally, PMMA polymer is useful in transferring of graphene film onto the surface of Ni electrode. In this work, the PMMA polymer coating ensured the integrity and homogeneity of the graphene film during the transfer process.

It is important to observe that the ammonia generation rate in the eU2A increased ~ 2 times after the Ni electrode was coated with the graphene film. This phenomenon offers a method to increase ammonia generation without increasing the geometric surface area of a working electrode. In this dissertation, the enhanced ammonia generation using graphene-coated Ni was found to not only come from the ammonia corrosion prevention (ammonia is saved from being ligands in Ni ammonia complex) but also from the enhancement of the catalytic effect of the Ni catalyst in the eU2A process. Botte [99] explained that the graphene acts as a diffusion control layer that enhances the diffusion of OH⁻ ions, thereby increasing the localized pH. The increase in localized pH at the electrode surface thus enhanced the ammonia generation in both the eU2A (according to the proposed mechanism in this investigation) and urea hydrolysis reactions.

7.2 Future Scope and Recommendations

Since the eU2A is an electrochemically induced process, the ammonia generation rate could be further improved by enlarging the contact area between the reagent solution
and catalyst surface such as by using fine Ni beads, Ni foam or Ni nano-composites as the working electrode. However, this brings difficulties for graphene coating on such forms of Ni electrodes. For example, it would be challenging to coat a Ni foam working electrode with graphene. As for future investigation, fostering CVD growth of graphene directly on a Ni electrode to give a firmer attachment should be considered. Additionally, the transportation conditions of eU2A could be improved by using a flow system. It could be valuable to investigate the mass transfer parameters inside the reactor to maximize the contact between the reagent solution and working catalyst.

In addition, understanding the effect of graphene coating on the enhancement of the catalytic effect on Ni electrode would be beneficial. A cost analysis for the eU2A process using the graphene coating is required in the future to reveal the cost of replacing the Ni electrodes with the graphene-coated Ni electrodes.

Furthermore, since the ammonia generation rate was reduced dramatically when the supporting electrolyte, KOH, was neutralized to K$_2$CO$_3$ during the eU2A process (Appendix Figure A8.3), the methods for increasing the pH inside the eU2A reactor, such as using Ca(OH)$_2$ to precipitate CO$_3^{2-}$ and regenerate KOH in the system (as shown in Eq. 47) [110] are worth investigating. The cost for the eU2A process would increase, because of the capital cost of Ca(OH)$_2$. The operating cost for the removal of the precipitated CaCO$_3$ would likely increase, and a special design for the reactor would be needed.

$$Ca(OH)_2 + K_2CO_3 \rightarrow CaCO_3 \downarrow +2KOH$$  \hspace{1cm} (47)

Last but not the least, the next step for the eU2A process investigated in this dissertation is to produce ammonia on-site for the SCR process. The gaseous products,
NH$_3$, N$_2$, H$_2$, and CO$_2$ will be generated at the same time in the eU2A reactor. Even though H$_2$ is beneficial for the SCR reaction, the optimized ratio of H$_2$ and NH$_3$ needs to be revealed. In addition, if N$_2$ and CO$_2$ are found to have negative effects for the SCR process, a separate step for removing these gases should be taken.
REFERENCES


APPENDIX A1: AMMONIA MEASUREMENT

The ammonia ISE (Thermo 710A+, measurement error is ± 2%) needs to be calibrated every day. Ammonia is soluble in DI water, but 50 % of ammonia solution can be lost every 6 hours [1]. Therefore before sampling, to preserve the sample, 0.5 mL H₂SO₄ solution was added to DI water (less than 50 mL) in the 100 mL of flask, after the sampled electrolyte from the reactor was dropped in, DI water was added to make a total 100 mL solution. The ammonia ISE was calibrated with 0.121, 1.21, 12.1, and 121 ppm (1 ppm = 5.87 x 10⁻⁵ M) of ammonia standard solutions, made by dilution from 1000 ppm as nitrogen standard (Thermo Scientific, Orion 951007, 1 ppm as nitrogen = 1.21 ppm of ammonia). The ammonia concentration of the diluted samples was measured after the calibration.

The diluted samples from the reactor was made by 0.5 mL of reactor’s solution diluted with ultra-pure water (Alfa Aesar, HPLC grade) to 100 mL (200 times dilution, volumetric flasks were used for accuracy). The concentration and amount of ammonia was calculated using Eqs. A1-A3. For the experiments in Chapter 4, the ammonia concentration of the solutions both in the reactor and trap were measured, while for the experiments in Chapter 5 and 6, the ammonia concentration of the solutions only in the reactor was measured.

\[
C_{NH_3} = C_{NH_3, \text{sample}} \times 200 \times 5.87 \times 10^{-5} \quad (A1)
\]

\[
n_{NH_3, r} = C_{NH_3, r} \cdot V_r \quad (A2)
\]

\[
n_{NH_3, t} = C_{NH_3, t} \cdot V_t \quad (A3)
\]

where,
$C_{NH_3, sample}$, the concentration of ammonia in the diluted sample, in ppm;

$C_{NH_3}$, the concentration of ammonia generated in the experiments, in M;

$n_{NH_3,r}$, the amount of ammonia generated in the experiments in the reactor, in mol;

$n_{NH_3,t}$, the amount of ammonia generated in the experiments in the trap, in mol;

$V_r$, the volume of the liquid (electrolyte, reactant, products) in the reactors, in L;

$V_r = 0.25 \text{ L}$ for the two-electrode reactor and $V_r = 0.125 \text{ L}$ for the three-electrode reactor;

$V_t$, the volume of the liquid (electrolyte, reactant, products) in the trap, in L; $V_t = 1 \text{ L}$ for the two-electrode eU2A reactor;
Table A1.1

Ammonia generation in the 24-hour eU2A (1.65 V, 70 °C) experiment in the two-electrode reactor using 7.0 M KOH supporting electrolyte

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>( C_{NH_3, \text{sample, reactor}} ) ppm</th>
<th>( C_{NH_3, \text{reactor}} ) M</th>
<th>( C_{NH_3, \text{sample, trap}} ) ppm</th>
<th>( C_{NH_3, \text{trap}} ) M</th>
<th>( n_{NH_3} ) mol</th>
<th>Generated ammonia mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.69</td>
<td>0.069</td>
<td>0</td>
<td>0</td>
<td>0.022</td>
<td>0</td>
</tr>
<tr>
<td>0.25</td>
<td>14.3</td>
<td>0.210</td>
<td>0.103</td>
<td>0.002</td>
<td>0.054</td>
<td>0.032</td>
</tr>
<tr>
<td>0.5</td>
<td>21.0</td>
<td>0.308</td>
<td>0.130</td>
<td>0.002</td>
<td>0.079</td>
<td>0.057</td>
</tr>
<tr>
<td>0.75</td>
<td>29.5</td>
<td>0.433</td>
<td>0.321</td>
<td>0.005</td>
<td>0.113</td>
<td>0.091</td>
</tr>
<tr>
<td>1.0</td>
<td>38.3</td>
<td>0.562</td>
<td>0.887</td>
<td>0.013</td>
<td>0.153</td>
<td>0.131</td>
</tr>
<tr>
<td>1.25</td>
<td>43.1</td>
<td>0.632</td>
<td>0.956</td>
<td>0.014</td>
<td>0.172</td>
<td>0.150</td>
</tr>
<tr>
<td>1.5</td>
<td>49.5</td>
<td>0.726</td>
<td>1.62</td>
<td>0.024</td>
<td>0.204</td>
<td>0.183</td>
</tr>
<tr>
<td>3.0</td>
<td>68.4</td>
<td>1.004</td>
<td>7.27</td>
<td>0.107</td>
<td>0.356</td>
<td>0.334</td>
</tr>
<tr>
<td>4.0</td>
<td>75.7</td>
<td>1.111</td>
<td>13.8</td>
<td>0.203</td>
<td>0.478</td>
<td>0.456</td>
</tr>
<tr>
<td>5.0</td>
<td>91.1</td>
<td>1.337</td>
<td>21.1</td>
<td>0.310</td>
<td>0.640</td>
<td>0.618</td>
</tr>
<tr>
<td>6.0</td>
<td>111</td>
<td>1.629</td>
<td>34.1</td>
<td>0.500</td>
<td>0.902</td>
<td>0.880</td>
</tr>
<tr>
<td>18.0</td>
<td>68.4</td>
<td>1.004</td>
<td>77.7</td>
<td>1.140</td>
<td>1.385</td>
<td>1.364</td>
</tr>
<tr>
<td>24.0</td>
<td>67.3</td>
<td>0.988</td>
<td>94.8</td>
<td>1.391</td>
<td>1.631</td>
<td>1.609</td>
</tr>
</tbody>
</table>

Measurement error is: ± 2 %
### Table A1.2

Ammonia generation in the 24-hour THU (70 °C) experiment in the two-electrode reactor using 7.0 M KOH supporting electrolyte

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>( C_{\text{NH}_3, \text{sample, reactor}} ) (M)</th>
<th>( C_{\text{NH}_3, \text{reactor}} ) (ppm)</th>
<th>( C_{\text{NH}_3, \text{sample, trap}} ) (M)</th>
<th>( C_{\text{NH}_3, \text{trap}} ) (M)</th>
<th>( n_{\text{NH}_3} ) (mol)</th>
<th>Generated Ammonia (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.96</td>
<td>0.117</td>
<td>0</td>
<td>0.001</td>
<td>0.030</td>
<td>0</td>
</tr>
<tr>
<td>0.25</td>
<td>12.4</td>
<td>0.182</td>
<td>0.035</td>
<td>0.001</td>
<td>0.046</td>
<td>0.016</td>
</tr>
<tr>
<td>0.5</td>
<td>17.8</td>
<td>0.261</td>
<td>0.042</td>
<td>0.001</td>
<td>0.066</td>
<td>0.036</td>
</tr>
<tr>
<td>0.75</td>
<td>21.9</td>
<td>0.321</td>
<td>0.078</td>
<td>0.001</td>
<td>0.081</td>
<td>0.052</td>
</tr>
<tr>
<td>1.0</td>
<td>24.7</td>
<td>0.362</td>
<td>0.106</td>
<td>0.002</td>
<td>0.092</td>
<td>0.062</td>
</tr>
<tr>
<td>1.25</td>
<td>28.8</td>
<td>0.423</td>
<td>0.257</td>
<td>0.004</td>
<td>0.109</td>
<td>0.079</td>
</tr>
<tr>
<td>1.5</td>
<td>29.3</td>
<td>0.430</td>
<td>0.263</td>
<td>0.004</td>
<td>0.111</td>
<td>0.081</td>
</tr>
<tr>
<td>3.0</td>
<td>36.5</td>
<td>0.536</td>
<td>1.19</td>
<td>0.017</td>
<td>0.151</td>
<td>0.121</td>
</tr>
<tr>
<td>4.0</td>
<td>42.3</td>
<td>0.621</td>
<td>1.53</td>
<td>0.022</td>
<td>0.177</td>
<td>0.147</td>
</tr>
<tr>
<td>5.0</td>
<td>43.4</td>
<td>0.637</td>
<td>1.54</td>
<td>0.023</td>
<td>0.181</td>
<td>0.151</td>
</tr>
<tr>
<td>6.0</td>
<td>46.8</td>
<td>0.687</td>
<td>1.59</td>
<td>0.023</td>
<td>0.194</td>
<td>0.164</td>
</tr>
<tr>
<td>18.0</td>
<td>67.8</td>
<td>0.995</td>
<td>1.67</td>
<td>0.025</td>
<td>0.271</td>
<td>0.241</td>
</tr>
<tr>
<td>24.0</td>
<td>66.6</td>
<td>0.977</td>
<td>2.99</td>
<td>0.044</td>
<td>0.286</td>
<td>0.256</td>
</tr>
</tbody>
</table>

Measurement error is: ± 2 %

### Table A1.3

Ammonia generation in the 3-hour eU2A (70 °C) experiments in the three-electrode reactor using 1.0, 2.5, and 7.0 M KOH supporting electrolyte

<table>
<thead>
<tr>
<th>Supporting Electrolyte</th>
<th>Generated ammonia in M</th>
<th>Generated ammonia in M</th>
<th>Generated ammonia in M</th>
<th>Generated ammonia in M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M KOH</td>
<td>0.532 V vs. Hg/HgO</td>
<td>0.502 V vs. Hg/HgO</td>
<td>0.462 V vs. Hg/HgO</td>
<td>0.434 V vs. Hg/HgO</td>
</tr>
<tr>
<td>2.5 M KOH</td>
<td>0.717±0.003</td>
<td>0.672±0.006</td>
<td>0.697±0.015</td>
<td>0.784±0.035</td>
</tr>
<tr>
<td>5.0 M KOH</td>
<td>0.908±0.024</td>
<td>0.966±0.010</td>
<td>1.042±0.010</td>
<td>1.143±0.044</td>
</tr>
<tr>
<td>7.0 M KOH</td>
<td>1.138±0.027</td>
<td>1.232±0.057</td>
<td>1.293±0.062</td>
<td>1.434±0.072</td>
</tr>
</tbody>
</table>

Ammonia generated in the ramping process (from room temperature to 70 °C) is subtracted.
Table A1.4

Ammonia generation in the 3-hour eU2A (70 °C) experiments in the three-electrode reactor using 5.0 M KOH supporting electrolyte at different applied potential

<table>
<thead>
<tr>
<th>Supporting electrolyte</th>
<th>Generated ammonia in M</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0 M KOH</td>
<td>0.425 V vs. Hg/HgO</td>
</tr>
<tr>
<td></td>
<td>0.462 V vs. Hg/HgO</td>
</tr>
<tr>
<td></td>
<td>0.485 V vs. Hg/HgO</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Applied potential</th>
<th>0</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30 min</td>
<td>0.348±0.003</td>
<td>0.417±0.010</td>
<td>0.455±0.012</td>
</tr>
<tr>
<td>60 min</td>
<td>0.542±0.003</td>
<td>0.697±0.015</td>
<td>0.770±0.016</td>
</tr>
<tr>
<td>90 min</td>
<td>0.688±0.015</td>
<td>0.908±0.024</td>
<td>0.966±0.067</td>
</tr>
<tr>
<td>120 min</td>
<td>0.826±0.006</td>
<td>1.042±0.010</td>
<td>1.079±0.014</td>
</tr>
<tr>
<td>150 min</td>
<td>0.935±0.034</td>
<td>1.138±0.027</td>
<td>1.259±0.015</td>
</tr>
<tr>
<td>180 min</td>
<td>1.024±0.019</td>
<td>1.232±0.057</td>
<td>1.394±0.023</td>
</tr>
</tbody>
</table>

Ammonia generated in the ramping process (from room temperature to 70 °C) is subtracted.

Table A1.5

Ammonia generation in the 3-hour THU (70°C) experiments in the three-electrode reactor using different concentrations of KOH supporting electrolyte

<table>
<thead>
<tr>
<th>Supporting electrolyte</th>
<th>Generated ammonia in M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M KOH</td>
<td>0.014</td>
</tr>
<tr>
<td>2.5 M KOH</td>
<td>0.050±0.001</td>
</tr>
<tr>
<td>5.0 M KOH</td>
<td>0.292±0.012</td>
</tr>
<tr>
<td>7.0 M KOH</td>
<td>0.353±0.004</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Applied potential</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>0.014</td>
<td>0.050±0.001</td>
<td>0.292±0.012</td>
<td>0.353±0.004</td>
</tr>
<tr>
<td>60</td>
<td>0.023±0.001</td>
<td>0.112±0.001</td>
<td>0.484±0.005</td>
<td>0.671±0.019</td>
</tr>
<tr>
<td>90</td>
<td>0.031</td>
<td>0.165±0.006</td>
<td>0.654±0.025</td>
<td>0.839±0.016</td>
</tr>
<tr>
<td>120</td>
<td>0.042±0.002</td>
<td>0.227±0.009</td>
<td>0.758±0.027</td>
<td>0.993±0.036</td>
</tr>
<tr>
<td>150</td>
<td>0.052±0.001</td>
<td>0.298±0.012</td>
<td>0.835±0.016</td>
<td>1.135±0.029</td>
</tr>
<tr>
<td>180</td>
<td>0.060±0.001</td>
<td>0.352±0.013</td>
<td>0.923±0.027</td>
<td>1.261±0.013</td>
</tr>
</tbody>
</table>

Ammonia generated in the ramping process (from room temperature to 70 °C) is subtracted.
Table A1.6

Ammonia generation in the 24-hour eU2A (0.75 V vs. Hg/HgO, 70 °C) and THU (70 °C) experiments in the three-electrode reactor using 2.5 M K$_2$CO$_3$ supporting electrolyte

<table>
<thead>
<tr>
<th></th>
<th>Generated ammonia in M</th>
<th>eU2A using Ni</th>
<th>eU2A using graphene-coated Ni</th>
<th>THU</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.023±0.001</td>
<td>0.016±0.004</td>
<td>0.009±0.000</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.032±0.004</td>
<td>0.027±0.001</td>
<td>0.020±0.001</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.043±0.004</td>
<td>0.042±0.000</td>
<td>0.026±0.001</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.057±0.003</td>
<td>0.057±0.005</td>
<td>0.031±0.001</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.073±0.004</td>
<td>0.070±0.006</td>
<td>0.034±0.000</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.086±0.006</td>
<td>0.081±0.003</td>
<td>0.038±0.003</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.099±0.001</td>
<td>0.087±0.002</td>
<td>0.045±0.001</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.109±0.006</td>
<td>0.096±0.003</td>
<td>0.050±0.004</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>-</td>
<td>0.053±0.004</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
<td>0.058±0.004</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.170±0.008</td>
<td>0.147±0.005</td>
<td>0.079±0.003</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>0.174±0.010</td>
<td>0.150±0.011</td>
<td>0.081±0.006</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>0.185±0.004</td>
<td>0.158±0.004</td>
<td>0.082±0.001</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>0.187±0.003</td>
<td>0.164±0.008</td>
<td>0.085±0.002</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>0.196±0.004</td>
<td>0.168±0.002</td>
<td>0.087±0.006</td>
<td></td>
</tr>
</tbody>
</table>

Ammonia generated in the ramping process (from room temperature to 70 °C) is subtracted.

Table A1.7

Ammonia generation in the 3-hour eU2A (0.965 V vs. Hg/HgO, 70 °C) and THU (70 °C) experiments in the three-electrode reactor using 3.0 M KHCO$_3$ supporting electrolyte

<table>
<thead>
<tr>
<th></th>
<th>Generated ammonia in M</th>
<th>eU2A using Ni</th>
<th>eU2A using graphene-coated Ni</th>
<th>THU</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>0.0055±0.0000</td>
<td>0.0050±0.0000</td>
<td>0.0031±0.0000</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.0093±0.0002</td>
<td>0.0087±0.0000</td>
<td>0.0055±0.0003</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>0.0133±0.0007</td>
<td>0.0128±0.0003</td>
<td>0.0069±0.0002</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>0.0158±0.0003</td>
<td>0.0147±0.0002</td>
<td>0.0084±0.0000</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>0.0180±0.0005</td>
<td>0.0167±0.0008</td>
<td>0.0092±0.0002</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>0.0191±0.0003</td>
<td>0.0177±0.0007</td>
<td>0.0102±0.0001</td>
<td></td>
</tr>
</tbody>
</table>

Ammonia generated in the ramping process (from room temperature to 70 °C) is subtracted.
Table A1.8

Ammonia generation in the 12-hour eU2A (0.85 V vs. Hg/HgO, 70 °C) experiments in the three-electrode reactor in the K₂CO₃/KHCO₃/NH₃/H₂O equilibrium system

<table>
<thead>
<tr>
<th></th>
<th>Generated ammonia in M</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni foil</td>
<td>Trap</td>
<td>Graphene-coated Ni</td>
<td>Reactor</td>
<td>Trap</td>
</tr>
<tr>
<td>0</td>
<td>2.712±0.071</td>
<td>0.779±0.017</td>
<td>2.815±0.000</td>
<td>0.849±0.002</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.735±0.042</td>
<td>0.782±0.013</td>
<td>2.829±0.050</td>
<td>0.859±0.017</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.829±0.021</td>
<td>0.784±0.020</td>
<td>2.832±0.071</td>
<td>0.864±0.010</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.794±0.050</td>
<td>0.786±0.013</td>
<td>2.821±0.008</td>
<td>0.880±0.007</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.821±0.058</td>
<td>0.786±0.020</td>
<td>2.809±0.033</td>
<td>0.902±0.003</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.865±0.066</td>
<td>0.791±0.007</td>
<td>2.835±0.012</td>
<td>0.904±0.003</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.879±0.079</td>
<td>0.794±0.020</td>
<td>2.841±0.054</td>
<td>0.909±0.020</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.832±0.017</td>
<td>0.798±0.020</td>
<td>2.829±0.033</td>
<td>0.920±0.020</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2.85±0.029</td>
<td>0.798±0.013</td>
<td>2.844±0.050</td>
<td>0.925±0.020</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>2.885±0.012</td>
<td>0.801±0.010</td>
<td>2.841±0.046</td>
<td>0.934±0.007</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.894±0.075</td>
<td>0.801±0.013</td>
<td>2.865±0.062</td>
<td>0.939±0.007</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>2.888±0.071</td>
<td>0.803±0.007</td>
<td>2.882±0.079</td>
<td>0.948±0.020</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>2.897±0.029</td>
<td>0.803±0.020</td>
<td>2.873±0.075</td>
<td>0.958±0.007</td>
<td></td>
</tr>
</tbody>
</table>

Ammonia generated in the ramping process (from room temperature to 70 °C) is NOT subtracted.
Table A1.9

Ammonia generation in the 12-hour THU (70 °C) experiment in the three-electrode reactor in the K₂CO₃/KHCO₃/NH₃/H₂O equilibrium system

<table>
<thead>
<tr>
<th></th>
<th>Generated ammonia in M Ni foil</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reactor</td>
<td>Trap</td>
</tr>
<tr>
<td>0</td>
<td>2.639±0.065</td>
<td>0.740±0.012</td>
</tr>
<tr>
<td>1</td>
<td>2.644±0.066</td>
<td>0.744±0.016</td>
</tr>
<tr>
<td>2</td>
<td>2.647±0.048</td>
<td>0.748±0.008</td>
</tr>
<tr>
<td>3</td>
<td>2.674±0.033</td>
<td>0.748±0.020</td>
</tr>
<tr>
<td>4</td>
<td>2.665±0.024</td>
<td>0.752±0.008</td>
</tr>
<tr>
<td>5</td>
<td>2.683±0.044</td>
<td>0.756±0.008</td>
</tr>
<tr>
<td>6</td>
<td>2.688±0.043</td>
<td>0.760±0.012</td>
</tr>
<tr>
<td>7</td>
<td>2.665±0.033</td>
<td>0.760±0.008</td>
</tr>
<tr>
<td>8</td>
<td>2.686±0.054</td>
<td>0.760±0.008</td>
</tr>
<tr>
<td>9</td>
<td>2.700±0.061</td>
<td>0.764±0.012</td>
</tr>
<tr>
<td>10</td>
<td>2.712±0.010</td>
<td>0.764±0.008</td>
</tr>
<tr>
<td>11</td>
<td>2.718±0.058</td>
<td>0.772±0.016</td>
</tr>
<tr>
<td>12</td>
<td>2.712±0.060</td>
<td>0.776±0.020</td>
</tr>
</tbody>
</table>

Ammonia generated in the ramping process (from room temperature to 70 °C) is NOT subtracted.

Figure A1.1. The concentration of ammonia in the eU2A and THU experiments in the three-electrode reactor using K₂CO₃/KHCO₃/NH₃/H₂O equilibrium supporting electrolyte.
APPENDIX A2: UREA MEASUREMENT

The standard solutions, 0.008, 0.016, 0.024, 0.032, and 0.040 M, were prepared by dilution from 1 M of urea solution made by urea powder (purity ≥ 99%, Fisher Scientific) to calibrate the UV-vis spectroscopy. The solution for each measurement was made by 0.2 mL testing sample (the standard solution or the diluted sample solution), 0.8 mL p-dye, and 1 mL DI water mixed in the UV cuvette (Section 3.4). After 20 minutes stabilization (no bubbles on the wall of the UV cuvettes), the UV-vis spectrum was measured using the Hewlett Packard Spectrophotometer HP 8452A. The residual urea concentrations were determined (see Section 3.5) and recorded in Table A2.1.

Table A2.1

The concentration of residual urea in the 24-hour eU2A (1.65 V, 70 °C) and THU (70 °C) experiments in the two-electrode reactor using 7.0 M KOH supporting electrolyte

<table>
<thead>
<tr>
<th>Time, h</th>
<th>eU2A</th>
<th>THU</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( C_{\text{urea, reactor}}, \text{M} )</td>
<td>( C_{\text{urea, reactor}}, \text{M} )</td>
</tr>
<tr>
<td>0</td>
<td>4.648±0.082</td>
<td>4.653±0.166</td>
</tr>
<tr>
<td>0.25</td>
<td>4.571±0.126</td>
<td>4.596±0.034</td>
</tr>
<tr>
<td>0.5</td>
<td>4.454±0.083</td>
<td>4.530±0.124</td>
</tr>
<tr>
<td>0.75</td>
<td>4.305±0.120</td>
<td>4.480±0.073</td>
</tr>
<tr>
<td>1.0</td>
<td>4.154±0.032</td>
<td>4.449±0.178</td>
</tr>
<tr>
<td>1.25</td>
<td>4.058±0.026</td>
<td>4.444±0.001</td>
</tr>
<tr>
<td>1.5</td>
<td>4.027±0.015</td>
<td>4.419±0.228</td>
</tr>
<tr>
<td>3.0</td>
<td>3.575±0.046</td>
<td>4.257±0.141</td>
</tr>
<tr>
<td>4.0</td>
<td>3.534±0.079</td>
<td>4.242±0.179</td>
</tr>
<tr>
<td>5.0</td>
<td>3.243±0.015</td>
<td>4.224±0.022</td>
</tr>
<tr>
<td>6.0</td>
<td>2.897±0.085</td>
<td>4.103±0.039</td>
</tr>
<tr>
<td>18.0</td>
<td>1.843±0.063</td>
<td>3.831±0.082</td>
</tr>
<tr>
<td>24.0</td>
<td>1.311±0.016</td>
<td>3.786±0.054</td>
</tr>
</tbody>
</table>
APPENDIX A3: GAS SAMPLING IN THE EU2A REACTORS

In the 24-hour eU2A experiments, the trapped gaseous products were sampled out from the sampling port in the two-electrode reactor system, as shown in Figure A10.1. Similarly, in 3-hour eU2A experiments, the collected gases were sampled out from the port in the three-electrode reactor system, as shown in Figure A3.2.

Figure A3.1. Gas sampling from the two-electrode eU2A reactor.
Figure A3.2. Gas sampling from the three-electrode eU2A reactor.
APPENDIX A4: GAS PRODUCTION AND SEPARATION

A4.1 Gas Production and Energy Consumption in the Two-Electrode eU2A Reactor

In the experiments using the two-electrode eU2A reactor, the active catalyst NiOOH was produced on the anode (the Ni working electrode) after applying a positive cell voltage and H₂ was generated on the cathode at the same time. The amount of H₂ was calculated according to Faraday’s Law based on 100% current efficiency \((z = 2\) for hydrogen evolution) as reported [2].

\[
\begin{align*}
n_{H_2} &= \left( \frac{\bar{I}}{F} \right) \left( \frac{1}{z} \right) = \frac{0.364 \text{ A} \times 24 \text{ h}}{26.8 \text{ Ah mol}^{-1}} \times \frac{1}{2} = 0.163 \text{ mol} \\
n_{\text{area, electrolysis}} &= n_{\text{N}_2, \text{ electrolysis}} = \frac{4.2 \pm 0.084}{61.9 \pm 1.238} \times n_{H_2} = (0.0110 \pm 0.0003) \text{ mol}
\end{align*}
\]  

(A4)  

(A5)

In the 24-hour experiments in the two-electrode reactor, a 10 mL sample of the gas was extracted out from the sampling port (Figure A10.1) for GC analysis. The sample gas consisted of H₂, O₂ and N₂. Table A4.1 gives the integrated area for each component and the corresponding volume and percentage volume of each component. In addition, by applying the ratio of O₂ and N₂ (79:21) in air, the percentages of the gases were recalculated in Table A4.2 indicating the volumetric percentage of air present. The presence of nitrogen implies that a fraction of the current is used to promote urea electrolysis (Eq. 27, Chapter 4).
Table A4.1

Composition of gas sample in the 24-hour eU2A (1.65 V, 70 °C) experiments in the two-electrode reactor

<table>
<thead>
<tr>
<th></th>
<th>Area</th>
<th>Volume, mL</th>
<th>Percentage, %</th>
<th>St. Dev., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1319.015</td>
<td>6.19</td>
<td>61.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Oxygen</td>
<td>44.011</td>
<td>0.72</td>
<td>7.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>189.16</td>
<td>3.09</td>
<td>30.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table A4.2

Composition of gas sample normalized with air in the 24-hour eU2A (1.65 V, 70 °C) experiments in the two-electrode reactor

<table>
<thead>
<tr>
<th></th>
<th>Volume, mL</th>
<th>Percentage, %</th>
<th>St. Dev., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>6.19</td>
<td>61.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Air</td>
<td>3.39</td>
<td>33.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.42</td>
<td>4.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The material balance for urea and ammonia in 24-hour eU2A and THU experiments is summarized in Table A4.3. The stoichiometric ratios of generated ammonia and converted urea are calculated as Eqs. A6 and A7:

\[
eU2A: \frac{1.609 \pm 0.032}{0.823 \pm 0.021} = 1.96 \pm 0.06 \quad (A6)
\]

\[
\text{THU}: \frac{0.256 \pm 0.005}{0.216 \pm 0.054} = 1.19 \pm 0.30 \quad (A7)
\]

The ammonia generation rate per effective volume (in g h\(^{-1}\) L\(^{-1}\)), which is the generation rate (in g h\(^{-1}\)) divided by the effective volume (in L), is summarized in Table A4.3. The effective volume is defined as the active volume for the reactions, 47 cm\(^3\) (Section 3.1, Chapter 3) for the eU2A process and 250 cm\(^3\) for the THU process. In the
calculation of the additional ammonia generation rate per effective volume of the eU2A process, the contribution of the thermal hydrolysis (0.256 mol) was subtracted.

The electrical energy consumed to generate the active catalyst in the 24-hour eU2A (1.65 V, 70°C) experiment in the two-electrode reactor was:

\[ E = UIt = 1.65 \, V \times (0.364 \pm 0.002) \, \text{A} \times 24 \, \text{h} = (14.414 \pm 0.029) \, \text{Wh} \]  \hspace{1cm} (A8)

For each gram of ammonia, the energy consumed was:

\[ \frac{E}{m_{NH_3}} = \frac{(14.414 \pm 0.029) \, \text{Wh}}{[(1.609 \pm 0.032) \, \text{mol} - (0.256 \pm 0.005) \, \text{mol}] \times 17 \, \text{g mol}^{-1}} = (0.63 \pm 0.02) \, \text{Wh g}^{-1} \]  \hspace{1cm} (A9)

Table A4.3

Material balance of urea and ammonia in the 24-hour eU2A and THU experiments (1.65 V, 70°C) in the two-electrode reactor

<table>
<thead>
<tr>
<th></th>
<th>eU2A</th>
<th>THU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles of urea converted, mol</td>
<td>0.834 ± 0.021</td>
<td>0.216 ± 0.044</td>
</tr>
<tr>
<td>Moles of urea converted to ammonia*, mol</td>
<td>0.823 ± 0.021</td>
<td>0.216 ± 0.044</td>
</tr>
<tr>
<td>Moles of ammonia produced, mol</td>
<td>1.609 ± 0.032</td>
<td>0.256 ± 0.005</td>
</tr>
<tr>
<td>Ammonia generation rate per effective volume**</td>
<td>( \hat{n}_{NH_3} = (20.39 \pm 0.49) , \text{g h}^{-1} , \text{L}^{-1} )</td>
<td>( \hat{n}_{NH_3} = (0.73 \pm 0.01) , \text{g h}^{-1} , \text{L}^{-1} )</td>
</tr>
</tbody>
</table>

* Moles of urea converted to nitrogen due to electrolysis (0.011 mol) were subtracted
** 47 cm³ (Section 3.1, Chapter 3) for eU2A and 250 cm³ for THU

A4.2 Gas Production in eU2A Experiments in the Three-Electrode Reactor

The gaseous products in 3-hour eU2A experiments using 5.0 M urea in the presence of 5.0 M KOH at different applied potentials (0.425 V, 0.462 V and 0.485 V vs. Hg/HgO) were collected in the gas collecting column. A 5.0 mL sample of the gas was
extracted from the sample port (Figure A3.2) of the collecting column and was injected into GC column for analysis. The volume of the gas in the head space of the reactor was measured by water replacement (44 mL). The volumetric percentages of N₂, O₂, and H₂ were determined by calibration with the peak area of standard gases and were shown in Table A4.4. In addition, by applying the ratio of O₂ and N₂ (79:21) in air, the percentage of the generated gases was recalculated in Table A3.5 indicating the volumetric percentage of air present.

Table A4.4

The composition of gas gaseous products at different applied potentials during in 3 hours of operation of the eU2A process using 5.0 M urea in the presence of 5.0 M KOH

<table>
<thead>
<tr>
<th>Applied potential, V vs. Hg/HgO</th>
<th>Volume of gas in the trap, mL</th>
<th>[H₂] , %</th>
<th>[N₂] , %</th>
<th>[O₂] , %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.425</td>
<td>13.4</td>
<td>7.24</td>
<td>73.66</td>
<td>19.10</td>
</tr>
<tr>
<td>0.462</td>
<td>62.2</td>
<td>5.29</td>
<td>75.30</td>
<td>19.41</td>
</tr>
<tr>
<td>0.485</td>
<td>78.8</td>
<td>8.93</td>
<td>72.67</td>
<td>18.41</td>
</tr>
</tbody>
</table>

Table A4.5

The composition of gas gaseous products at different applied potentials during in 3 hours of operation of the eU2A process using 5.0 M urea in the presence of 5.0 M KOH

<table>
<thead>
<tr>
<th>Applied potential, V vs. Hg/HgO</th>
<th>Volume of gas in the trap, mL</th>
<th>[H₂] , %</th>
<th>[N₂] , %</th>
<th>Air, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.425</td>
<td>13.4</td>
<td>7.24</td>
<td>1.78</td>
<td>90.98</td>
</tr>
<tr>
<td>0.462</td>
<td>62.2</td>
<td>5.29</td>
<td>2.30</td>
<td>92.41</td>
</tr>
<tr>
<td>0.485</td>
<td>78.8</td>
<td>8.93</td>
<td>3.42</td>
<td>87.65</td>
</tr>
</tbody>
</table>

The amount of gas was determined by ideal gas law approximately. The generated N₂ and H₂ were calculated by using Eq. A10 and Eq. A11 separately in atmospheric pressure, and the results were shown in Table A4.6.
The amount of generated gaseous products at different applied potentials during in 3 hours of operation of the eU2A process using 5.0 M urea in the presence of 5.0 M KOH

Table A4.6

<table>
<thead>
<tr>
<th>Applied potential V vs. Hg/HgO</th>
<th>Volume of gas in the trap mL</th>
<th>Produced N$_2$ mol</th>
<th>Produced H$_2$ mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.425</td>
<td>13.4</td>
<td>3.76×10$^{-5}$</td>
<td>1.53×10$^{-4}$</td>
</tr>
<tr>
<td>0.462</td>
<td>62.2</td>
<td>9.44×10$^{-5}$</td>
<td>2.17×10$^{-4}$</td>
</tr>
<tr>
<td>0.485</td>
<td>78.8</td>
<td>1.64×10$^{-4}$</td>
<td>4.27×10$^{-4}$</td>
</tr>
</tbody>
</table>

By comparing the theoretical nitrogen, calculated by using Faraday’s law, and the measured nitrogen, the current efficiencies for urea electrolysis were determined and shown in Table A4.7.

Table A4.7

Comparison of nitrogen production between theoretical and actual value amount at different applied potentials during in 3 hours of operation of the eU2A process using 5.0 M urea in the presence of 5.0 M KOH

<table>
<thead>
<tr>
<th>Applied potential V vs. Hg/HgO</th>
<th>Average current A cm$^{-2}$</th>
<th>Theoretical N$_2$ mol</th>
<th>Measured N$_2$ mol</th>
<th>Current efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.425</td>
<td>7.75×10$^{-4}$</td>
<td>8.67×10$^{-5}$</td>
<td>3.76×10$^{-5}$</td>
<td>43.4</td>
</tr>
<tr>
<td>0.462</td>
<td>1.69×10$^{-3}$</td>
<td>1.89×10$^{-4}$</td>
<td>9.44×10$^{-5}$</td>
<td>49.8</td>
</tr>
<tr>
<td>0.485</td>
<td>2.22×10$^{-3}$</td>
<td>2.48×10$^{-4}$</td>
<td>1.64×10$^{-4}$</td>
<td>65.9</td>
</tr>
</tbody>
</table>
APPENDIX A5: REACTION RATE FOR EU2A AND THU IN THE TWO-ELECTRODE REACTOR

First-order reaction as a function of the concentration of urea [3] was assumed for the calculation of the overall reaction rate constants for eU2A and THU. Because pH is higher than 12, no backward reaction occurs [3]. Let \(- r_A\) be the rate of forward reaction, \(C_{A,0}\) is the initial concentration, \(C_{A,i}\) is the concentration of urea at any sample time (see Table A2.1), \(\Delta t_i\) is the time interval between two samples. The average rate of forward reaction, \(k\), can be obtained through Eqs. A9 and A10 and the results are shown in Table A5.1.

\[
-r_A = \frac{-dC_A}{dt} = \frac{C_{A,i-1} - C_{A,i}}{\Delta t_i} = k_i C_{A,i} (i = 1, 2, 3, \ldots, n) \tag{A9}
\]

\[
\overline{k} = \frac{\sum_{i=1}^{n} k_i}{n} \tag{A10}
\]

Table A5.1

<table>
<thead>
<tr>
<th>Operation condition</th>
<th>Reaction rate constant, (k) min(^{-1})</th>
<th>St. dev. min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>eU2A (in 7 M KOH)</td>
<td>1.65 V, 70 °C</td>
<td>0.00140</td>
</tr>
<tr>
<td>THU (in 7 M KOH)</td>
<td>70 °C</td>
<td>0.00039</td>
</tr>
<tr>
<td>Urea hydrolysis [4]</td>
<td>140 °C, 100 kg cm(^{-2})</td>
<td>0.00457</td>
</tr>
</tbody>
</table>
APPENDIX A6: PH MEASUREMENT

The pH value of reagent solutions in the experiments was measured with a pH electrode connected to the digital meter (OAKTON Acorn Meter pH 5) in this dissertation. To ensure the accuracy of the measurement, 3-point calibration with standard pH buffers 4.01, 7.00, and 10.00 was conducted before measuring. At each point, open the cap (see Figure A6.1) for the measurement. For the eU2A experiments using 2.5 M K₂CO₃ at 70 °C, the amount of ammonia generated was small so the ammonia was dissolved in the electrolyte in the reactor, the loss of ammonia is subtle. However, when conducting the eU2A experiments in the K₂CO₃/KHCO₃/NH₃/H₂O equilibrium system, large amount of ammonia escaped from the reactor. Therefore, the pH value was only measured when the experiments were finished. Since most of the ammonia generated would emit out from the reactor in this situation, an acid trap was used to trap the emitted ammonia.

Figure A6.1. The three-electrode eU2A reactor using a three-neck flask. The reference electrode was supported by a homemade Luggin capillary.
APPENDIX A7: \textit{IN-SITU} RAMAN EU2A CELL

The main body of the homemade \textit{in-situ} Raman EU2A cell -designed and fabricated at CEER- was made by Teflon and the dimensions are shown in Figure A7.1a. The three-electrode system consists with Ni foil (1.0 cm x 1.0 cm, > 99\%, Alfa Aesar) as the working electrode, and Ni foil (0.5 cm x 2.0 cm, > 99\%, Alfa Aesar) as the counter electrode, and a Hg/HgO electrode as the reference electrode. The Raman laser beam passed through the silica window, and focused on Ni working electrode during \textit{in-situ} experiments. The counter electrode was arranged around the working electrode as shown in Figure A7.1b.

Figure A7.1. (a) The electrochemical cell for \textit{in-situ} Raman spectroscopy; (b) the schematic arrangement of the working electrode and counter electrode.
APPENDIX A8: FACTORS THAT AFFECT THE EU2A TECHNIQUE

A8.1 Working Electrode

Three kinds of working electrodes were investigated in this study: the packed Ni beads (Chapter 4), the Ni foil, and the graphene-coated Ni foil (Chapters 5 and 6). The Normalized additional ammonia generation rate for different operation conditions could be calculated using Eqs. A11-14.

\[
C_{i, \text{add}} = C_{i, \text{eU2A}} - C_{i, \text{THU}} \quad (i = 1, 2, 3, ..., n)
\] (A11)

\[
r_i = \frac{dC_{i, \text{add}}}{dt} = \frac{C_{i+1, \text{add}} - C_{i, \text{add}}}{\Delta t_i} \quad (i = 1, 2, 3, ..., n)
\] (A12)

\[
r = \frac{\sum_{i=1}^{n} r_i}{N}
\] (A13)

\[
\bar{r}_A = \frac{r}{A}
\] (A14)

where,

\( C_{i, \text{add}} \), the concentration of the additional ammonia generated on the working electrode in the eU2A process, in M;

\( C_{i, \text{eU2A}} \), the concentration of the ammonia generated in the reactor during the eU2A experiments, in M;

\( C_{i, \text{THU}} \), the concentration of the ammonia generated in the reactor during the THU experiments, in M;

\( i \), the sample point;

\( r_i \), the additional ammonia generation rate between two adjacent sample points, in M h\(^{-1}\);
$r$, the additional ammonia generation rate in the eU2A process, in M h$^{-1}$;

$\bar{r}_d$, the normalized additional ammonia generation rate in the eU2A process; in M h$^{-1}$ cm$^{-2}$;

$\Delta t_i$, time intervals between two adjacent sampling points, in h;

$N$, total numbers of the sampling points;

$A$, geometric surface area of working electrode used in eU2A process, in cm$^2$;

The additional ammonia generation rate in the eU2A process using 7.0 M KOH supporting electrolyte was compared between using the Ni beads and the Ni foil in Figure A8.1. It demonstrates that the rate was increased significantly using the Ni beads due the enlarged surface area. However, the normalized additional ammonia generation rate was much higher using the Ni foil. The surface of the Ni beads working electrode in the two-electrode reactor was not sufficiently used as the catalyst in the eU2A process.

![Figure A8.1](image)

**Figure A8.1.** (a) Additional ammonia generation rate of eU2A using 7.0 KOH with the Ni beads and Ni foil as the working electrode. (b) Normalized additional ammonia generation rate (per cm$^2$) of eU2A using 7.0 KOH with the Ni beads and Ni foil as the working electrode.
The eU2A experiment using the graphene-coated Ni as the working electrode has higher normalized ammonia generation rate compared to using the Ni foil (Figure A8.2). However, it is a challenge to coat graphene on Ni based electrodes with non-flat surface such as Ni beads or Ni form. In this case, the direct growth of graphene on the Ni surface should be considered [5].

Figure A8.2. Normalized additional ammonia generation rate (per cm²) in the 24-hour eU2A experiments using 2.5 M K₂CO₃ as the supporting electrolyte with the Ni foil and graphene-coated Ni as the working electrode.

A8.2 Supporting Electrolyte

A series of eU2A experiments, using different supporting electrolytes with the Ni foil or the graphene-coated Ni as the working electrodes, were conducted in this study. Figure A8.3 shows that the ammonia generation rate varies at different supporting electrolyte which has different concentration of OH⁻. In the eU2A process, the additional ammonia generation rate using 2.5 M K₂CO₃ supporting electrolyte (0.001 M h⁻¹ cm⁻²) is ~5.9% of the maximum rate that was achieved using 5.0 M KOH (0.017 M h⁻¹ cm⁻²). By using the graphene-coated Ni as the working electrode, the rate could be increased to ~
13.7% of the maximum rate. This result gives evidence that the concentration of OH⁻ has positive correlation with ammonia generation in the eU2A process.

Figure A8.3. Normalized additional ammonia generation rate (per cm²) of eU2A using different supporting electrolytes with the Ni foil and graphene-coated Ni as the working electrode.

The actual supporting electrolyte is complicate during eU2A process in practical applications since the system is finally becoming a vapor liquid NH₃/CO₂/H₂O equilibrium with the K₂CO₃/KHCO₃ equilibrium as the supporting electrolyte. The loading of the system is binary since urea is decomposed to NH₃ and CO₂ gas in the eU2A process. No investigation was conducted in such equilibrium system with ammonia and CO₂ loading at the same time. Haynes et al. studied the equilibrium of potassium carbonate, potassium bicarbonate, carbon dioxide, and water with 20-30-40 percent equivalent potassium carbonate concentrations in the solution [6].
In practical applications of eU2A, urea is continuously refilled and it will dynamically build the equilibrium of NH₃/CO₂/H₂O and equilibrium of K₂CO₃ and KHCO₃ in the solution. The solution in the eU2A reactor will eventually be saturated with CO₂ and NH₃ and the head space in the reactor will be filled with CO₂ and NH₃ in the mole ratio of 1:2. In this case, the partial pressure of CO₂ at 14.7 psi (1 atm) is 4.9 psi. Therefore the percentage of K₂CO₃ converted to KHCO₃ is ~ 70% according to Figure A8.4.

![Figure A8.4. Equilibrium pressure of carbon dioxide over (a) 30 percent and (b) 40 percent equivalent potassium carbonate solution [6].](image)

If 2.5 M K₂CO₃ solution (34.5%) is utilized in the eU2A reactor, it will eventually become 0.75 M K₂CO₃/3.5 M KHCO₃ (70% of 2.5 M K₂CO₃ converted to KHCO₃) with
saturated ammonia in the reactor. To simulate this situation, 0.75 M K$_2$CO$_3$/3.5 M KHCO$_3$ in the presence of 5.0 M NH$_4$OH (which is the approximate solubility of ammonia in DI water at 70 °C, see Appendix A12) was prepared. The mixture was preheated to and maintained at 70 °C for 30 minutes in the three-electrode eU2A reactor to build a K$_2$CO$_3$/KHCO$_3$/NH$_3$/H$_2$O equilibrium system. After adding urea into the reactor to make the urea in the concentration of 5.0 M, the system was heated back to 70 °C (because the temperature was dropped with the adding of urea). The 24-hour eU2A and THU experiments were conducted afterwards and the results are shown in Figure A8.5.

Figure A8.5: Ammonia generation in the eU2A and THU experiments for 5.0 M urea in the K$_2$CO$_3$/KHCO$_3$/NH$_3$/H$_2$O equilibrium system at 70 °C.
The normalized additional ammonia generation rate in the eU2A experiments in the $K_2CO_3/KHCO_3/NH_3/H_2O$ equilibrium system with the Ni foil and graphene-coated Ni working electrode is compared in Figure A8.6. At equilibrium of $K_2CO_3/KHCO_3/NH_3/H_2O$, the ammonia generation rate was stabilized at $\sim 0.0008 \, \text{M h}^{-1} \, \text{cm}^{-2}$ using the Ni foil as the working electrode and $\sim 0.0014 \, \text{M h}^{-1} \, \text{cm}^{-2}$ using the graphene-coated Ni as the working electrode. The measured pH value of the equilibrium system is 10.64 and 10.68 after the 24-hours eU2A experiments using the Ni foil and graphene-coated Ni separately.

However, severe corrosion of the Ni electrode was observed using Ni foil as the working electrode in the $K_2CO_3/KHCO_3/NH_3/H_2O$ equilibrium system, as shown in Figure 8.7A. In the contrast, the corrosion is reduced considerably using the graphene-coated Ni. In the eU2A experiments in the $K_2CO_3/KHCO_3/NH_3/H_2O$ equilibrium system, the normalized concentration of Ni ions in the reactor was higher than using 2.5 M
K$_2$CO$_3$ as the supporting electrolyte because the ammonia concentration was much higher in the reactor.

Figure A8.7. Concentration of the Ni ions in the reagent solution in the 12-hours eU2A (0.85 V vs. Hg/HgO, 70 °C) experiments with the Ni foil and graphene-coated Ni as the working electrodes and the 12-hour THU (70 °C) experiment for 5.0 M urea in the K$_2$CO$_3$/KHCO$_3$/NH$_3$/H$_2$O equilibrium system.
APPENDIX A9: CORROSION OF THE NI ELECTRODE IN THE EU2A EXPERIMENTS

After the 24-hour eU2A (0.750 V vs. Hg/HgO, 70 °C) experiments for 5.0 M urea in the presence of 2.5 M K₂CO₃, the solution in the reactor turned to blue, as shown in Figure A9.1. At each sample point, a 0.5 mL sample solution was extracted from the reactor and then diluted to 10 mL as the testing samples. The concentration of Ni ions in the testing samples was measured by AAS equipped with the Ni hollow cathode lamp, and the concentration of the Ni ions in the reagent solution in the reactor was calculated by using Eq. 24 and the result was plotted in Figure A9.2.

Figure A9.1. The reagent solution turned to blue indicating the corrosion of the Ni electrode. The solution changes from transparent to bluish color after the 24-hour eU2A (0.750 V vs. Hg/HgO, 70 °C) experiment for 5.0 M urea in the presence of 2.5 M K₂CO₃.
Figure A9.2: Concentration of the Ni ions in the reagent solution in the 24-hour eU2A experiments (0.75 V vs. Hg/HgO, 70 °C) with the Ni foil and graphene-coated Ni working electrodes using 5.0 M urea in the presence of 2.5 M K$_2$CO$_3$. 
APPENDIX A10: REMOVING COPPER FOIL FROM THE GRAPHENE/COPPER STACK

Figure A10.1. Copper melting in the Mable agent.

Figure A10.2. Graphene being cleaned in DI water.
The graphene-coated Ni electrode was characterized by SEM using a JEOL JSM-6390 scanning electron microscope (15kV, 14 mm working distance). The images were obtained before masking the edge of graphene on Ni substrate for the eU2A experiments. In Figure A11.1, the morphology of the graphene-coated Ni electrode shows that graphene is homogenously covered on the Ni substrate with small defects.

Figure A11.1. SEMs of the graphene-coated Ni with magnification of (a) 50, (b) 500, (c) 3000, and (d) 5000. The area highlighted with a green rectangle corresponds to the higher magnification on the next image pointed out by a green arrow.
APPENDIX A12: THE AMMONIA-WATER SYSTEM

The solubility of ammonia is ~130 g per kg water (~7.6 M) at 70 °C as demonstrated in Figure A12.1 [7].

![Figure A12.1. Solubility of ammonia in water [7].](image)

The vapor-liquid distribution ratio, $K$, refers to the mole fraction of components $i$ in the vapor phase $y$ and liquid phase $x$ respectively [8].

$$ K_i = \frac{y_i}{x_i} \quad (A11) $$

At atmospheric pressure (0.1 MPa), the equilibrium ratio $K$ is about 0.5 (Figure A12.2) [9]. According to Eq. A11, at equilibrium, the concentration of ammonia in the electrolyte is ~5.0 M. Therefore 5.0 M NH$_4$OH was added with 0.75 M K$_2$CO$_3$/3.5 M KHCO$_3$ in the reagent solution. After preheating at 70 °C for 30 minutes, the vaporized ammonia was absorbed in DI water. It is found that the ammonia concentration in the reactor in equilibrium is ~ 2.8 M (Figure A1.1) in the eU2A experiments. Figure A12.3
demonstrated the migration of ammonia in the eU2A process. Ammonia is generated from urea via the eU2A reaction and absorbed in the reagent solution. After the solution was saturated with ammonia, it is emitted from the reactor.

Figure A12.2. Equilibrium ratios for ammonia-water up to the critical point of ammonia [9].

Figure A12.3. Schematic diagram for the migration of ammonia in the eU2A system.
APPENDIX A13: REFERENCES FOR THE APPENDICES
