ELECTROCHEMICAL NO_X REDUCTION USING A CARBON NANOSPIKED CATALYST

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ABSTRACT

Electrochemical NO_x reduction was studied using a novel, nanostructured nitrogen-doped carbon nanospikes catalyst (CNS). NOx is a major environment and health concern that is typically eliminated using noble-metal gas-phase catalytic reactors. Alternatively, an electrocatalytic approach may reduce NO_x to N_2 using electric potential and reaction, foregoing noble metal catalysis. For these studies nitrate (NO_3^-) and nitrite (NO_2^-) (the end products of dissolved NOx in water) were used as surrogate reagents. Basic solutions were more favorable than acidic solutions for nitrate reduction. The nitrate reduction reaction with three different electrolytes, Lithium hydroxide, Sodium hydroxide, and Potassium hydroxide has been compared. Identification and quantification tests for nitrate, nitrite, and ammonia indicated that nitrite is an intermediate product during nitrate reduction. The final product with sodium hydroxide is ammonia. Potassium hydroxide and lithium hydroxide suggested no formation of ammonia. However, it suggested a possibility of formation of nitrogen and oxygen.

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CHAPTER 1

INTRODUCTION

Abundant amount of Nitrogen Oxide (NO_x) emission is of a major concern because of its harmful health and environmental effects. It is known to be the primary cause for smog and acid rain (Jiang, Luo, & Li, 2007; Krivoruchenko, Telegina, Bokarev, & Stakheev, 2015; Sheridan et al., 2014) . It is also known to cause low lung function and increased risk of cancer (O'Driscoll et al., 2016). One of the major source of NO_x pollutant is car exhaust stream. In the past decade, US, EU, China, Japan, and several other countries have constantly lowered the emission limit for NOx as a remediation measure. In the New England states, NO_x emission control was implemented sequentially through the reasonably available control technology (RACT) and ozone transport region (OTR) NO_x cap and allowance trading program. Further, to address long-range NOx transport outside the OTR, Environmental Protection Agency (EPA) identified and evaluated specific regulation strategies through a two-year effort in partnership with the eastern-US states, industry representatives, and environmental groups ("Nitrogen oxides (NOx) control regulations," 2016). As part of this NO_x SIP rule, EPA designed a “cap and trade” regulation model to achieve the specified NO_x level.

To address the lowering NO_x emission limits, several different catalysts have been investigated (Shimazu et al., 2007). Catalysts such as rhodium, platinum, and palladium are commonly used in the process of NO_x reduction. Catalytic activity essentially gives a measure of the NO_x reduction reaction and the final catalyst performance. Ideally, a high catalytic activity, increased surface area, and wide temperature range for NO_x reduction reactions are desired in a catalyst. Catalyst composition and physical properties are major influences on the catalyst performance, reliability, and cost.

1.1 Current Systems and Drawbacks

1.1.1 Selective Catalytic Reduction

Current methods include selective catalytic reduction where a liquid reductant reagent is introduced. Commonly in a diesel engine, diesel exhaust fluid (DEF) called Adblue is added. Adblue is composed of around 32.5% urea and 67.5% deionized water (Katsounaros et al., 2012). Adblue is injected in the exhaust stream which sets off a chemical reaction that converts NO_x into Nitrogen and Water in the presence of a catalyst. Most of the catalysts investigated here so far are rare and expensive metals. One of the major disadvantages of this system is the expensive catalysts. The other disadvantage is that the catalytic converters only operate at high temperatures. Temperature is one of the biggest limitation for SCR.

Some other disadvantages include SCR being sensitive to contamination. Apart from being expensive, it also has finite life. Another possible issue that can occur is the ammonia slip, where excess ammonia is injected into the system. This method also requires a continuous supply of the reductant into the exhaust.

1.1.2 NO_x adsorbers

This method isn’t a stand by method. This is normally used along with selective catalytic reduction. This method involves storage of nitrogen oxides on the catalyst during lean condition and release during rich condition. One of the major drawbacks of using a NO_x adsorber is the emptying out of the washcoat.

1.2 Purpose of the study

The purpose of the study is to investigate a new catalyst using an electrochemical approach. The catalyst investigated here is composed of carbon and nitrogen. This catalyst has been designed for the first time by Rondinone *et. Al* (Sheridan et al., 2014). The key advantage of this catalyst is that these electrodes wouldn't need complicated pretreatment or activation procedures (Sheridan et al., 2014). NO_x reduction is studied using this novel nanostructured nitrogen-doped carbon nanospikes catalyst (CNS) for the first time. Nitrate (NO_3^-) and Nitrite (NO_2^-), the end products of dissolved NO_x in water, were used as surrogate reagents. One promising approach is electrochemical reduction of nitrate. Using an electrochemical approach would eliminate the need of injecting urea. It would simplify the process. It would also eliminate the need to operate at significantly high temperatures. The reduction wouldn't require high temperatures or expensive catalysts. Figure 1.2.1 shows a typical denitrification cycle.

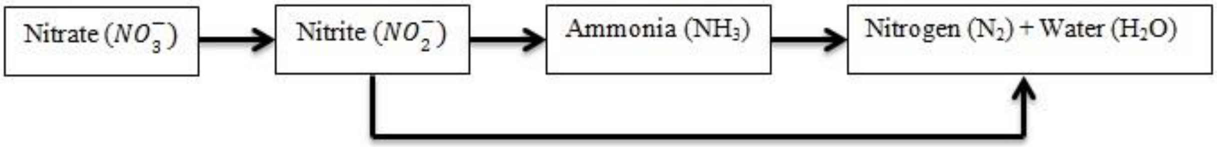


Figure 1.2.1 Typical Denitrification Cycle

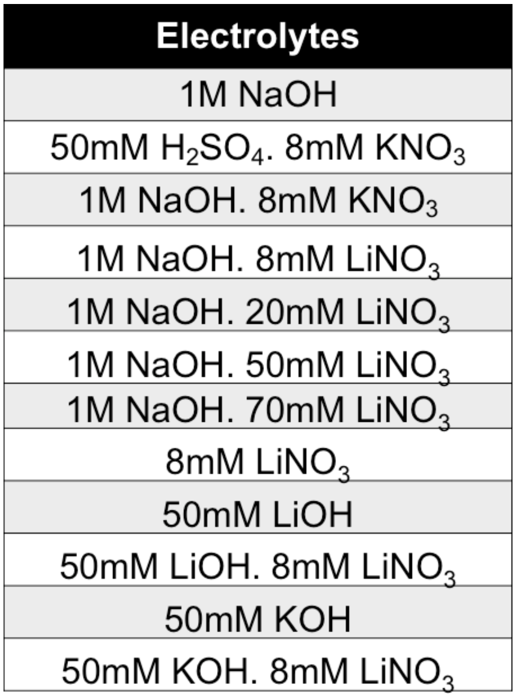
CHAPTER 2

METHODOLOGY

2.1 Reagents

The stock solutions were prepared using 18 MΩ ultrapure water supplied by milipore. 50mM H_2SO_4, 1M $NaOH$, 50mM $LiOH$, 50mM KOH, and 50mM $NaOH$ blank stock solutions were prepared by direct dissolution in water. All the blank experiments were carried out without the addition of nitrate ($\mathrm{NO_3^-}$). Nitrate stock solutions were prepared by direct dissolution of nitrate in blank stock solutions. Tests with $\mathrm{NO_3^-}$ in the blank stock solutions featured the addition of $\mathrm{NO_3^-}$ in the form of Potassium nitrate (KNO_3), and Lithium nitrate ($LiNO_3$). Table 2.1.1 shows the composition of the stock solutions with $\mathrm{NO_3^-}$. All the experiments were carried out at ambient temperature and pressure.

Table 2.1.1 List of electrolytes investigated



Electrolytes
1M NaOH
50mM H_2SO_4. 8mM KNO_3
1M NaOH. 8mM KNO_3
1M NaOH. 8mM $LiNO_3$
1M NaOH. 20mM $LiNO_3$
1M NaOH. 50mM $LiNO_3$
1M NaOH. 70mM $LiNO_3$
8mM $LiNO_3$
50mM LiOH
50mM LiOH. 8mM $LiNO_3$
50mM KOH
50mM KOH. 8mM $LiNO_3$

2.2 Preparation of the electrode

A nanostructured nitrogen doped carbon catalyst was investigated. Figure 1 shows the transmission electron microscope (TEM) images of the Carbon nanospikes. The Plasma enhanced chemical vapor deposition (PECVD) is used in fabricating the carbon nanospiked (CNS) Si wafers (Sheridan et al., 2014). The carbon nanospikes coated Si wafer was cut into 1 cm^2 sections. Indium is a conductive post transition metal. It was used to ensure that the current passes from the copper wire to the electrode surface. Silver paint is used as an adhesive for the copper wire. Industrial grade epoxy is used to cover the uncoated side of the Si wafer. It is also used to seal the copper wire to the CNS itself. This is done so that only the surface of the CNS electrode is exposed to the electrolyte. This helps prevent the reaction from occurring anywhere other than the surface. Figure 2.2.2 shows the image and the schematic of the CNS electrode.

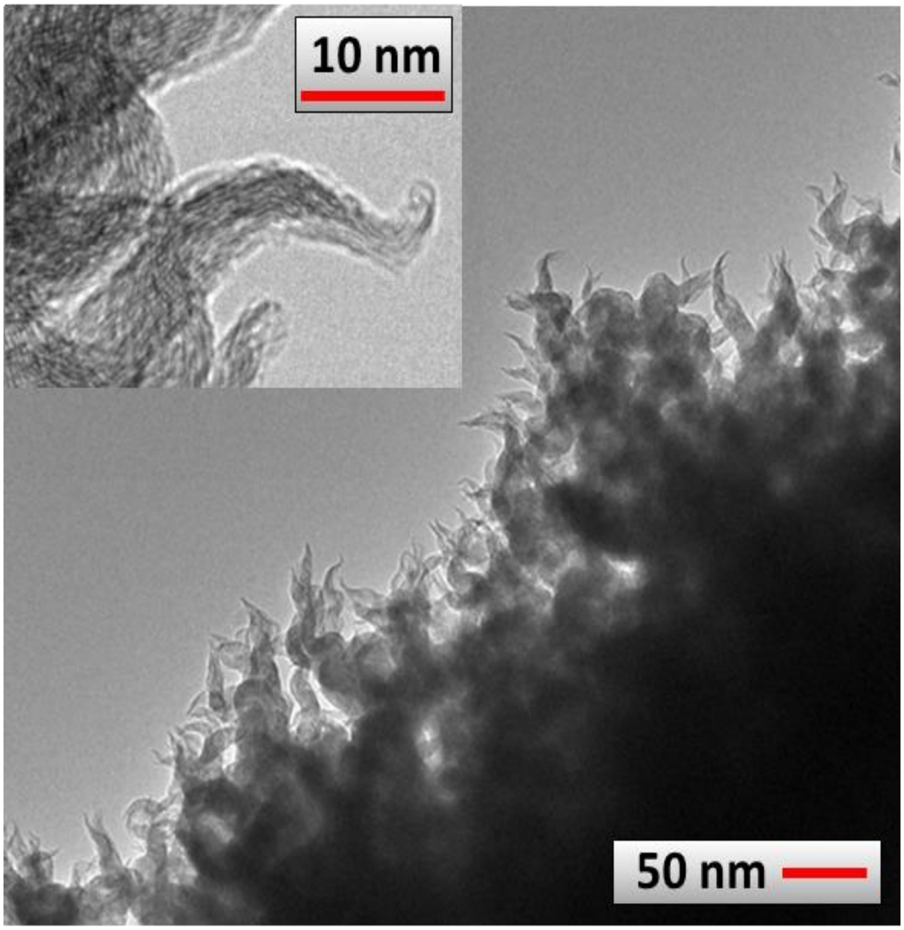


Figure 2.2.1 Representative TEM images of the CNS electrode. The inset is a HR-TEM image of an individual spike of CNS. Reproduced with permission from J. Electrochem. Soc., **161**, H558 (2014).

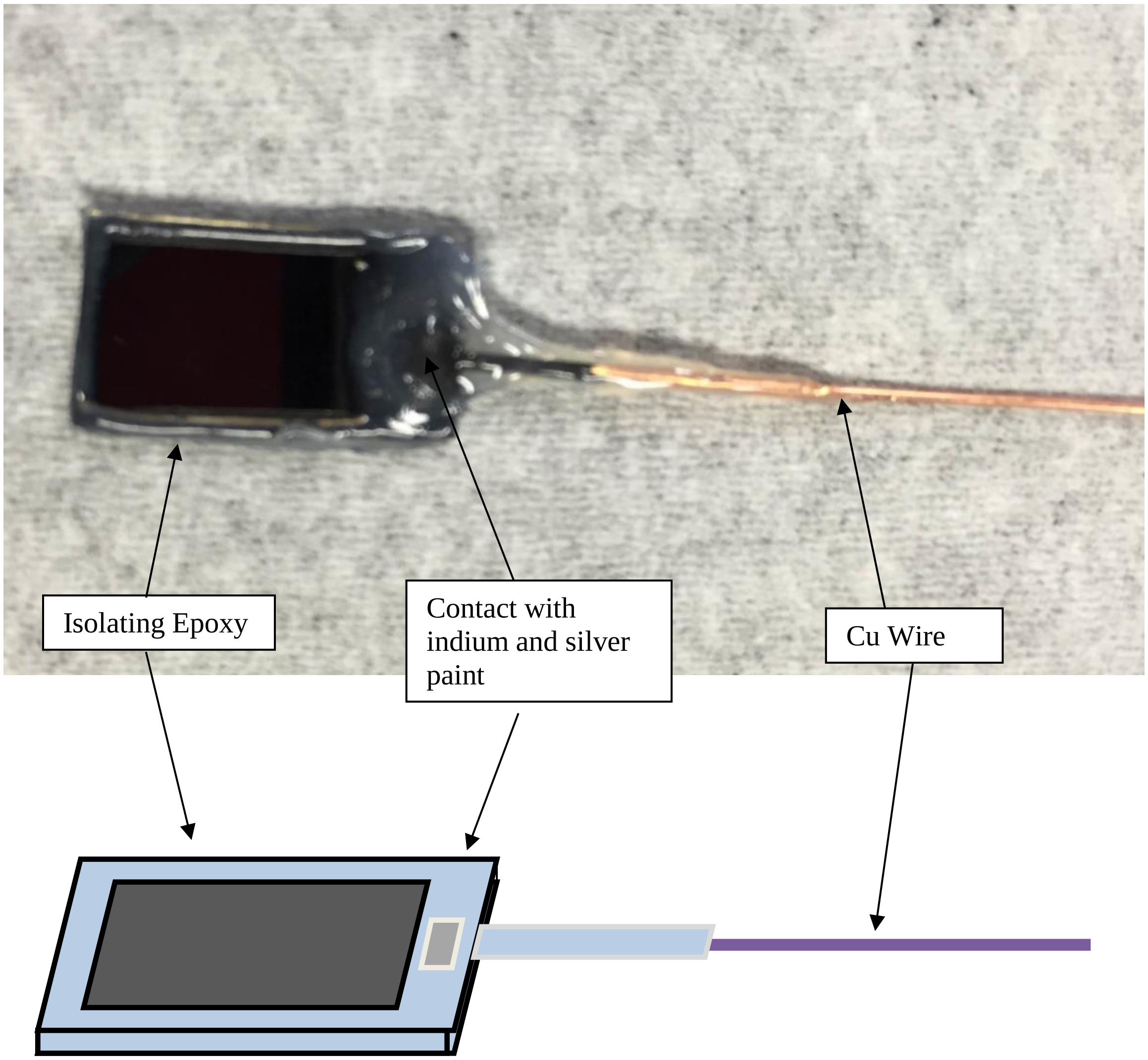

Isolating Epoxy
Contact with indium and silver paint
Cu Wire

Figure 2.2.2 A picture (top) and schematic of CNS electrode

2.3 Electrochemical Cell

Typically, an electrochemical cell is where a working electrode, reference electrode, and a counter electrode are immersed in a solution, and the potential difference between the electrodes is varied by means of an external power supply (Bard & Faulkner, 2004). This variation in potential, E, can produce a current flow in the external circuit, because electrons transfer across the electrode/solution interface as the reaction takes place (Bard & Faulkner, 2004). Reactions like these are governed by faraday’s law (i.e. the amount of chemical reaction occurred is proportional to the electricity passed) (Bard & Faulkner, 2004).

2.3.1 Preparation of an Electrochemical Cell

Electrochemical characterization was done using the nanostructed nitrogen-doped carbon catalyst as the working electrode, an Ag/AgCl reference electrode and a platinum mesh counter electrode. A three-electrode electro catalytic cell is set up to accurately measure the current characteristics of the carbon nanospiked electrode. This helps us carefully control and measure the potential and current through the cell ("Two, three and four electrode experiments,"). The reference electrode has a stable and well known potential. The reference electrode helps determine the potential of the working electrode. The counter electrode ensures that the current does not pass through the reference electrode. Electrolyte is necessary because it provides ions, which assures the conductivity of the solution. The solutions were deoxygenated by bubbling helium for at least 30 minutes.

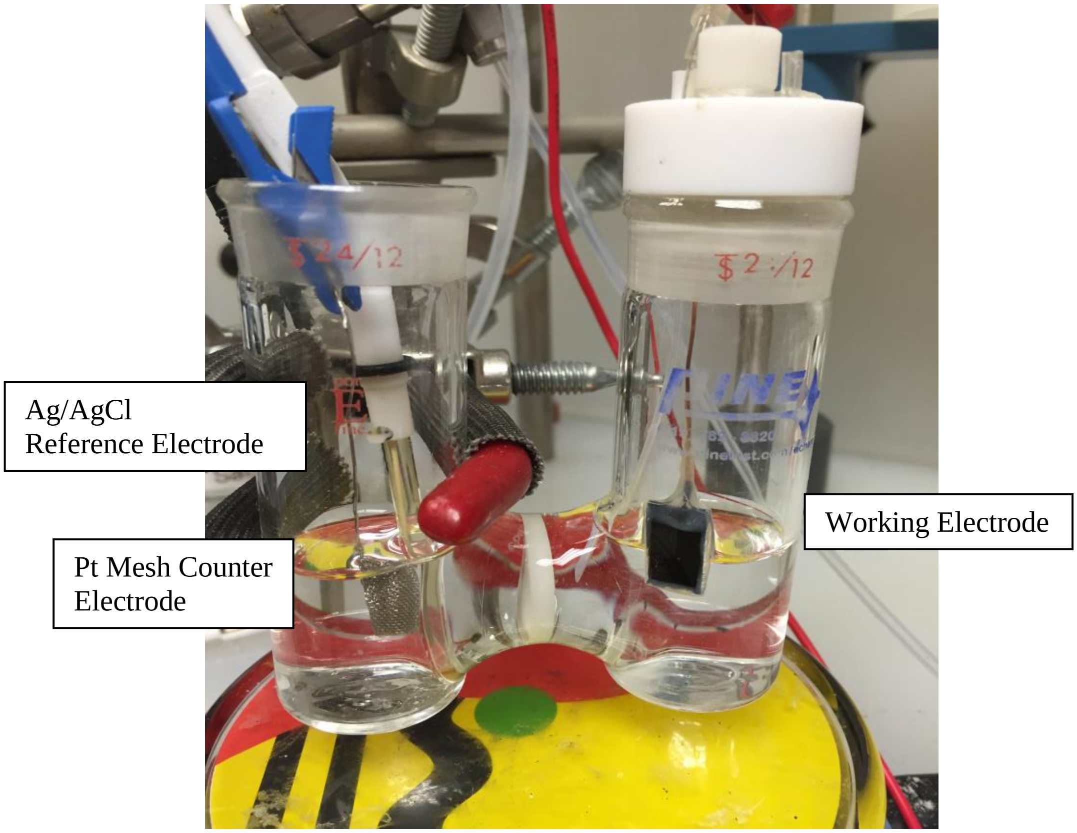


Figure 2.3.1 A picture of the electrochemical cell

2.4 Instruments

Electrochemical analysis was done using cyclic voltammetry (CV) and chronoamperometry (CA). Electrochemical measurements were performed using a Biologic VSP potentiostat (Biol-logic USA, LLC) controlled by a personal computer equipped with EC-Lab software. Cyclic Voltammetry was performed to determine the electrochemical potential of the reaction. In cyclic voltammetry, the voltage is swept between two predetermined values at a fixed scan rate (Jiang et al., 2007). Once it reaches the first value, the scan is reversed and the voltage is swept back to the first value. This helps us determine the reduction potential of the ongoing electrochemical reaction. The potential of the working electrode determines if any redox reactions occur at the surface of the electrode ("Cyclic voltammetry,"). Once the reduction potential is determined, chronoamperometry is performed.

Chronoamperometry is one of the most used electroanalytical technique. The electrode potential is stepped from an initial potential to the final potential. At the initial potential, no significant current flows through the working electrode, however, after stepping the potential to the final potential the analyte begins to be consumed at the electrode surface via reduction. The potential is set in chronoamperometry so the reduction can possibly go to completion at the surface electrode (Bard & Faulkner, 2004). Faraday's law governs this process. In Faraday's law, the amount of substance produced at the electrode is directly proportional to the electric current passed i.e. for every mole of nitrate being reduced at the electrode there is a mole of electrons leaving or entering the electrode. Per Allen J. Bard et. al. "The relationship between charge and amount of product formed is given by *Faraday's law;* that is, the passage of 96,485.4 C causes 1 equivalent of reaction (e.g., consumption of 1 mole of reactant or production of 1 mole of product in a one-electron reaction)." Faradaic law provides the link between current and analyte concentration (Shimazu et al., 2007).

The Scanning Electron Microscopy (SEM) was used for imaging and elemental analyses of the electrode. This was used in order to study the difference between the surface composition of the electrode before the reaction and after the reaction.

2.5 Quantification of Nitrate, Nitrite, and Ammonia

Ammonia was quantified using salicylate-hypochlorite test. API Ammonia test kit was used to quantify the ammonia. Solution 1 contains the sodium salicylate and polyethylene glycol.

Solution 2 contains sodium hydroxide and sodium hypochlorite ("Ammonia," 2016). Ammonia reacts with hypochlorite ions to form monochloroamine, which further reacts with salicylate to give 5-amino salicylate ("Ammonia," 2016). 5-amino salicylate creates varying shades of green. Quantification of nitrate and nitrite was done using the Tetra easy strips. The test strips indicated the amount in ppm.

CHAPTER 3

RESULTS and DISCUSSION

The reduction of nitrate at a carbon nanospike electrode was studied in various media using Cyclic voltammetry and chronoamperometry. The studies were carried out in 1 M NaOH, 50 mM H_2SO_4, 50 mM NaOH, 50 mM KOH, or 50 mM LiOH with additions of varying concentrations of NO_3^-.

3.1 Using Acid as an Electrolyte and Potassium nitrate as the nitrate donor

The purpose of an electrolyte is to allow ion flow between the cathode and the anode in order to balance the charges so that the reaction can continue. Acids, bases, and salts act as good electrolytes as they can form ions when dissolved in water. These solutions conduct electricity due to the mobility of the cations and anions. However, choosing a strong acid over a weak acid is more efficient because it dissociates completely in water providing the maximum number of ions for the reduction process (Bard & Faulkner, 2004).

3.1.1 Using 50 mM H_2SO_4, and 50 mM H_2SO_4. 8 mM KNO_3 as the electrolytes

Strong electrolytes are fully dissociated when dissolved in water. Here, sulfuric acid was selected as a model strong electrolyte because it is a strong acid. Potassium nitrate was chosen to be the nitrate donor. Blank experiments were conducted using just the sulfuric acid first, and then the nitrate was added to the solution. Table 3.1.1 shows the quantitative test results before and after the reaction. We detected the presence of nitrite using the tetra test strips. Based on this initial analysis, no nitrate or ammonia was detected in the control experiment with just H_2SO_4, as expected. However, the absence of nitrite or ammonia with the nitrogen donor (KNO_3) and H_2SO_4, suggests that the nitrate reduction reaction is not facilitated in these conditions. To investigate the implications of these initial results with KNO_3 as the nitrate donor, cyclic voltammetry studies were conducted.

Table 3.1.1 Quantitative tests before and after the reaction with 50 mM H_2SO_4 and 8 mM KNO_3

	Before Reaction		**After Reaction**		
Electrolyte	**Nitrate (ppm)**	**Ammonia (ppm)**	**Nitrate (ppm)**	**Nitrite (ppm)**	**Ammonia (ppm)**
50mM H_2SO_4	Negative	Negative	Negative	Negative	Negative
50mM H_2SO_4. 8mM KNO_3		Negative		Negative	Negative

Figure 3.1.1 compares the Cyclic Voltammograms observed for the carbon nanospiked electrode at 100mV s^{-1} in 50 mM H_2SO_4 and 50 mM H_2SO_4. 8 mM KNO_3 as the electrolyte. Voltammograms of 50mM H_2SO_4 were recorded at different scan rates to establish reference behavior without the addition of the nitrate. Lack of peak suggests that the reaction might not have occurred. There was no activity for nitrate reduction on carbon nanospiked electrode. The possible noise could be due to excess helium bubbles in the solution.

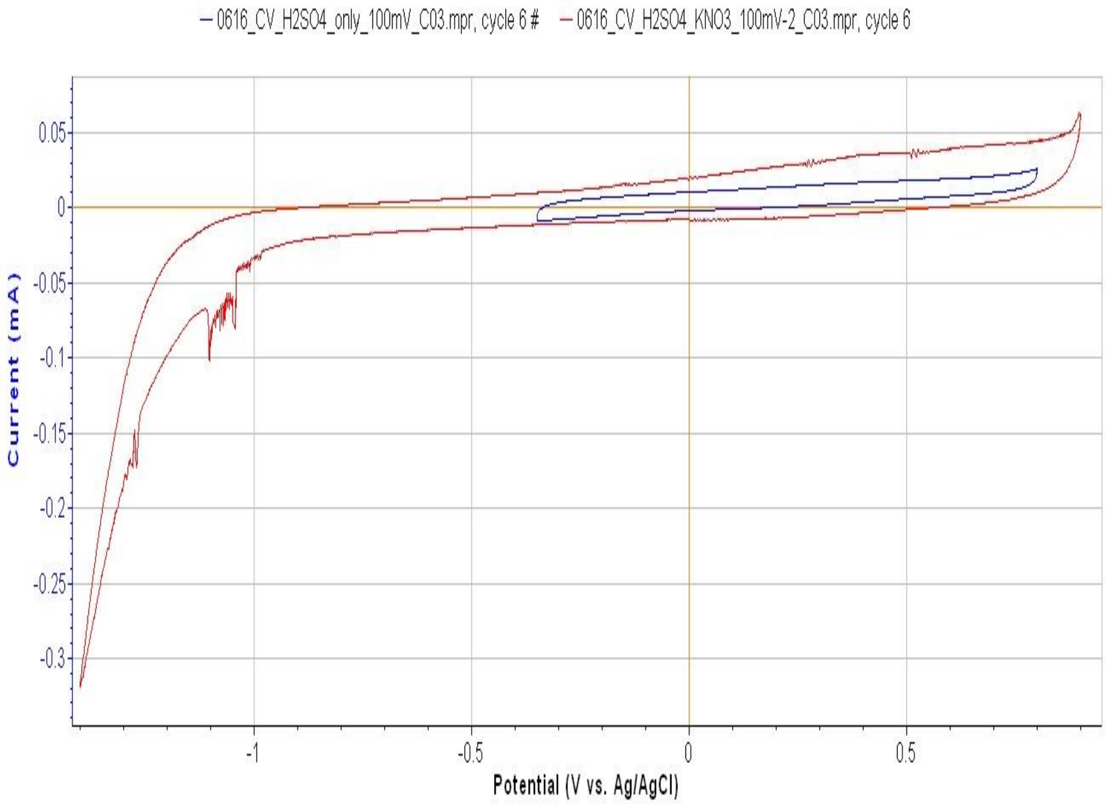


Figure 3.1.1 Redox behavior of CNS with 50 mM H_2SO_4 and 50 mM H_2SO_4. 8 mM KNO_3 as the electrolyte. Scan Rate 100mV s^{-1}. The voltammogram represents 4th cycle.

3.2 Using Base as an electrolyte with Potassium nitrate as the nitrate donor

After testing the strong acid as an electrolyte, a strong base was tested as the electrolyte.

3.2.1 Using 1 M NaOH and 1 M NaOH. 8 mM KNO_3

Table 3.2.1 shows quantitative tests before and after the cyclic voltammograms were conducted. We detected the presence of nitrite using the tetra test strips, and the presence of ammonia using the salicylate-hypochlorite test. Based on this initial analysis, no nitrate or ammonia was detected in the control experiment with just NaOH, as expected. However, the absence of nitrite or ammonia with the nitrogen donor (KNO_3) and NaOH, suggests that the nitrate reduction reaction is not facilitated in these conditions. To investigate the implications of these initial results with KNO_3 as the nitrate donor, cyclic voltammetry studies were conducted.

Table 3.2.1 Quantitative tests before and after the reaction with 1 M NaOH and 8 mM KNO_3

	Before Reaction		**After Reaction**		
Electrolyte	**Nitrate (ppm)**	**Ammonia (ppm)**	**Nitrate (ppm)**	**Nitrite (ppm)**	**Ammonia**
1M NaOH	Negative	Negative	Negative	Negative	Negative
1M NaOH. 8mM KNO_3		Negative		Negative	Negative

Voltammograms of 1M NaOH were recorded at different scan rates to establish reference behavior without the addition of the nitrate. Figure 3.2.1 compares the Cyclic Voltammograms observed for the carbon nanospiked electrode at 100mV s^{-1} in 1M NaOH and 1M NaOH. 8mM KNO_3 as the electrolyte. The representative scan rate was the best suitable scan rate amongst the ones tested. The predominant sharp peak towards the negative sweep is possibly due to hydrogen adsorption (Casella & Contrusi, 2014). It inhibits the reduction of nitrates at potentials that execute a high hydrogen coverage (Dima, A de Vooys, & Koper, 2003). The noise could be possibly due to the air bubbles at the working electrode.

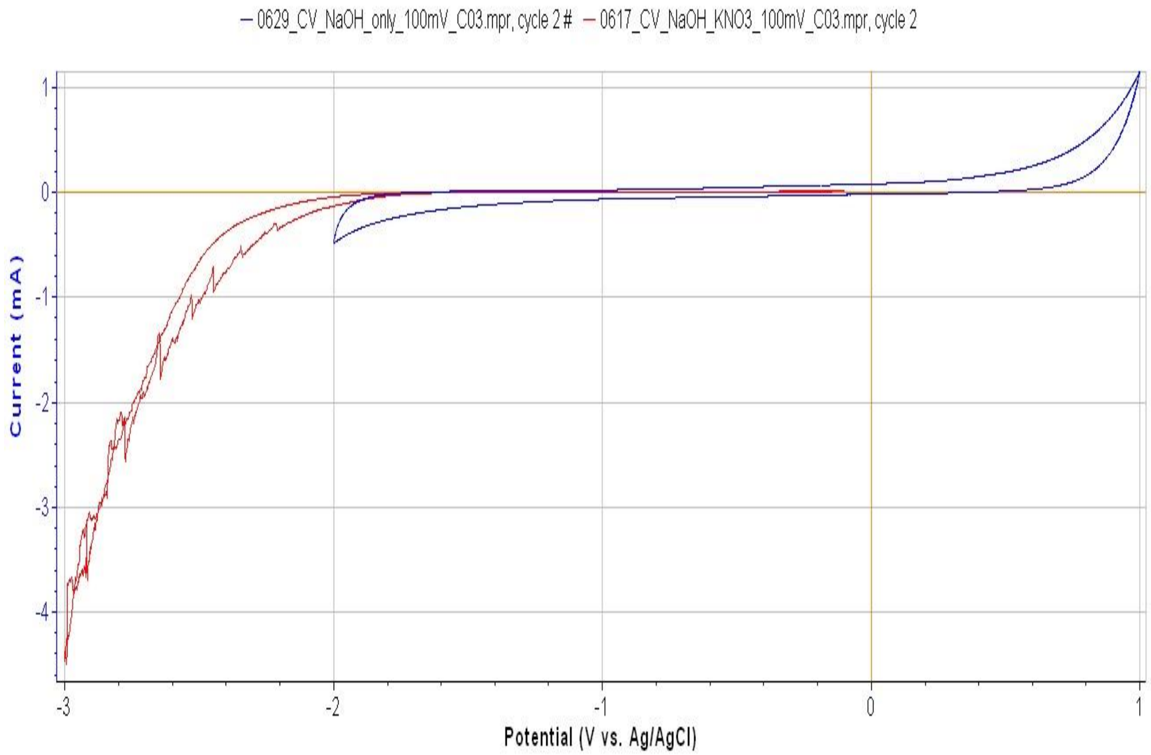


Figure 3.2.1 Redox behavior of CNS with 50mM NaOH and 50mM NaOH. 8mM $LiNO_3$ as the electrolyte. Scan rate 100mV s^{-1}. The voltammogram represent 2^{nd} cycle.

Therefore, the change in electrolyte did not show any statistically significant change in initiating the NO_x reduction reaction, as suggested by the absence of nitrite or ammonia in both NaOH and H_2SO_4 based reactions. Our next step was to investigate the effect of nitrate donor ions on the NO_x reduction reaction. We chose $LiNO_3$ as our second nitrate donor because it is a better reducing agent.

3.3 Using Acid as an electrolyte with Lithium nitrate as the nitrate donor

3.3.1 Using 50 mM H_2SO_4, and 50 mM H_2SO_4. 8 mM $LiNO_3$ as the electrolyte

After getting negative results, another nitrate donor was investigated. Table 3.3.1 shows the quantitative tests before and after the reaction. Presence of nitrite suggested that some reaction had occurred, but lack of ammonia possibly contradicted the assumption. Results suggest that nitrite could be the intermediate product.

Table 3.3.1 Quantitative tests before and after the reaction with 50 mM H_2SO_4 and 8 mM $LiNO_3$

	Before Reaction		**After Reaction**		
Electrolyte	**Nitrate (ppm)**	**Ammonia (ppm)**	**Nitrate (ppm)**	**Nitrite (ppm)**	**Ammonia**
50mM H_2SO_4	Negative	Negative	Negative	Negative	Negative
50mM H_2SO_4. 8mM $LiNO_3$	80-160	Negative	80-160	0.5-1	Negative

Figure 3.3.1 compares the Cyclic Voltammograms observed for the carbon nanospiked electrode at 100mV s^{-1} in 50 mM H_2SO_4 and 50 mM H_2SO_4. 8 mM KNO_3 as the electrolyte. Lack of a strong peak at higher potentials also suggests lack of nitrate reduction. The predominant sharp current drop towards the negative sweep is possibly due to the hydrogen adsorption. Hydrogen adsorption possibly contaminates the surface of the electrode thereby hindering the nitrate reduction (Casella & Contrusi, 2014).

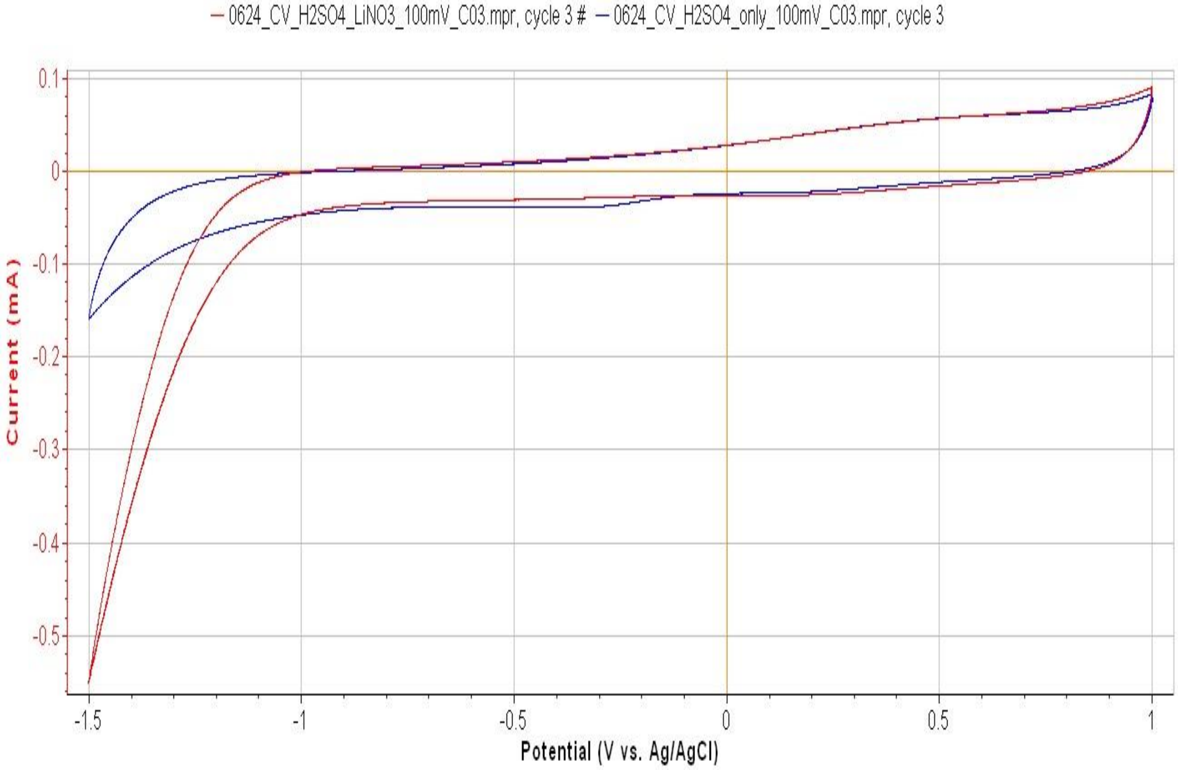


Figure 3.3.1 Redox behavior of CNS with 50 mM H_2SO_4 and 50 mM H_2SO_4. 8 mM $LiNO_3$ as the electrolyte. Scan rate 100mV s^{-1}. The voltammogram represent 3rd cycle.

3.4 Using Base as an electrolyte with Lithium nitrate as the nitrate donor

3.4.1 Using 1 M NaOH and 1 M NaOH. 8 mM $LiNO_3$

After getting negative results while testing certain acids and bases as electrolyte, a strong base was tested with lithium nitrate. Cyclic volammograms were recorded for sodium hydroxide, and sodium hydroxide with nitrate in it. Table 3.4.1 shows the quantitative tests before and after the cyclic volammograms and chronoamperometry were recorded. It suggests the presence of ammonia and nitrite. Usually use of acid or base as an electrolyte helps maintain a constant pH. However, pH was still recorded to ensure that the reaction wasn't pH forwarding. The low pH produces less reduction of NO_3^- because the electro reduction reaction favors the production of H_2 gas.

Results suggest that nitrite is the intermediate product while ammonia could be the end product of the reaction. The need for lithium is consistent with literature reports for the electrochemical formation of ammonia from N_2 gas (Giddey, Badwal, & Kulkarni, 2013; Kordali, Kyriacou, & Lambrou, 2000). The detailed mechanism of the reaction is currently under investigation.

Table 3.4.1 Quantitative tests before and after the reaction with 1 mM NaOH and 8mM $LiNO_3$

	Before Reaction			**After Reaction**				
Electrolyte	**Nitrate (ppm)**	**Ammonia (ppm)**	**pH**	**Nitrate (ppm)**	**Nitrite (ppm)**	**Ammonia**	**pH (WE)**	**pH (CE)**
1M NaOH	Negative	Negative	13.44	Negative	Negative	Negative	13.42	
1M NaOH. 8mM $LiNO_3$	0-20	Negative	13.37	0-20	<0.5	0.25	13.36	13.35

Figure 3.4.1 compares the Cyclic Voltammograms observed for the carbon nanospiked electrode at 5 mV s^{-1} in 1 M NaOH and 1M NaOH. 8 mM $LiNO_3$ as the electrolyte. Figure 7 compares the blank experiment and the one with the presence of nitrate. The reduction starts at -1.5 V. Voltammograms were run at several different scan rates. Chronoamperometry was performed for 15 h at -1.5 V to possibly have the reaction to go to completion.

Equations below show the possible reaction mechanism for the nitrate reduction, based on our cyclic voltammogram data.

$$\boldsymbol{NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O}$$

$$\boldsymbol{NO_2^- + 7H^+ + 6e^- \rightarrow NH_3 + 2H_2O}$$

$$\boldsymbol{NH_4^+ + NO_2^- \rightarrow N_2 + H_2O}$$

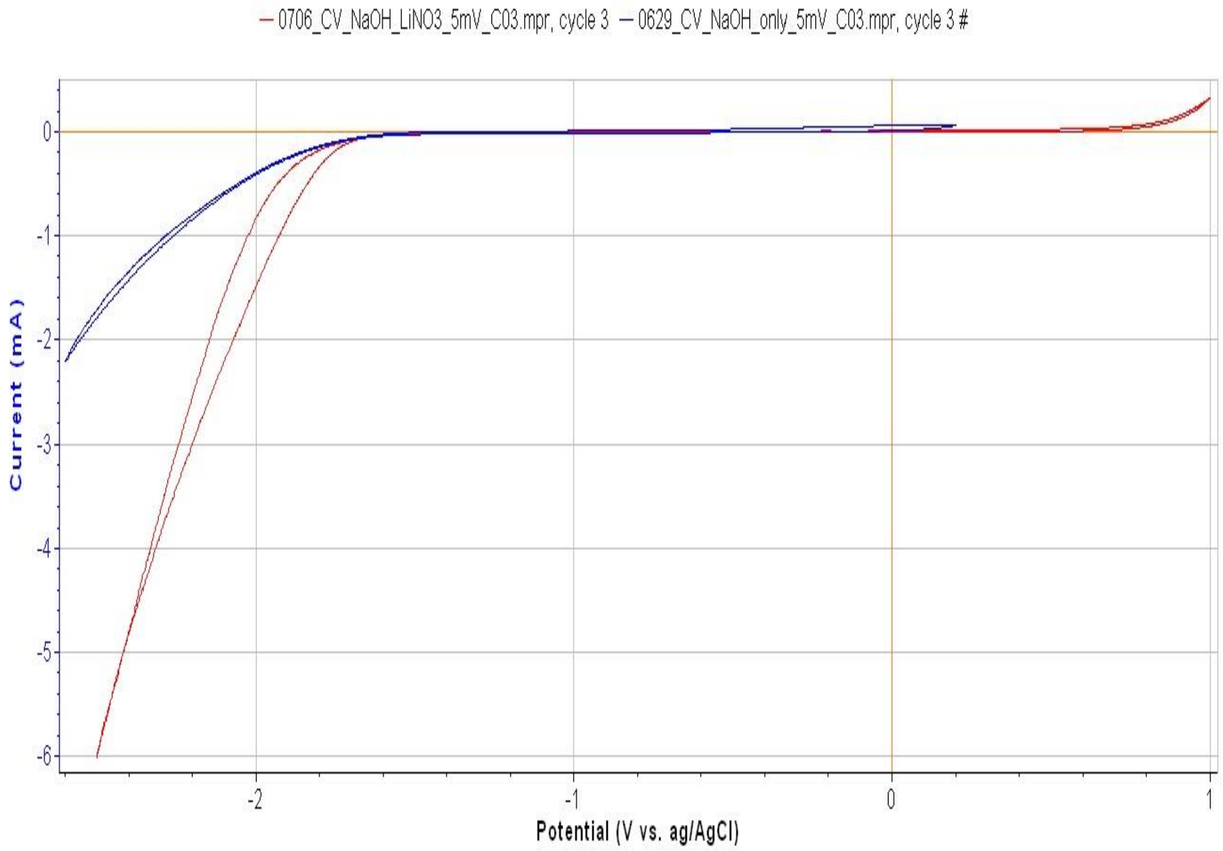


Figure 3.4.1 Redox behavior of CNS with 50 mM NaOH and 50 mM NaOH. 8 mM $LiNO_3$ as the electrolyte. Scan Rate 5mV s^{-1}. The voltammograms represent the 3rd cycle.

Figure 3.4.2 shows the SEM image of the carbon nanospike electrode after the reaction. The TEM of the CNS before the reaction showed the curled tips, however the SEM after the reaction shows a visibly different topography. Presence of salts can be seen on the surface of the electrode.

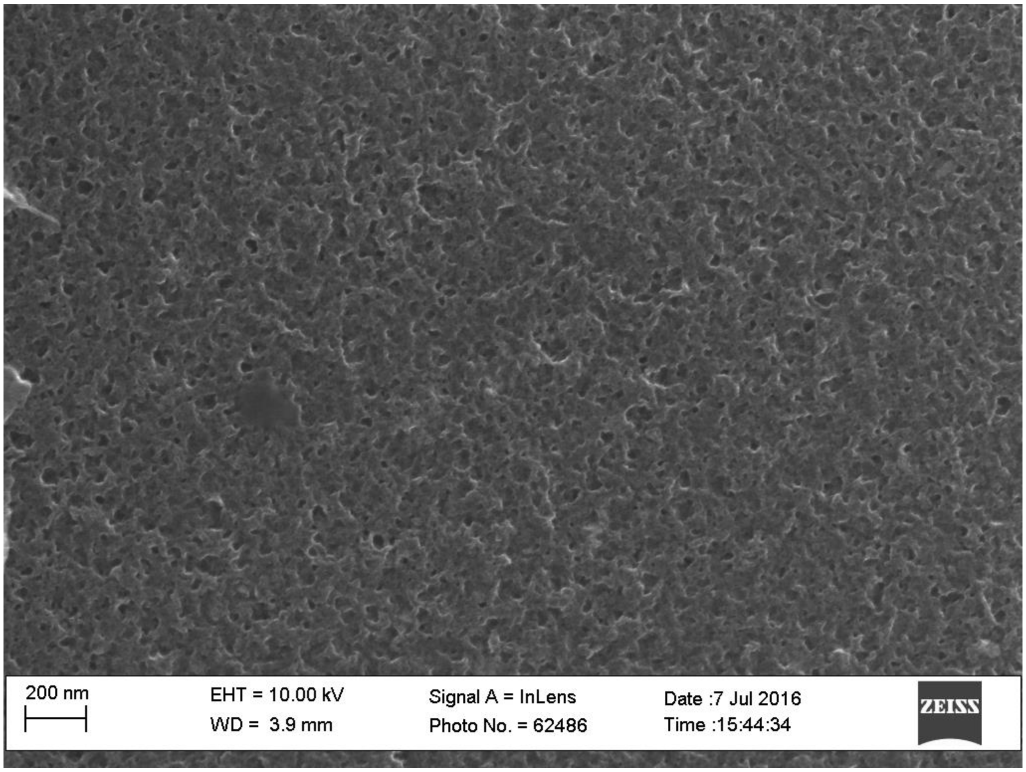

200 nm
EHT = 10.00 kV
WD = 3.9 mm
Signal A = InLens
Photo No. = 62486
Date :7 Jul 2016
Time :15:44:34
ZEISS

Figure 3.4.2 SEM of Carbon nanospike electrode after the reaction.

3.4.2 Comparing different concentrations of nitrate

After getting positive results using lithium as the nitrate donor, and a strong base as the electrolyte, the concentration of the nitrate was fluctuated to see how it affected the reaction. Table 3.4.2 shows the quantitative tests before and after the reaction. No presence of ammonia was found with higher concentrations of nitrate.

Another possibility is that excess nitrite reacts with ammonia ion to further produce nitrogen and water. Further tests need to be done to quantify and confirm the nitrogen production.

Table 3.4.2 Quantitative tests before and after running CV's and CA with 1 M NaOH and different concentrations of $LiNO_3$

	Before Reaction			**After Reaction**				
Electrolyte	**Nitrate (ppm)**	**Ammonia (ppm)**	**pH**	**Nitrate (ppm)**	**Nitrite (ppm)**	**Ammonia**	**pH (WE)**	**pH (CE)**
1M NaOH	Negative	Negative	13.44	Negative	Negative	Negative	13.42	
1M NaOH. 8mM $LiNO_3$	0-20	Negative	13.37	0-20	<0.5	0.25	13.36	13.35
1M NaOH. 20mM $LiNO_3$	0-20	Negative	13.43	0-20	0.5	0.25-0.5	13.34	13.34
1M NaOH. 50mM $LiNO_3$	0-20	Negative	13.39	0-20	0.5	Negative	13.39	13.44
1M NaOH. 70mM $LiNO_3$	0-20	Negative	13.38	0-20	0-0.5	Negative	13.33	13.33

Figure 3.4.3 compares the Cyclic Voltammograms observed for the carbon nanospiked electrode at 5mV s^{-1} in 1 M NaOH and 1 M NaOH with different concentrations of $LiNO_3$ as the electrolyte. Red line represents the voltammogram of 1 M NaOH with 8 mM of $LiNO_3$. Blue line represents the voltammogram of 1 M NaOH with 20 mM $LiNO_3$. Pink line represents the voltammogram of 1 M NaOH with 50 mM $LiNO_3$, and green line represents the voltammogram of 1 M NaOH with 70 mM $LiNO_3$. Typically, with increase in the concentration of the nitrate the current vs. potential becomes more negative. However, there is an exception with 20 mM $LiNO_3$ possibly due to faradaic losses.

Faradaic loss occurs when electrons or ions participates in side reactions (Bard & Faulkner, 2004; "Cyclic voltammetry,").

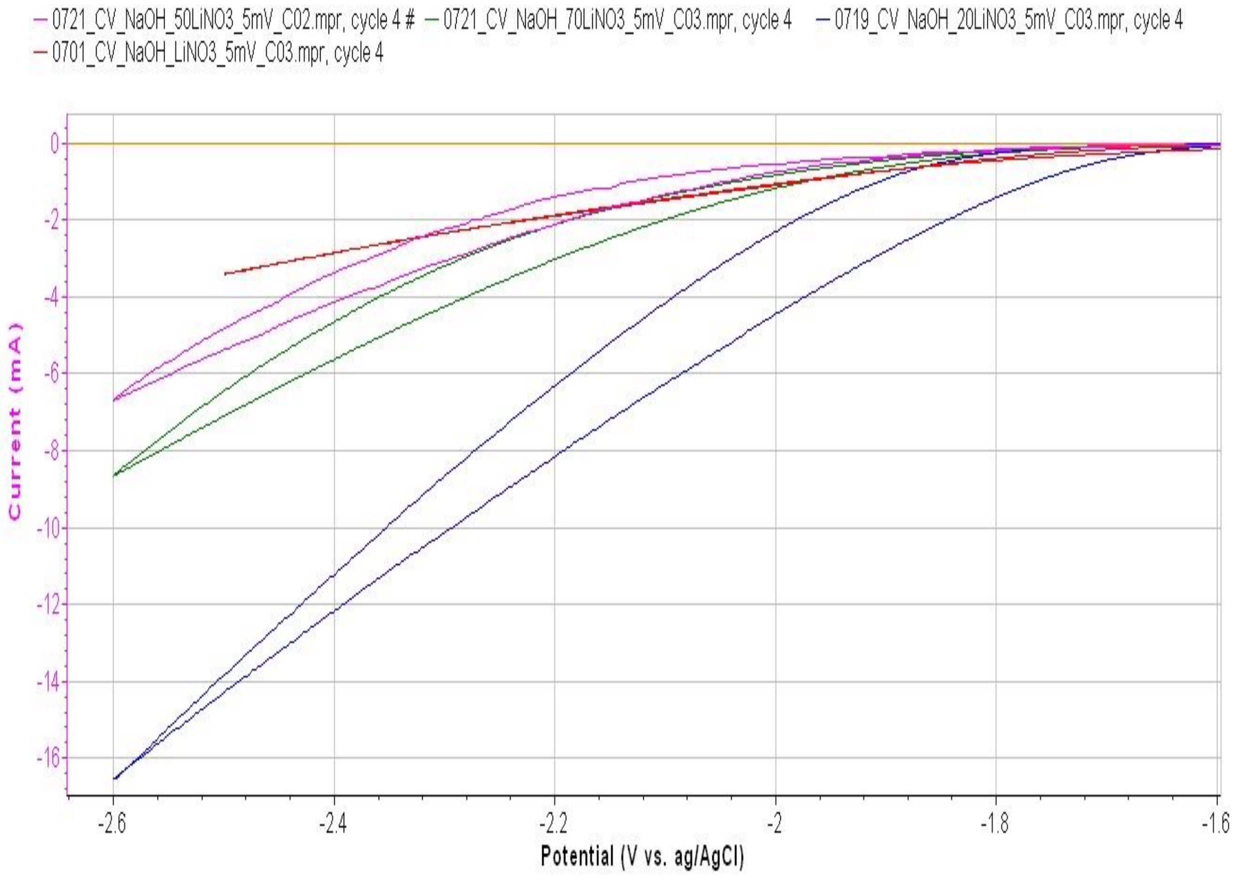


Figure 3.4.3 Redox behavior of CNS with 1 M NaOH and different concentrations of $LiNO_3$ as the electrolyte. Scan Rate 5mv s^{-1}. The voltammogram represents the 4th cycle.

3.4.3 Comparing different bases with 8 mM $LiNO_3$

Once promising results were obtained by using a base with $LiNO_3$ as the nitrate donor, different bases were investigated to further understand the reactions. Table 3.4.3 compares different bases with $LiNO_3$ as the nitrate donor. The highest reduction efficiency was observed with lithium hydroxide as the base and lithium nitrate as the nitrate donor. Lithium ions play an important role in reducing nitrate. The ionization energies would suggest that lithium would be the weakest reducing agent out of the alkali metals. However, the reduction potential implies that lithium is the strongest reducing agent.

Table 3.4.3 Quantitative tests before and after the reaction with different bases

	Before Reaction			**After Reaction**				
Electrolyte	**Nitrate (ppm)**	**Ammonia (ppm)**	**pH**	**Nitrate (ppm)**	**Nitrite (ppm)**	**Ammonia**	**pH (WE)**	**pH (CE)**
1M NaOH	Negative	Negative	13.44	Negative	Negative	Negative	13.42	
1M NaOH. 8mM $LiNO_3$	0-20	Negative	13.37	0-20	<0.5	0.25	13.36	13.35
50mM LiOH	Negative	Negative		Negative	Negative	Negative	12.58	12.59
50mM LiOH. 8mM $LiNO_3$	160	Negative	12.71	40	3	0-0.25	12.57	12.50
50mM KOH	Negative	Negative		Negative	Negative	Negative	12.68	11.34
50mM KOH. 8mM $LiNO_3$	160	Negative	12.76	80<x<160	3	Negative	12.72	11.22
50mM NaOH	Negative	Negative		Negative	Negative	Negative		
50mM NaOH. 8mM $LiNO_3$	160	Negative	12.71	80<x<160	5-10	Negative		11.36

Figure 3.4.4 compares the Cyclic Voltammograms observed for the carbon nanospiked electrode at 100 mV s^{-1} in different bases with 8 mM $LiNO_3$ as the electrolyte. Purple line represents 50 mM NaOH with 8 mM $LiNO_3$. Red line represents 50 mM LiOH with 8mM $LiNO_3$.

Green line represents 50 mM KOH with 8 mM $LiNO_3$. LiOH has a more steeper slope than NaOH. This could be possible due to a lower ionic resistance.

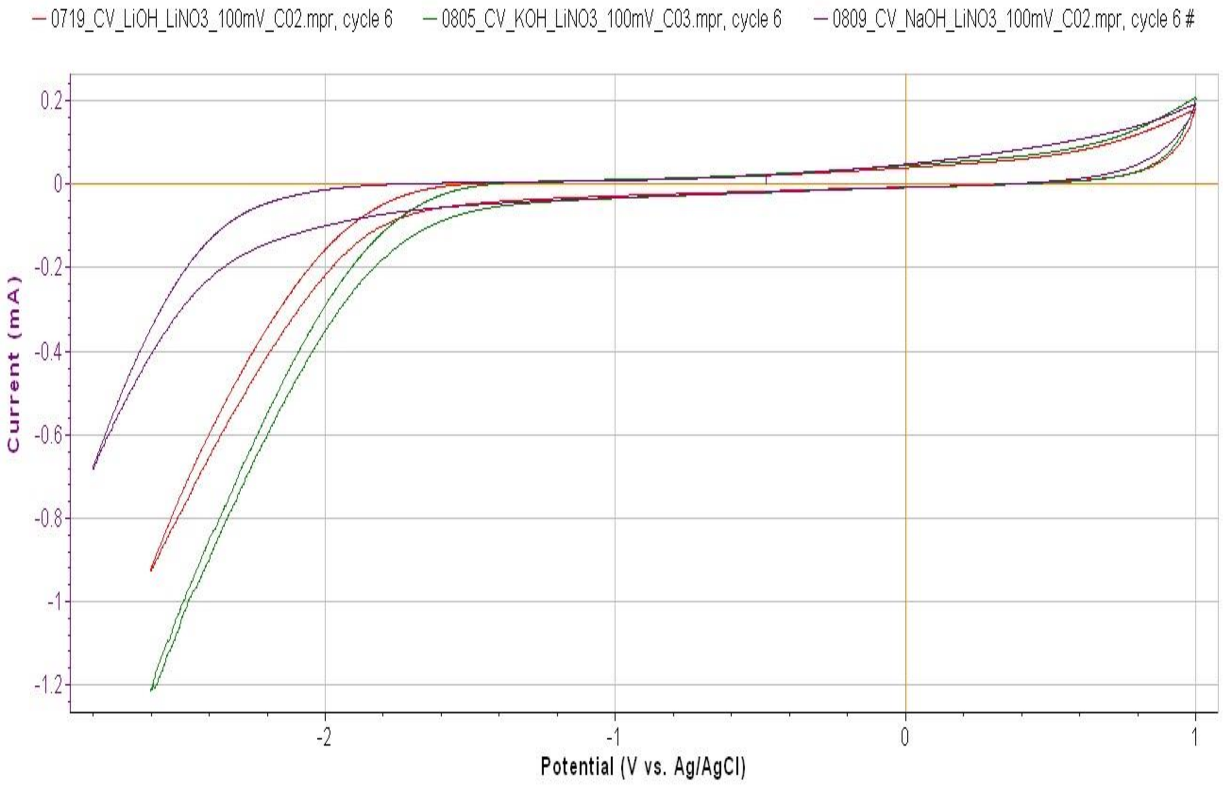
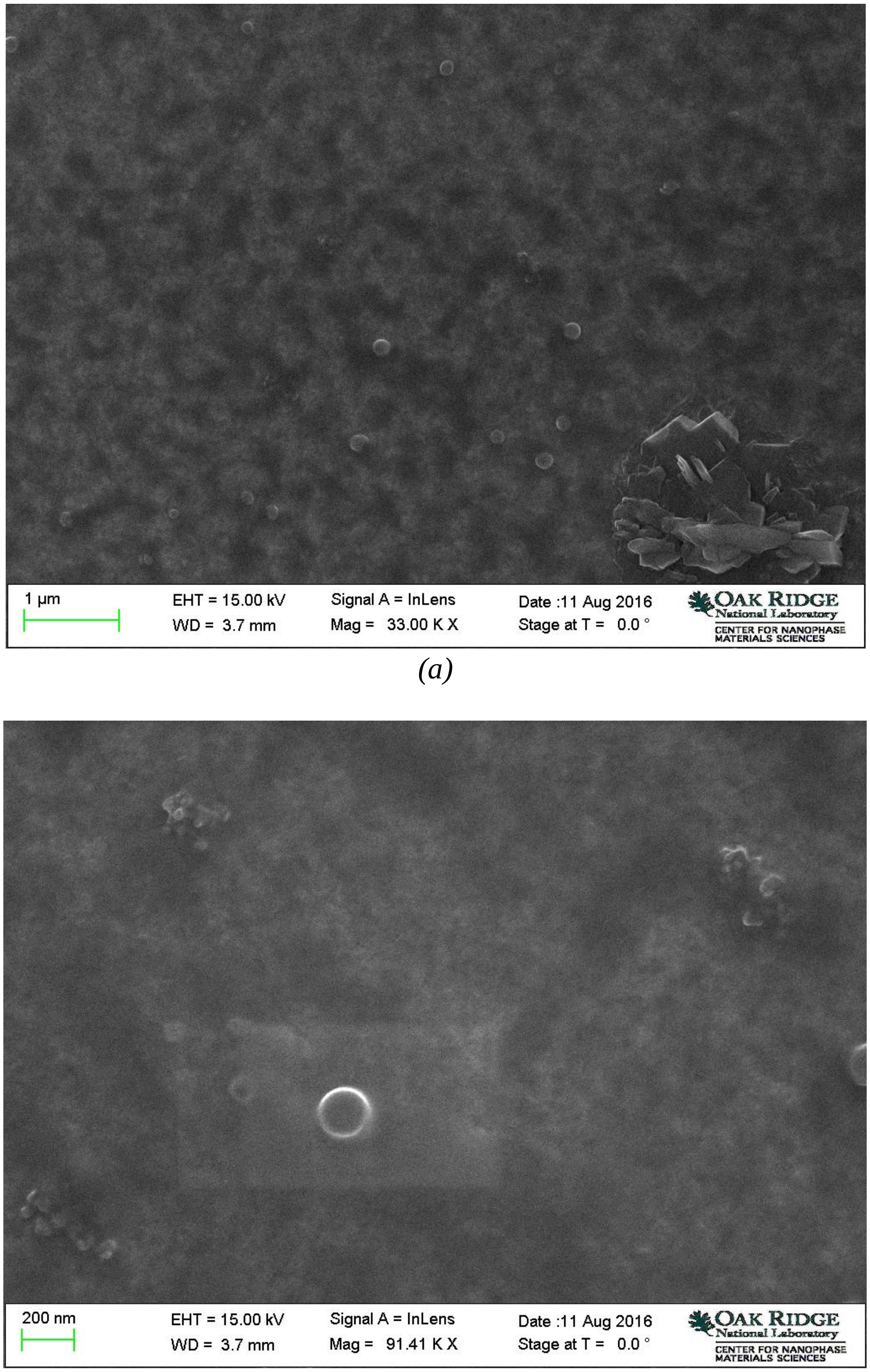


Figure 3.4.4 Redox behavior of CNS with 1M NaOH 8 mM $LiNO_3$, 50 mM LiOH 8 mM $LiNO_3$, and 50 mM OH 8 mM $LiNO_3$ as the electrolyte

Figure 3.4.5 shows the SEM images of the carbon nanospiked electrode after the reaction occurred. Elemental analyses show presence of nitrogen, carbon, lithium, oxygen, and sodium on the surface of the electrode. Big white structure at the right end corner is likely salt.

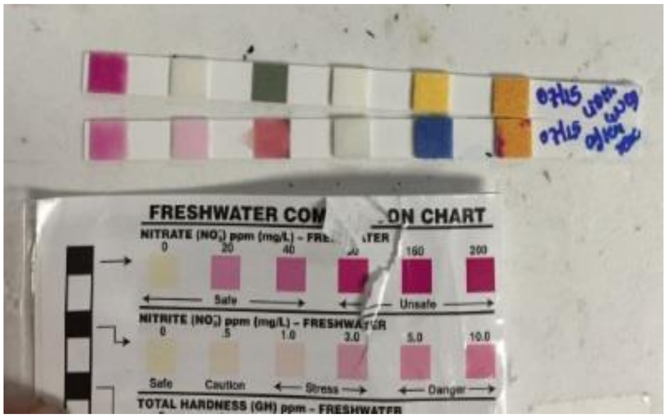

1 µm
EHT = 15.00 kV
WD = 3.7 mm
Signal A = InLens
Mag = 33.00 K X
Date :11 Aug 2016
Stage at T = 0.0 °
OAK RIDGE National Laboratory
CENTER FOR NANOPHASE MATERIALS SCIENCES
200 nm
EHT = 15.00 kV
WD = 3.7 mm
Signal A = InLens
Mag = 91.41 K X
Date :11 Aug 2016
Stage at T = 0.0 °
OAK RIDGE National Laboratory
CENTER FOR NANOPHASE MATERIALS SCIENCES

(a)

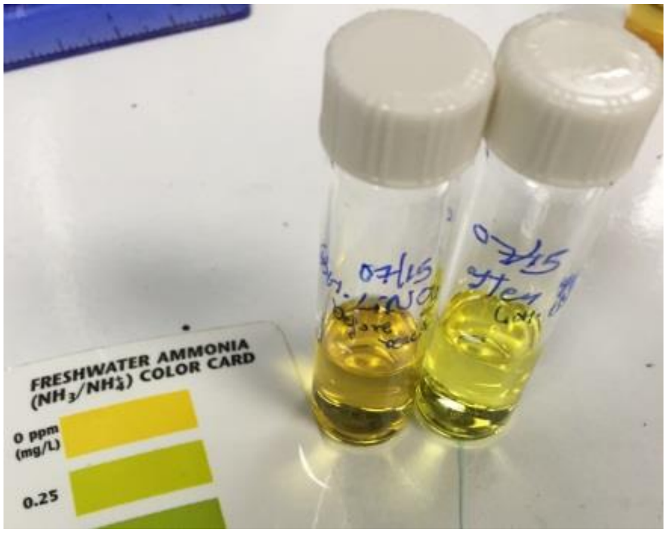
(b)

Figure 3.4.5 SEM images of 50 mM LiOH. 8 mM $LiNO_3$ after the reaction a) with salt deposit on it b) zoomed in on the unknown white circular disk

Figure 3.4.6 shows the quantitative tests for 50 mM LiOH. 8 mM $LiNO_3$ before and after the reaction. Figure 3.4.6.a shows the concentration nitrate and nitrite tests before and after the reaction. The nitrate concentration changes from 160 ppm to 40 ppm, while the concentration nitrite changes from 0ppm to 3 ppm. Salicylate-hypochlorite tests give a light green color, suggesting the presence of moderately low amount of ammonia.


FRESHWATER COM ON CHART
NITRATE (NO3) ppm (mg/L) - FRE TER
0
20
40
160
200
Safe
Unsafe
NITRITE (NO2) ppm (mg/L) - FRESHWATER
0
.5
1.0
3.0
5.0
10.0
Safe
Caution
Stress
Danger
TOTAL HARDNESS (GH) ppm - FRESHWATER

(a)


FRESHWATER AMMONIA
(NH3/NH4+) COLOR CARD
0 ppm
(mg/L)
0.25
07/15
07/15

(b)

Figure 3.4.6 Quantification Tests for 50 mM LiOH. 8 mM $LiNO_3$ a) nitrite and nitrate test strip before and after the reaction b) salicylate-hypochlorite test for ammonia

3.5 Possible reaction mechanism

Nitrite is a possible intermediate product. The presence of ammonia suggests that the nitrite was further reduced. Absence of ammonia possibly suggests that the ammonia was further reduced to nitrogen and water. The hydrogen ions are supplied from the water in the electrolyte.

$$\boldsymbol{NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O}$$

$$\boldsymbol{NO_2^- + 7H^+ + 6e^- \rightarrow NH_3 + 2H_2O}$$

$$\boldsymbol{NH_4^+ + NO_2^- \rightarrow N_2 + H_2O}$$

CHAPTER 4

CONCLUSION and FUTURE WORK

Strong electrolytes dissociate completely in water. It also conducts current efficiently. After testing acid and bases, the results indicated that bases were preferred for nitrate reduction over acids. The results clearly suggest that lithium ion is necessary in the electrochemical reduction of nitrate. Using high concentrations of nitrate hasn’t been beneficial. However, there is a possibility of nitrite further reaction with ammonia ion to form nitrogen and water. Further tests need to be conducted to prove this hypothesis.

Further, low pH produces less reduction of NO_3^- because the electro reduction reaction favors the production of H_2 gas. Lithium is an excellent reducing agent, and highest reduction efficiency was observed while using LiOH as the electrolyte with $LiNO_3$ at the nitrate source. Furthermore, faradaic efficiency needs to be calculated in order to quantify the products in moles.

This is a novel method and the reactions are not fully understood, which is why it is necessary to conduct further experiments to fully understand the nature of the reactions. Preliminary results also suggest that there is a possibility of nitrite reacting with NH_4^+ and forming N_2 and H_2O. Quantification tests needs to be run to confirm the formation of N_2 and H_2O. IR spectroscopy or Differential electrochemical mass spectroscopy (DEMS) could be used to quantify the presence of nitrogen.

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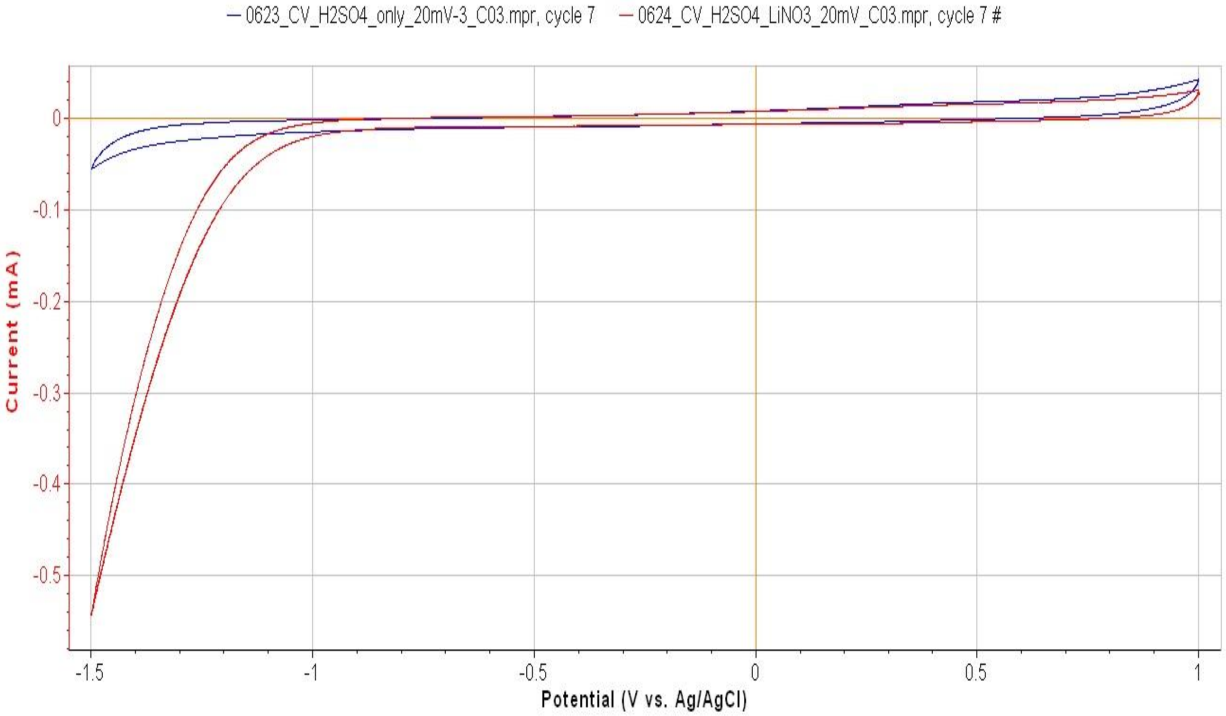
APPENDIX A

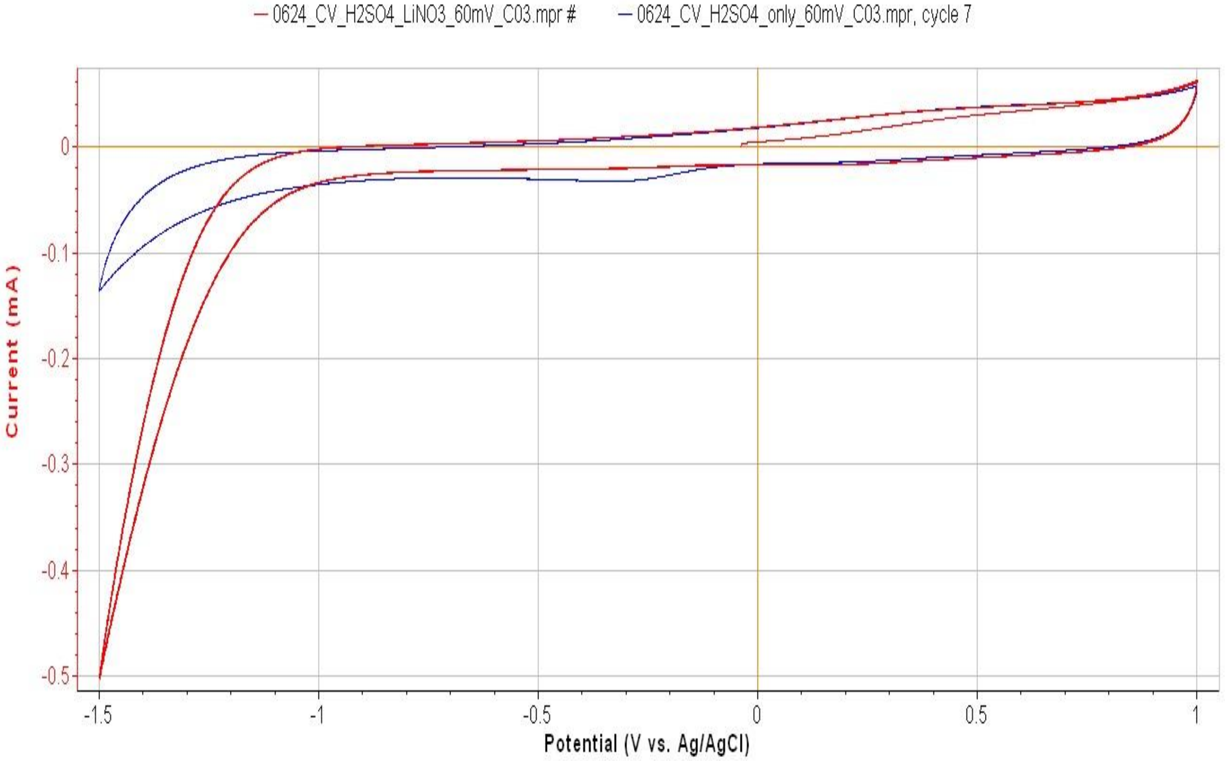
LIST OF ALL THE EXPERIMENTS CONDUCTED

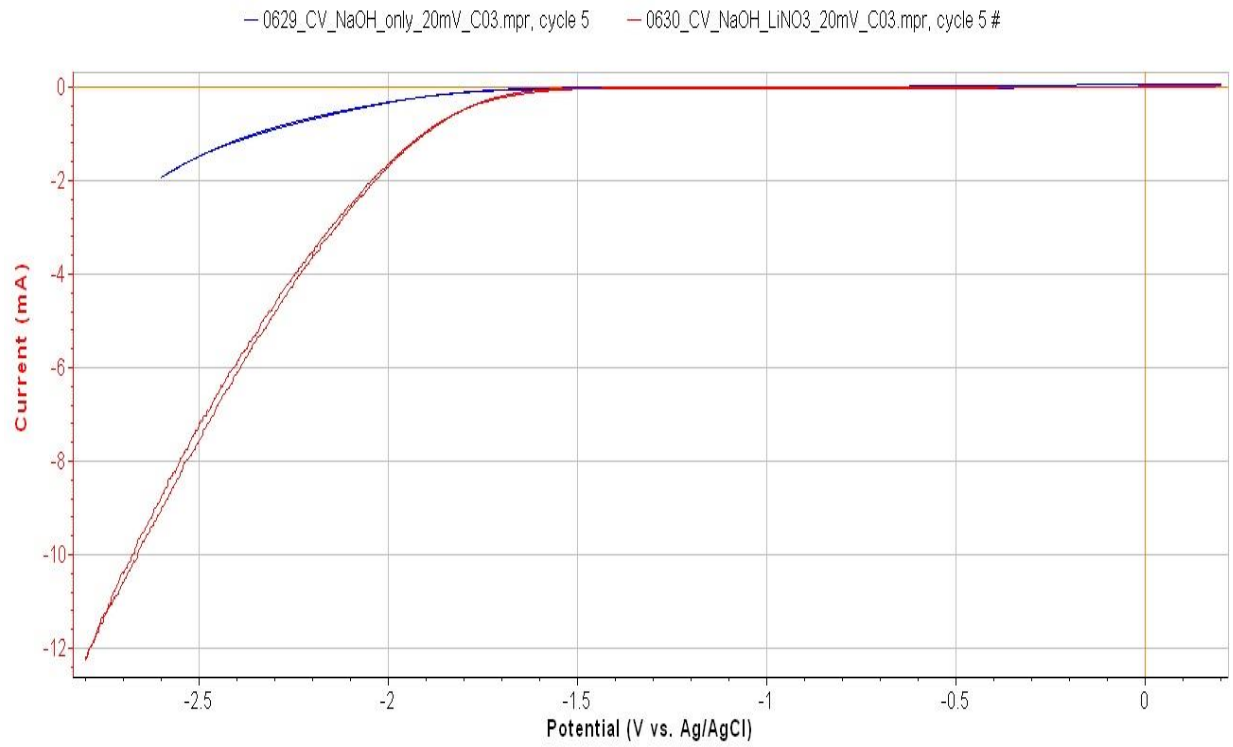
Date	**Electrolyte**	**Before Nitrate (ppm)**	**reaction Ammonia (ppm)**	**Nitrate (ppm)**	**After Nitrite (ppm)**	**Reaction Ammonia (ppm)**
6/14/16	**50mM H_2SO_4**					
6/15/16	**50mM H_2SO_4**					
6/16/16	**50mM H_2SO_4. 8mM KNO_3**		Negative			Negative
6/17/16	**1M NaOH. 8mM KNO_3**		Negative			Negative
6/21/16	**50mM H_2SO_4**		Negative			Negative
6/23/16	**50mM H_2SO_4**		Negative			Negative
6/24/16	**50mM H_2SO_4**		Negative			Negative
6/24/16	**50mM H_2SO_4. 8mM $LiNO_3$**		Negative			Negative
6/27/16	**50mM H_2SO_4. 8mM $LiNO_3$**		Negative			Negative
6/28/16	**50mM H_2SO_4. 8mM $LiNO_3$**	80-160	Negative	80-160	0.5-1.00	Negative
6/29/16	**1M NaOH**		Negative			Negative
6/30/16	**1M NaOH. 8mM $LiNO_3$**		Negative			Negative
7/5/16	**1M NaOH. 8mM $LiNO_3$**			0-20	Negative	Positive
7/6/16	**1M NaOH. 8mM $LiNO_3$**			0-20	Negative	0.25
7/7/16	**1M NaOH. 8mM $LiNO_3$**			0-20	Negative	0.25
7/11/16	**8mM $LiNO_3$**	200	Negative	160	3	0.25
7/12/16	**8mM $LiNO_3$**	200	Negative	160	3	0.25
7/14/16	50mM LiOH	Negative	Negative			Negative
7/15/16	**50mM LiOH. 8mM $LiNO_3$**	160	0.25	40	3	0.25
7/19/16	**50mM LiOH. 8mM $LiNO_3$**	160	Negative	40	3	Negative
7/19/16	**1M NaOH. 20mM $LiNO_3$**	0-20	Negative	0-20	0.5	0.25-0.50
7/21/16	**1M NaOH. 50mM $LiNO_3$**	0-20	Negative	0-20	0.5	Negative
7/25/16	50mM KOH					
7/26/16	**50mM KOH. 8mM $LiNO_3$**	160	Negative	80<x<160	3	Negative
8/3/16	**1M NaOH. 20mM $LiNO_3$**	0-20	Negative	0-20	Negative	Negative
8/4/16	**50mM KOH. 8mM $LiNO_3$**		Negative			Negative
8/5/16	**50M NaOH. 8mM $LiNO_3$**	160	Negative	80<x<160	5-10ppm	Negative

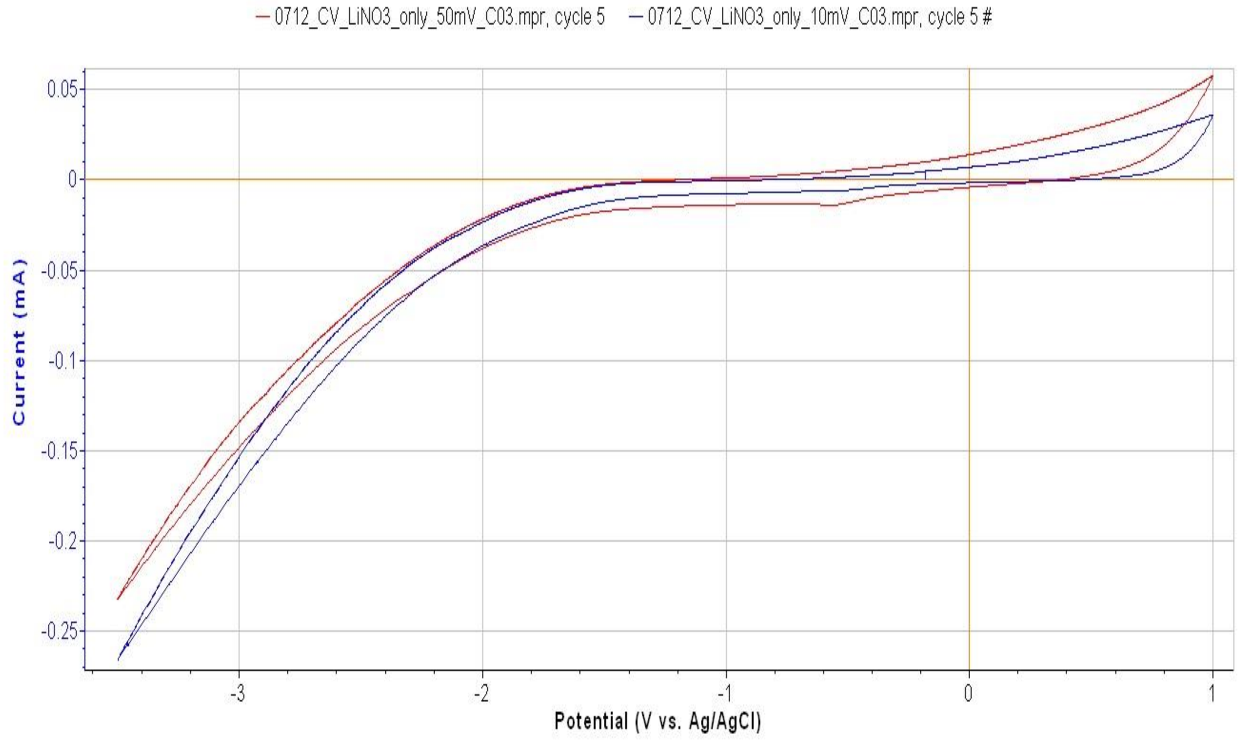
APPENDIX B

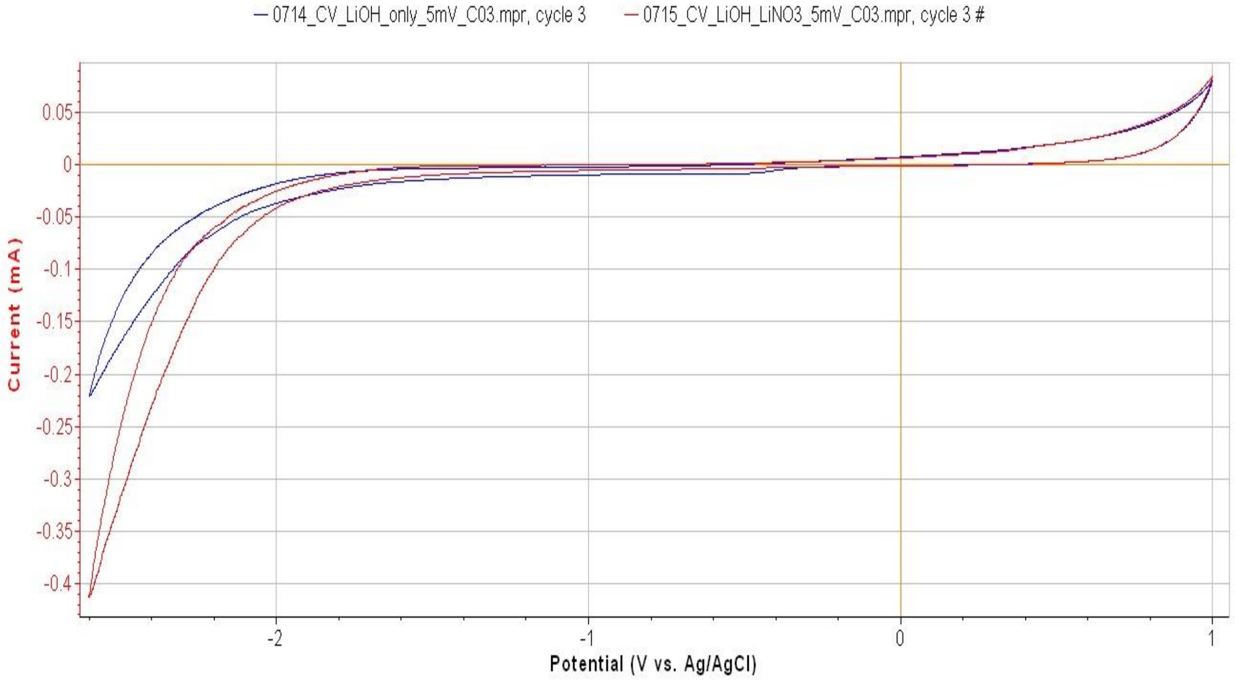
CYCLIC VOLTAMMOGRAMS OF EXPERIMENTS WITH VARIOUS SCAN RATES


0623_CV_H2SO4_only_20mV-3_C03.mpr, cycle 7
0624_CV_H2SO4_LiNO3_20mV_C03.mpr, cycle 7 #
Current (mA)
0
-0.1
-0.2
-0.3
-0.4
-0.5
-1.5
-1
-0.5
0
0.5
1
Potential (V vs. Ag/AgCl)

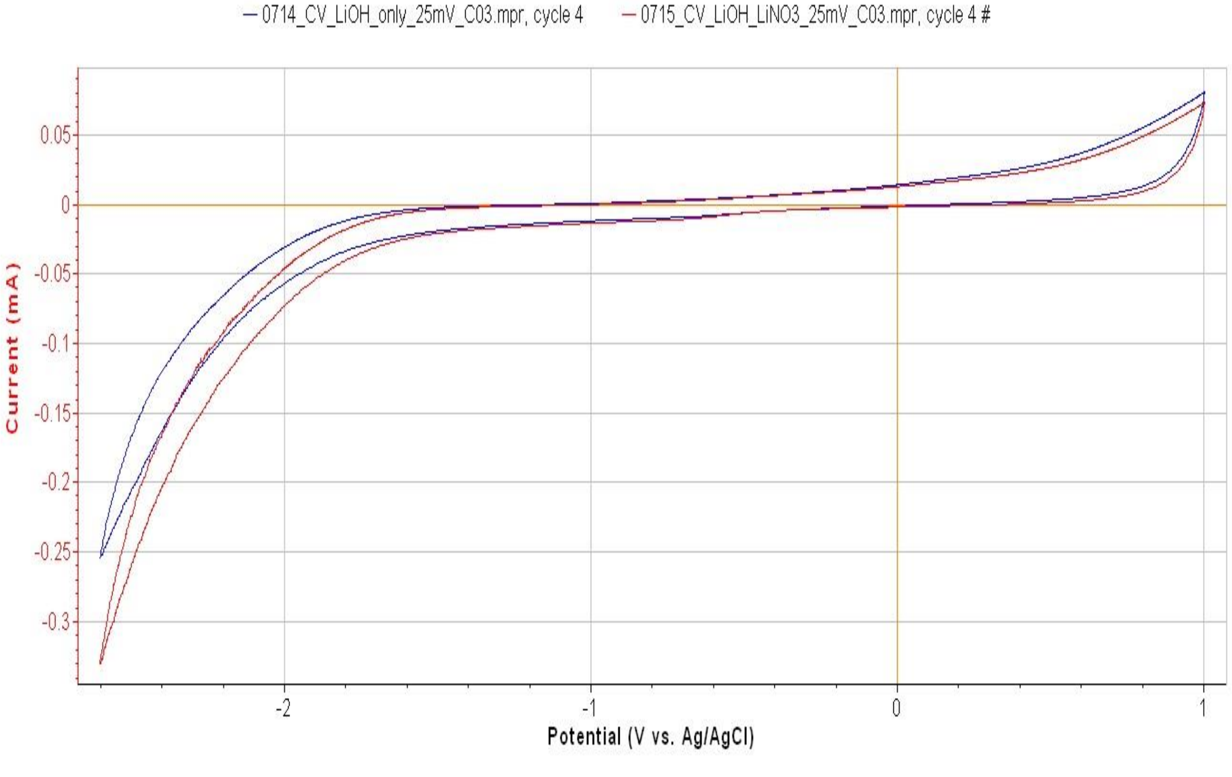

0624_CV_H2SO4_LiNO3_60mV_C03.mpr #
0624_CV_H2SO4_only_60mV_C03.mpr, cycle 7
Current (mA)
0
-0.1
-0.2
-0.3
-0.4
-0.5
-1.5
-1
-0.5
0
0.5
1
Potential (V vs. Ag/AgCl)


— 0629_CV_NaOH_only_20mV_C03.mpr, cycle 5
— 0630_CV_NaOH_LiNO3_20mV_C03.mpr, cycle 5 #
Current (mA)
0
-2
-4
-6
-8
-10
-12
-2.5
-2
-1.5
-1
-0.5
0
Potential (V vs. Ag/AgCl)

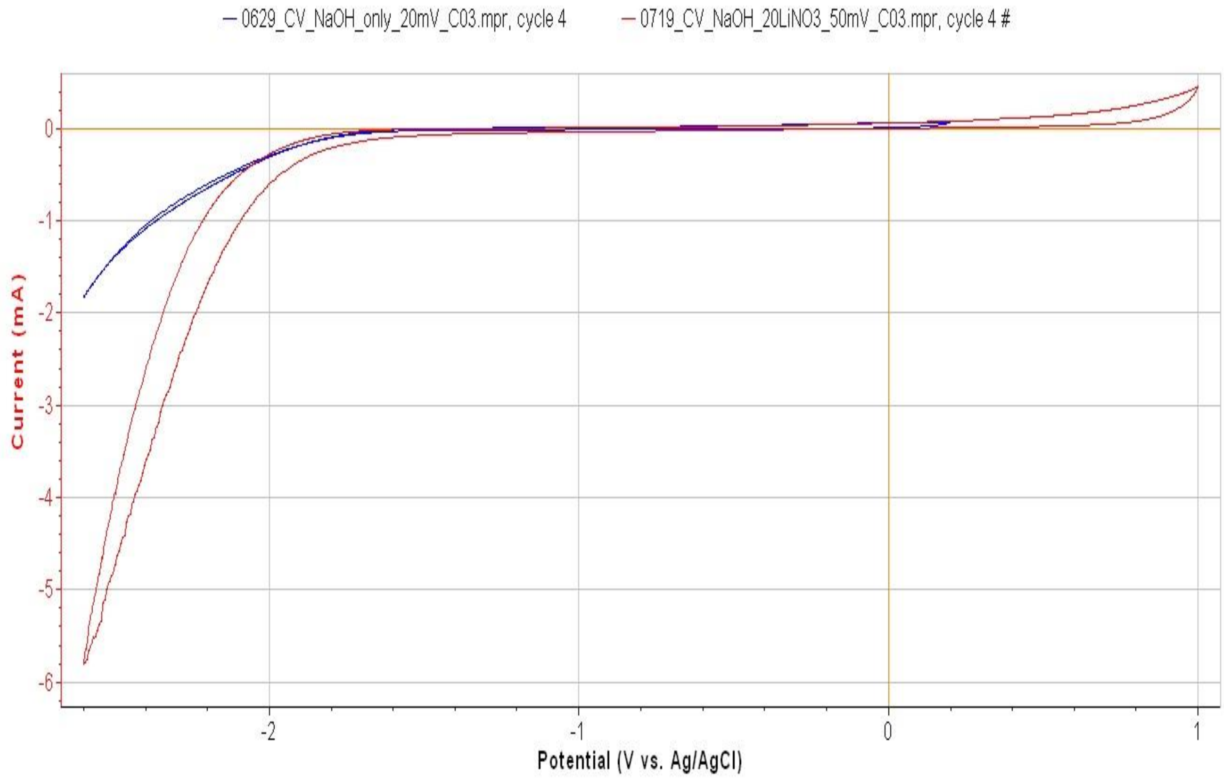

— 0712_CV_LiNO3_only_50mV_C03.mpr, cycle 5
— 0712_CV_LiNO3_only_10mV_C03.mpr, cycle 5 #
Current (mA)
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
-3
-2
-1
0
1
Potential (V vs. Ag/AgCl)



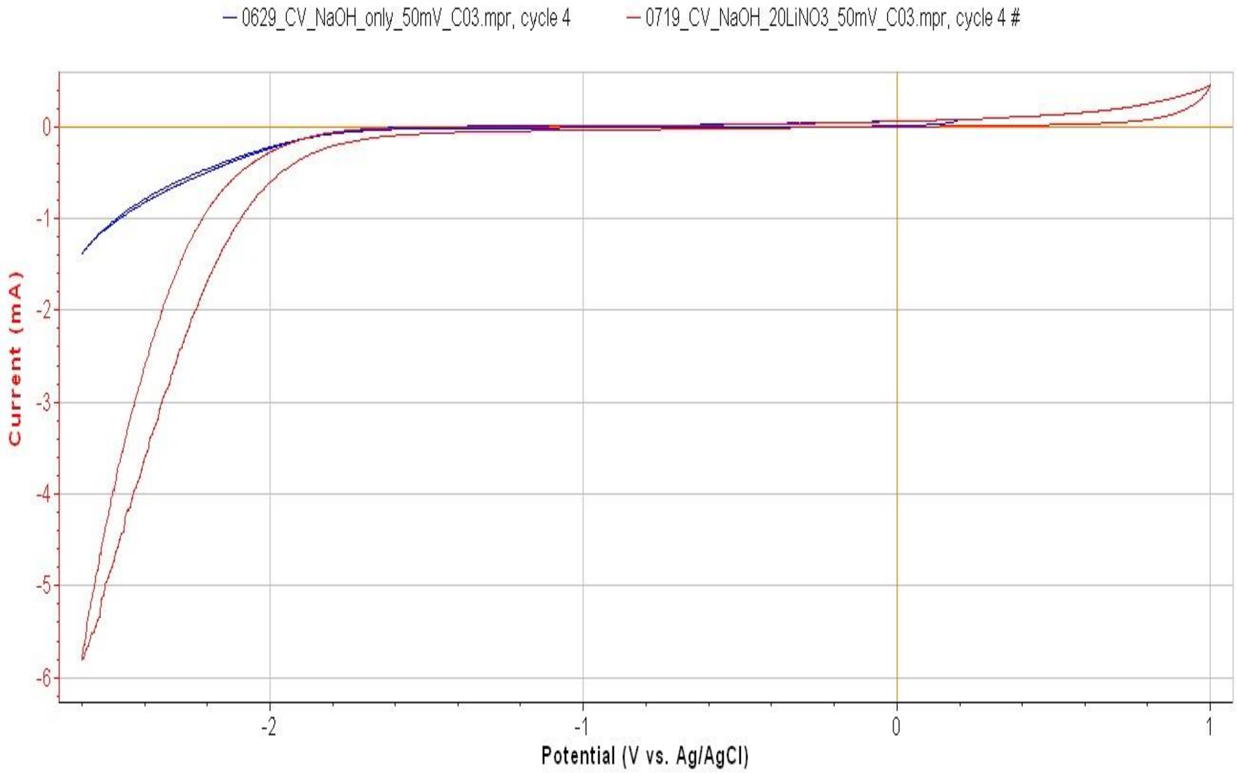
0714_CV_LiOH_only_5mV_C03.mpr, cycle 3
0715_CV_LiOH_LiNO3_5mV_C03.mpr, cycle 3 #
Current (mA)
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
-0.35
-0.4
-2
-1
0
1
Potential (V vs. Ag/AgCl)



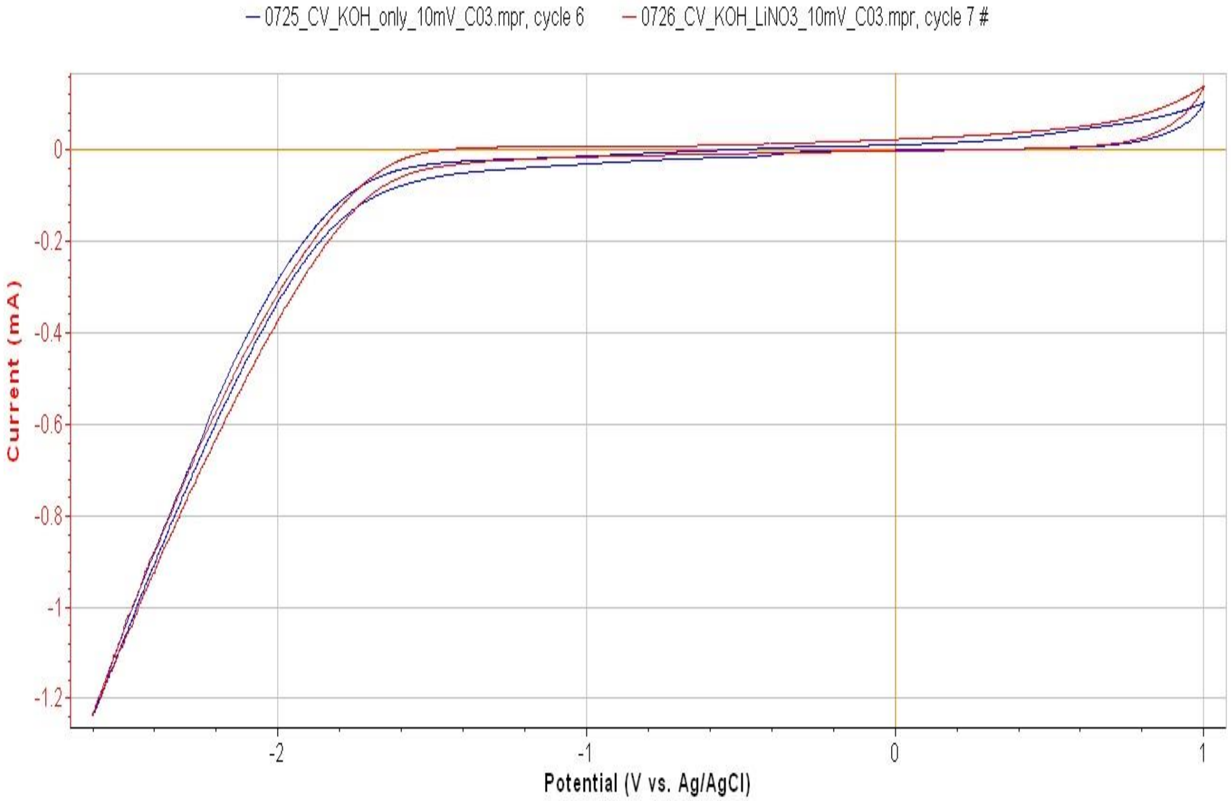
0714_CV_LiOH_only_25mV_C03.mpr, cycle 4
0715_CV_LiOH_LiNO3_25mV_C03.mpr, cycle 4 #
Current (mA)
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
-2
-1
0
1
Potential (V vs. Ag/AgCl)

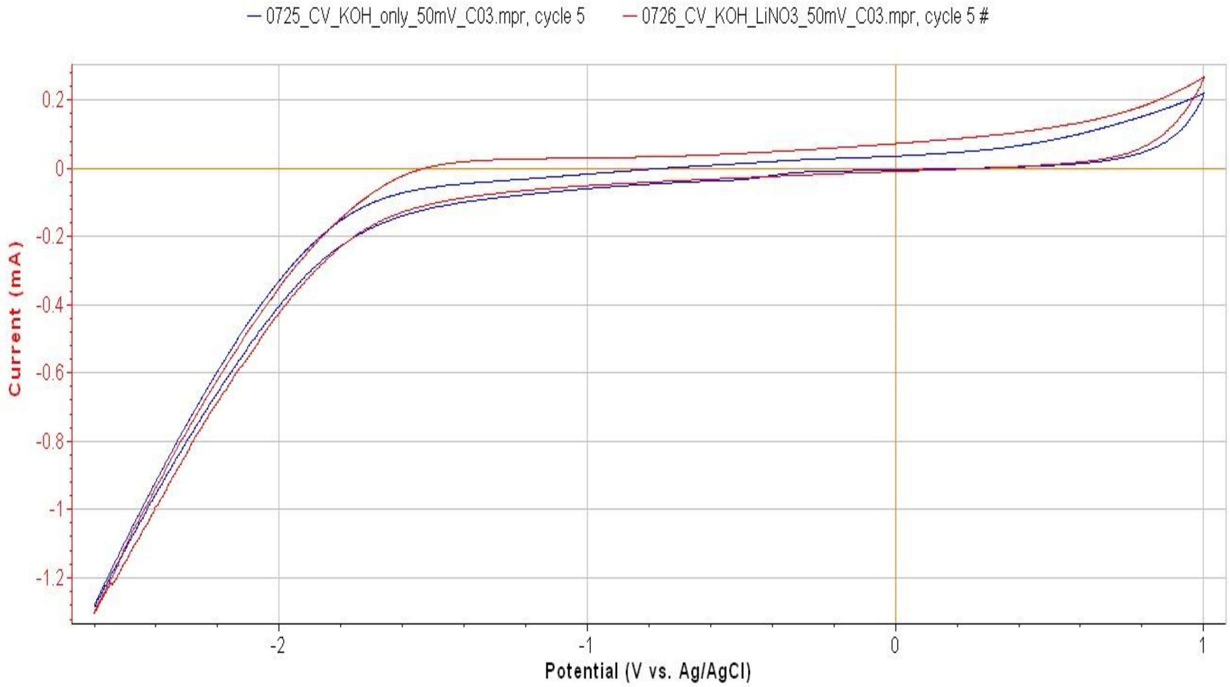


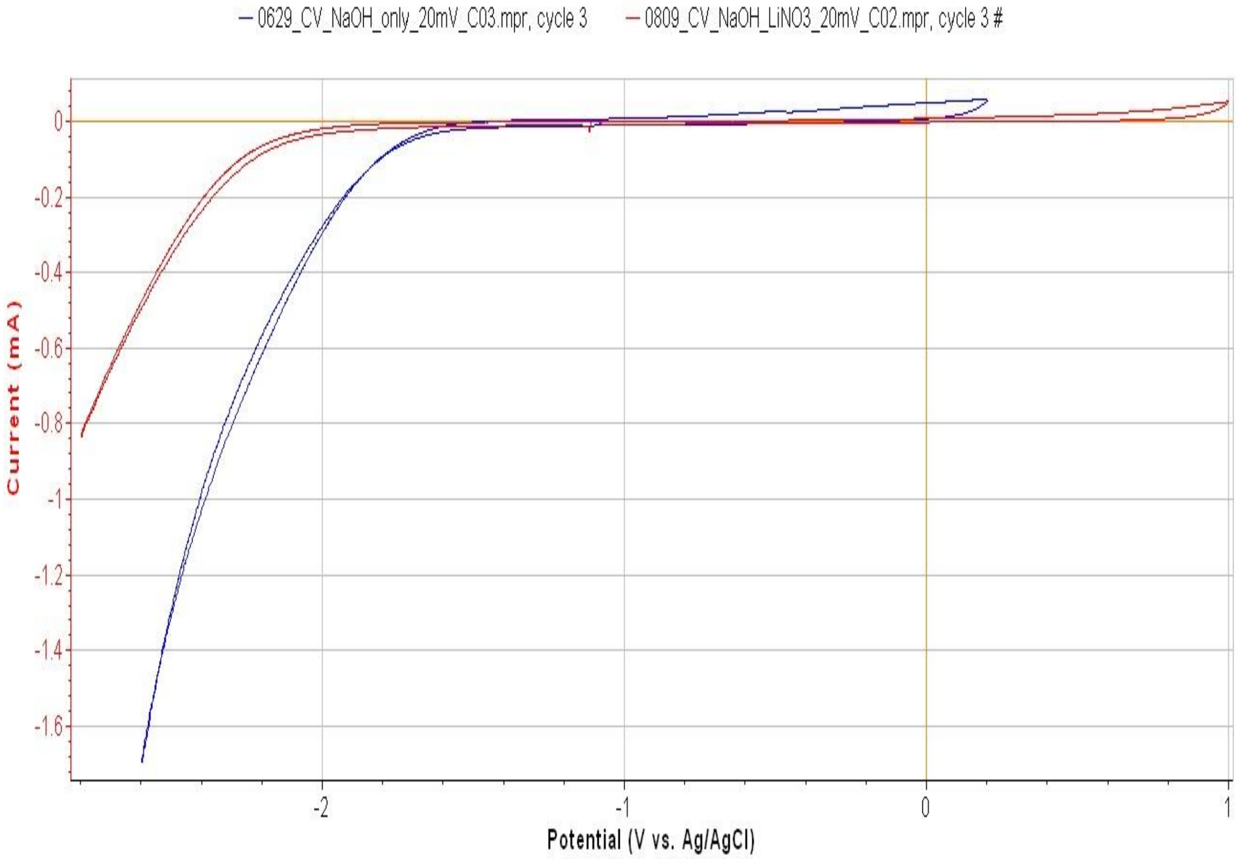
— 0629_CV_NaOH_only_20mV_C03.mpr, cycle 4
— 0719_CV_NaOH_20LiNO3_50mV_C03.mpr, cycle 4 #
Current (mA)
0
-1
-2
-3
-4
-5
-6
-2
-1
0
1
Potential (V vs. Ag/AgCl)



— 0629_CV_NaOH_only_50mV_C03.mpr, cycle 4
— 0719_CV_NaOH_20LiNO3_50mV_C03.mpr, cycle 4 #
Current (mA)
0
-1
-2
-3
-4
-5
-6
-2
-1
0
1
Potential (V vs. Ag/AgCl)


0725_CV_KOH_only_10mV_C03.mpr, cycle 6
0726_CV_KOH_LiNO3_10mV_C03.mpr, cycle 7 #
Current (mA)
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-2
-1
0
1
Potential (V vs. Ag/AgCl)


0725_CV_KOH_only_50mV_C03.mpr, cycle 5
0726_CV_KOH_LiNO3_50mV_C03.mpr, cycle 5 #
Current (mA)
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-2
-1
0
1
Potential (V vs. Ag/AgCl)


0629_CV_NaOH_only_20mV_C03.mpr, cycle 3
0809_CV_NaOH_LiNO3_20mV_C02.mpr, cycle 3 #
Current (mA)
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
-2
-1
0
1
Potential (V vs. Ag/AgCl)

VITA

Shikha Patel was born in Gujarat, India, to the parents of Paresh and Taruna Patel. She attended Sant Kabir school in Ahmedabad, Gujarat, India. Upon graduation from high school in Gujarat, India Shikha immigrated to Chattanooga, TN in 2008 with her family. She moved to Murfreesboro, TN to attend Middle Tennessee University for a Bachelor's of Science degree in chemistry with a minor in psychology. After graduation, she attended University of Tennessee at Chattanooga for a Master's of Science degree in Chemical and Mechanical Engineering. As part of the Volkswagen's distinguished scholar program Shikha worked as a summer intern at the Oakridge national laboratory. There she worked with Dr. Adam Rondinone on electrochemical NO_x reduction using a carbon nanospiked electrode.