

***Final Technical Report***

***for:***

**Electrochemical Oxidation of  
Alkyl Nitro Compounds  
PP-1345**

***A SERDP 'SEED' Activity***

**Initial Submittal: June 30, 2004**

**Amended: August 17, 2004**

***Prepared for:*** Strategic Environmental Research and Development  
Programs Office

***Under Contract:*** DACA72-03-P-0009

***Submitted by:***



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This research is supported wholly by the US Department of Defense, through the Strategic Environmental Research and Development Program (SERDP).

| Report Documentation Page                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                    |                                     | Form Approved<br>OMB No. 0704-0188               |                                  |                                 |
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| 1. REPORT DATE<br><b>17 AUG 2004</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                    | 2. REPORT TYPE<br><b>Final</b>      |                                                  | 3. DATES COVERED<br><b>-</b>     |                                 |
| 4. TITLE AND SUBTITLE<br><b>Electrochemical Oxidation of Alkyl Nitro Compounds</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                    |                                     | 5a. CONTRACT NUMBER<br><b>DACA72-03-P-0009</b>   |                                  |                                 |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                    |                                     | 5b. GRANT NUMBER                                 |                                  |                                 |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                    |                                     | 5c. PROGRAM ELEMENT NUMBER                       |                                  |                                 |
| 6. AUTHOR(S)<br><b>Scott K. Lusk</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                    |                                     | 5d. PROJECT NUMBER<br><b>PP-1345</b>             |                                  |                                 |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                    |                                     | 5e. TASK NUMBER                                  |                                  |                                 |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                    |                                     | 5f. WORK UNIT NUMBER                             |                                  |                                 |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br><b>ATK Thiokol Inc. P.O. Box 707, M/S 230, Brigham City, Utah 84302</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                    |                                     | 8. PERFORMING ORGANIZATION REPORT NUMBER         |                                  |                                 |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)<br><b>Strategic Environmental Research &amp; Development Program 901 N Stuart Street, Suite 303 Arlington, VA 22203</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                    |                                     | 10. SPONSOR/MONITOR'S ACRONYM(S)<br><b>SERDP</b> |                                  |                                 |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                    |                                     | 11. SPONSOR/MONITOR'S REPORT NUMBER(S)           |                                  |                                 |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT<br><b>Approved for public release, distribution unlimited</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                    |                                     |                                                  |                                  |                                 |
| 13. SUPPLEMENTARY NOTES<br><b>The original document contains color images.</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                    |                                     |                                                  |                                  |                                 |
| 14. ABSTRACT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                    |                                     |                                                  |                                  |                                 |
| 15. SUBJECT TERMS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                    |                                     |                                                  |                                  |                                 |
| 16. SECURITY CLASSIFICATION OF:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                    |                                     | 17. LIMITATION OF ABSTRACT<br><b>UU</b>          | 18. NUMBER OF PAGES<br><b>30</b> | 19a. NAME OF RESPONSIBLE PERSON |
| a. REPORT<br><b>unclassified</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | b. ABSTRACT<br><b>unclassified</b> | c. THIS PAGE<br><b>unclassified</b> |                                                  |                                  |                                 |

## **Electrochemical Synthesis of Alkyl Nitro Compounds**

### **Final Technical Report**

#### **EXECUTIVE SUMMARY**

Current chemical oxidative methods for the production of dinitroalkanes such as 2,2-dinitropropane (the precursor to the taggant 2,3-dimethyl-2,3-dinitrobutane (DMDNB)) and 2,2-dinitropropanol (DNPOH, the precursor to the energetic plasticizer BDNPA/F) yield as byproducts large amounts of chemical process waste in the form of corrosive inorganic salts. Similarly inefficient and polluting processes are now used in the oxidation of many other chemicals important to Defense programs. Particular to this contract, the conversion of trinitrotoluene (TNT) to hexanitrostilbene (HNS), phloroglucinol to trinitrophloroglucinol (a precursor material to the fuze system explosive triaminotrinitrobenzene (TATB)), and 1-*t*-butyl-3-hydroxymethyl-3-nitroazetidine (HMNAz) to 1,3,3-trinitroazetidine (TNAZ, a next generation explosive ingredient were also considered). The large excess of necessary oxidizing reagents in these chemistries and the significantly large resulting waste streams requiring treatment and disposal after the manufacturing chemistry is completed for these commodities add a great deal of cost to these processes.

In contrast, the use of modern electrochemical oxidation methodologies to conduct the same chemical synthesis could eliminate or significantly reduce the need for strong chemical oxidizing agents in manufacture of the above fielded materials and many others, and thus avoid their byproducts and large waste streams. This proven electrochemical oxidation technology, employed today in application to manufacture of non-energetic materials, synthesis applications, could potentially produce the desired energetic ingredients more efficiently and in an environmentally responsible fashion.

To this end, cursory studies conducted within this 'SEED' activity have been made. These studies indicate that the electrochemical oxidation methodology to manufacture targeted energetic materials is feasible, though not in all applications, and could provide a substantial savings to the cost of producing several energetic materials. In the studies conducted it was shown that some materials, phloroglucinol in particular, do not respond to electrochemical stimulus and will not lend itself to processing in this manner. Other chemical processes studied showed varying degrees of response to electrochemical oxidation and thus could be processed in this manner. Of particular note, DNPOH was shown after cursory experimentation to be manufactured at 40% molar yield through electrochemical methods.

By way of evaluation of the advantages of electrochemical synthesis, the economics and the environmental discharge of the chemical and the electrochemical synthetic routes to DNPOH were compared. This material was manufactured by ATK Thiokol in 1998 at production scale and good manufacturing cost and waste history data are available. Approximately 100,000 pounds of this material was manufactured in the production effort but the traditional manufacturing methods resulted in generation of over 1.6 million pounds of waste stream products (see the table below). The reaction is necessarily dilute. A large amount of water is dictated by the amount required to keep the byproduct,

sodium sulfate in solution. Premature precipitation of that salt causes the process tubes to clog with solids.

**Composition of the DNPOH Waste Stream for the Production Run of 1998**

| Reagent                    | Thousands of Pounds Produced |
|----------------------------|------------------------------|
| Trisodium Phosphate        | 34                           |
| Water                      | 836                          |
| Sodium Hydroxide           | 69                           |
| Sodium Nitrite             | 303                          |
| Potassium Ferricyanide     | 72                           |
| Sodium Persulfate          | 263                          |
| Formaldehyde               | 17                           |
| Phosphoric Acid            | 32                           |
| Ethyl Acetate              | 23                           |
| <b>Total Aqueous Waste</b> | <b>1,649</b>                 |

If the oxidative nitration were carried out electrochemically, the potassium ferricyanide and sodium persulfate reagents would be completely eliminated. The water content could be significantly reduced since the sodium sulfate would no longer drive the reaction concentration. The sodium nitrite could also be reduced from the current 10 equivalents to near 4. Finally, large amounts of ethyl acetate remain dissolved in the wastewater from the extraction of the DNPOH. Reduction of the water would also proportionately diminish the ethyl acetate lost into the waste stream. In summary the waste stream would be reduced from roughly 25 pounds per pound of DNPOH to near 16 pounds per pound.

The material and waste costs associated with producing DNPOH would be reduced from \$9.18 per pound (traditional synthesis methods) to an estimated \$4.59 per pound of DNPOH produced by using the electrochemical synthesis route (a 50% reduction), assuming the current electrochemical yield of the reaction achieved in this report (unoptimized) is improved from 40% to 70% in an optimization study. Overall, even if the yield was not improved over this 'first try' level, the electrochemical route is still found to be a more environmentally friendly route than the current traditional chemical synthesis route.

The next logical step to develop this technology would be to fund and conduct a developmental effort to optimize an electrochemical synthesis route to one or more target chemicals (from those listed above), to determine scalability to pound-per-hour levels, and refine/re-evaluate the economic feasibility and manufacturing scale potential. Scale up and implementation of this technology will result in the introduction of significantly more environmentally friendly manufacturing processes for energetic materials synthesis than is currently employed in production today.

## **PERFORMING ORGANIZATION**

ATK Thiokol Inc. located in Brigham City, Utah has directed this activity. The basic research activity was performed under subcontract by the Department of Chemistry at the University of Utah located in Salt Lake City, Utah.

## **BACKGROUND**

Energetic materials such as bis-dinitropropyl acetal-formal (BDNPA/F), 2,2',4,4',6,6'-hexanitrostilbene (HNS), 2,3-dimethyl-2,3-dinitrobutane (DMDNB), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), and 1,3,3-trinitroazetidine (TNAZ) are of strategic interest to the Department of Defense (DoD). These compounds all share energetic structural elements consisting of nitro groups bound to carbon atoms, and the production of such materials is generally accomplished with numerous powerful chemical oxidizers. Use of these reagents generate pernicious waste streams, and these chemical oxidizers are themselves environmentally costly to produce. Many of these materials are used in current DoD systems. Therefore, it was felt to be beneficial if more environmentally benign production methods for these materials were developed.

## **OBJECTIVE**

The objective of this 'SEED' program was the development and preliminary evaluation of general technology for the synthesis of *gem* and *vic*-dinitroalkanes using clean electrochemical oxidation methodology. Successful application of this approach could eliminate the use of strong chemical oxidizing agents and thus their byproducts, providing a more environmentally sound approach to manufacture of these strategic materials.

## **TECHNICAL APPROACH**

This SEED program conducted cursory experiments of the five different chemistries identified above for effective application of the electrochemical oxidation approach. To this end the oxidation of trinitrotoluene (TNT), 1-*t*-butyl-3-hydroxymethyl-3-nitroazetidine (HMNAz), phloroglucinol, and nitroethane were carried out under electrochemical conditions to manufacture the target compounds. These oxidations were evaluated for their efficacy and ability to be scaled to industrially useful quantities. Cursory economic feasibility of the approach at a production scale was estimated and recommendations made for further pursuit.

## **SUMMARY**

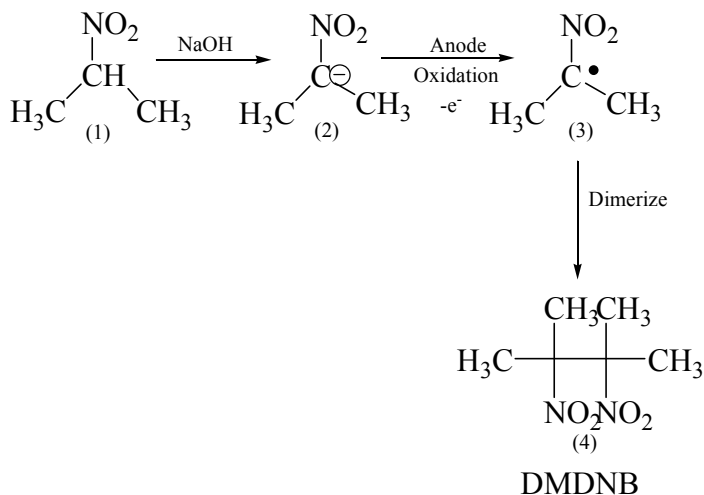
The voltammetric investigations and electrochemical synthesis of the targeted chemistries are reported. Several of these applications appear to be very promising to pursue. An electrochemical oxidation cell has been established and it has met the near-term objective to perform bulk electrolysis experiments to isolate quantities of some of these materials for chemical identification. Application of this chemistry method to manufacture of these materials appears feasible, pending further development.

The economics and the environmental discharge of the chemical synthesis and the electrochemical synthesis routes to 2,2-dinitropropanol (DNPOH) were compared as the test case. The material and waste costs associated with producing DNPOH would be reduced from \$9.18 to \$4.59 (50%) per pound of DNPOH by using the electrochemical

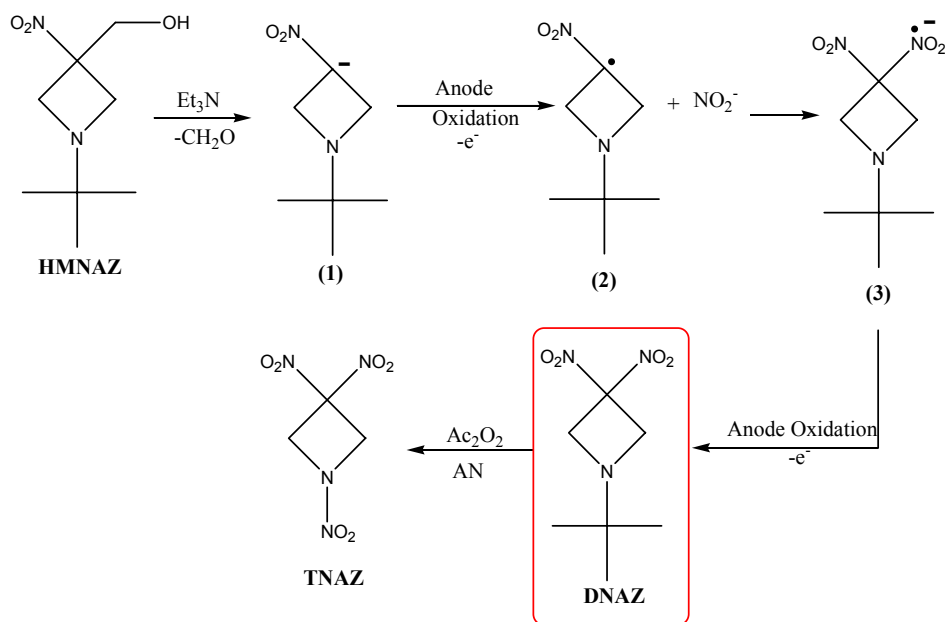
synthesis route if the yield of the reaction is improved from 40% to 70%. Overall, if the yield is not improved, the electrochemical route is still a more environmentally friendly route than the ATK Thiokol chemical synthesis route.

### ACCOMPLISHMENTS

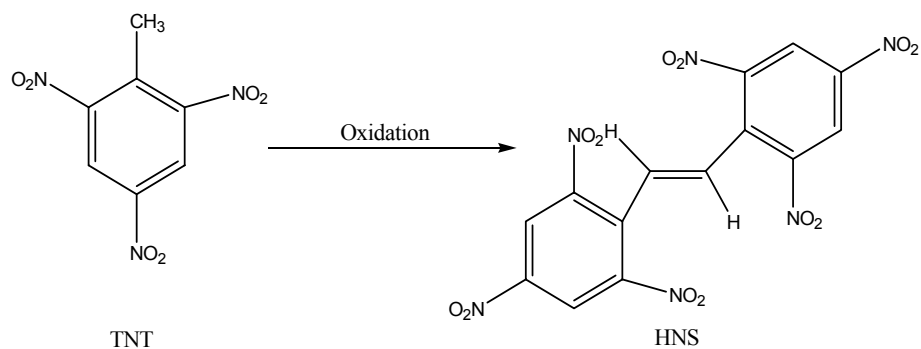
The electrosynthesis of the target materials is shown in Schemes 1-4:



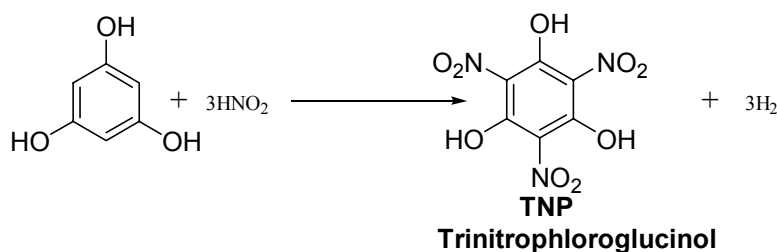
**Scheme 1. Electrosynthesis of 2- Nitropropane to DMDNB**



**Scheme 2. Electrochemical Oxidation of HMNAz**



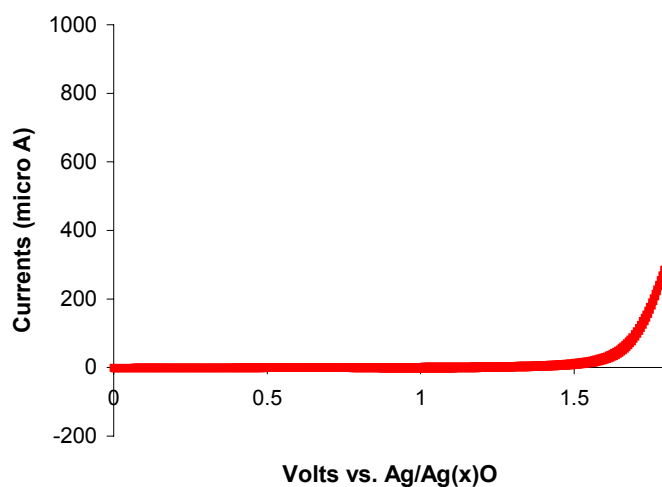
**Scheme 3: Electrochemical Oxidation of TNT**



**Scheme 4: Electrochemical Oxidative nitration of Phloroglucinol**

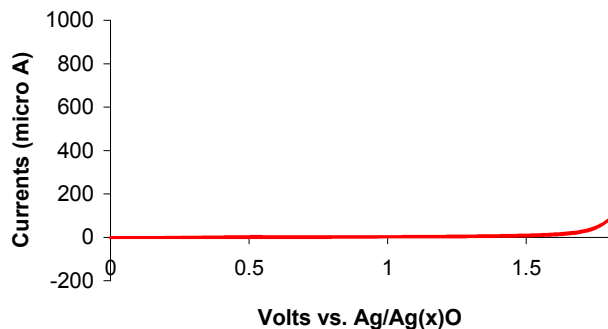
#### Oxidation of 2-Nitropropane

Evaluation of background ‘noise’ influence or interference in the process is first evaluated. The background voltammogram of the GC electrode in methanol containing only 0.2 M LiClO<sub>4</sub> is shown in Figure 1. The background curve is featureless on this current scale, indicating no significant interfering reactions are occurring up to potentials of ~1.6 V. The increase in current at 1.6 V is probably due to water oxidation, a kinetically slow process at GC electrodes.



**Figure 1. Voltammogram of Glassy Carbon (GC) Electrode in CH<sub>3</sub>OH/0.2M LiClO<sub>4</sub>**

Addition of 100 mM 2-nitropropane to the CH<sub>3</sub>OH/0.2M LiClO<sub>4</sub> (Figure 2) results in very little change to the voltammetric response, indicating that the protonated form of 2-nitropropane is electrochemically inactive.

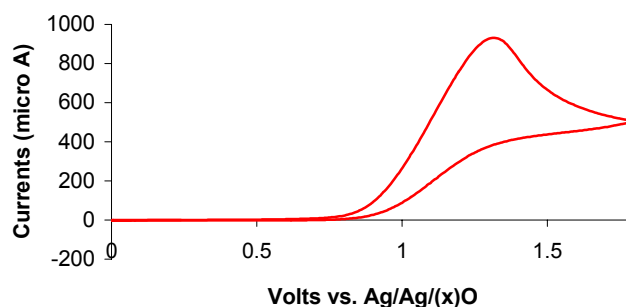


**Figure 2. Voltammogram of Glassy Carbon (GC) Electrode in CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>/0.1 M 2-nitropropane**

The above experiments were repeated after the addition of 0.1 M NaOH to the solution, with the intent of deprotonating the carbon atom directly adjacent to the NO<sub>2</sub> group (scheme 1). Figure 3 shows the voltammetric response recorded in a CH<sub>3</sub>OH/0.2M LiClO<sub>4</sub> solution containing 0.1 M NaOH. A large wave with peak potential at ca. 1.35 V is observed corresponding to the oxidation of OH<sup>-</sup> directly at the GC electrode (equation 1).

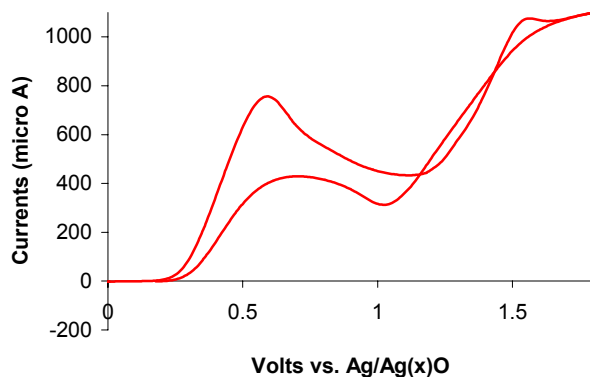


The standard redox potential for this reaction is 0.401 V, consistent with onset of current at 0.7 V (a slow electron-transfer kinetics introduces a significant overpotential for this reaction).



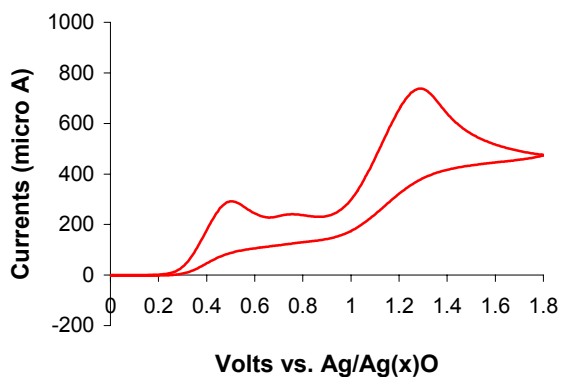
**Figure 3. Voltammogram of Glassy Carbon (GC) Electrode in CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>/0.1 M NaOH**

Addition of 0.1 M 2-nitropropane to the basic solution ( $\text{CH}_3\text{OH}/0.2\text{M LiClO}_4/0.1\text{ M NaOH}$ ) results in the appearance of a new oxidation wave, beginning at 0.2 V, and shown in Figure 4. We assign this wave to the oxidation of deprotonated 2-nitropropane (scheme (1)) which is consistent with what we would expect.

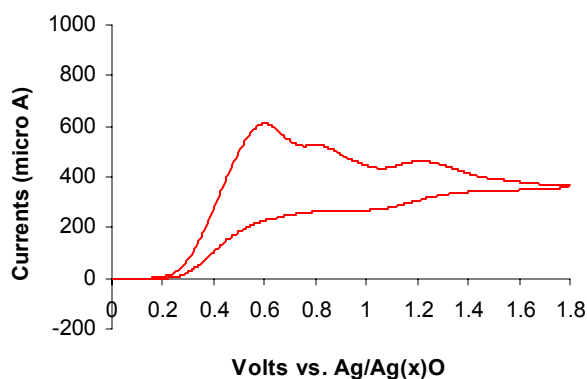


**Figure 4. Voltammogram of Glassy Carbon (GC) Electrode in  $\text{CH}_3\text{OH}/0.2\text{ M LiClO}_4/0.1\text{ M NaOH}/0.1\text{ M 2-nitropropane}$**

Figures 5 and 6 show voltammograms for 0.01 and 0.05 M 2-nitropropane solutions (each containing 0.1 M NaOH).



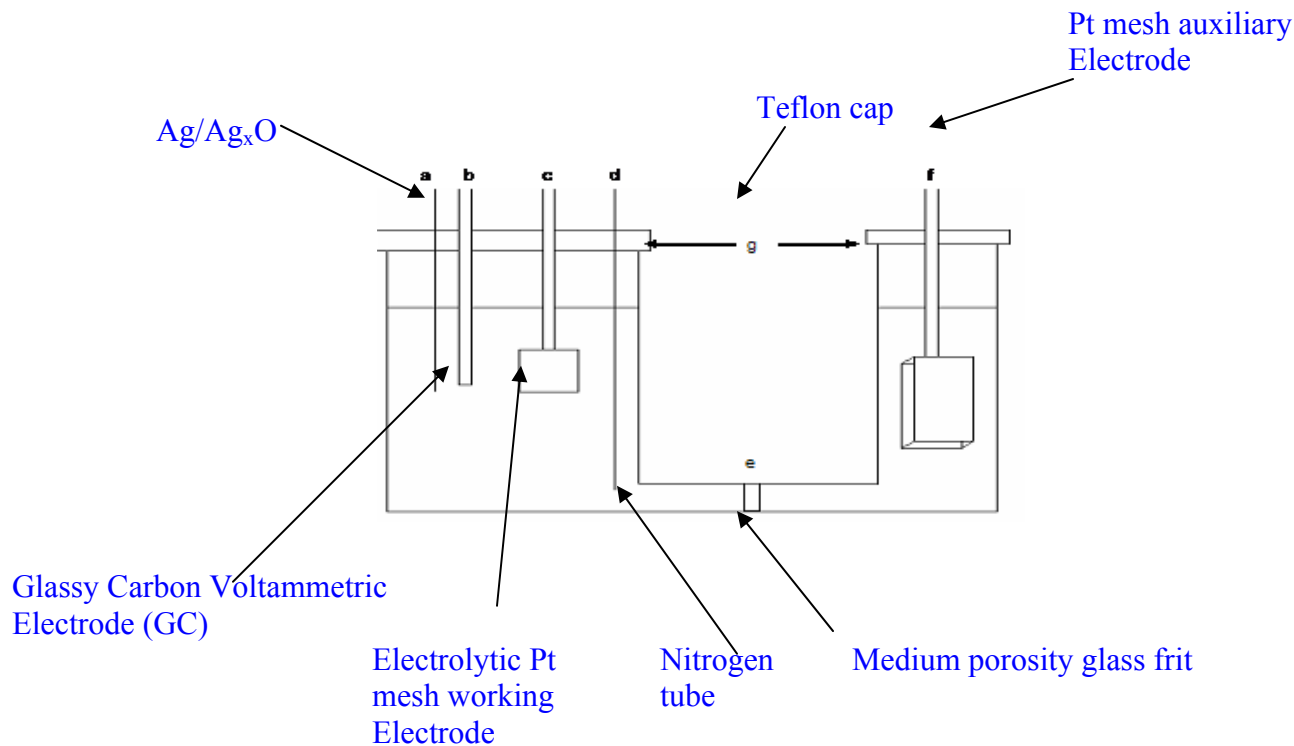
**Figure 5. Voltammogram of Glassy Carbon (GC) Electrode in  $\text{CH}_3\text{OH}/0.2\text{ M LiClO}_4/0.1\text{ M NaOH} /0.01\text{ M 2-nitropropane}$**



**Figure 6. Voltammogram of Glassy Carbon (GC) Electrode in  $\text{CH}_3\text{OH}/0.2 \text{ M LiClO}_4/0.1 \text{ M NaOH} / 0.05 \text{ M 2-nitropropane}$**

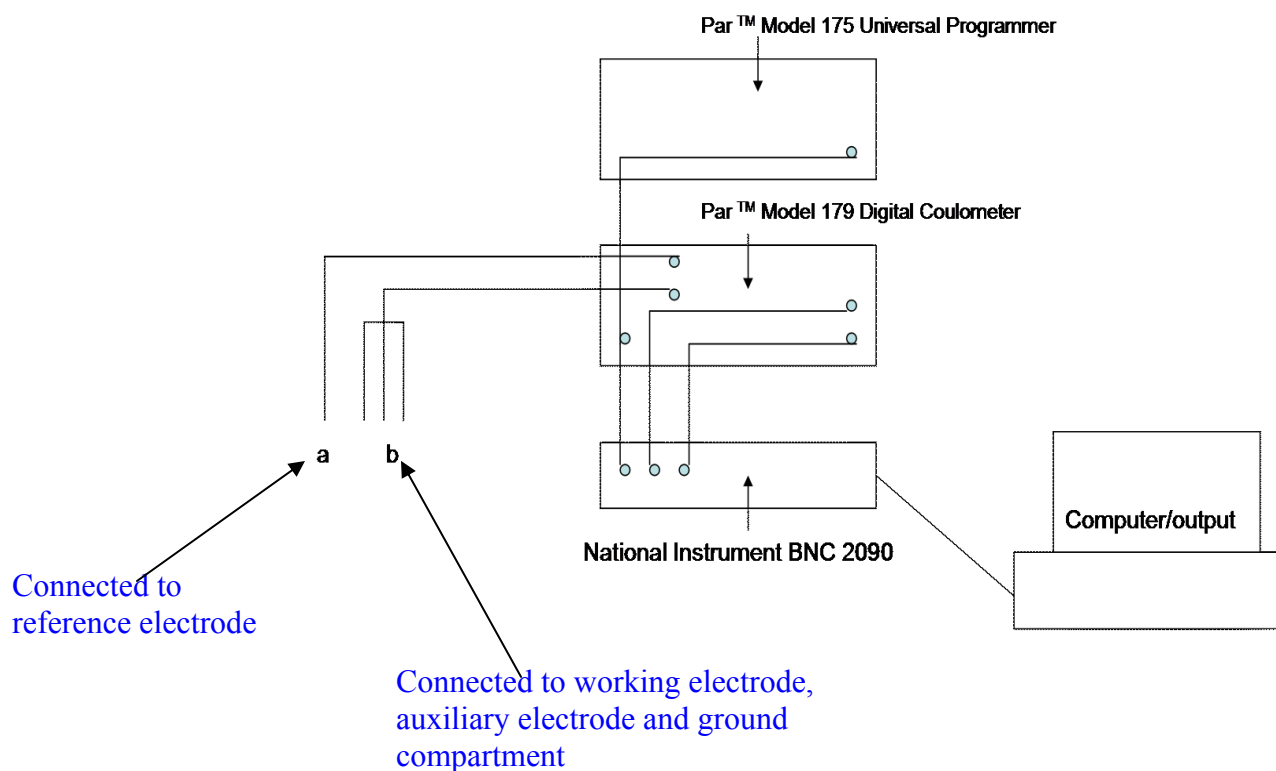
### Electrochemical Synthesis of DMDNB

A laboratory scale electrochemical cell has been established for evaluation of the identified chemistries. The electrochemical cell configuration, shown in Figure 7, has two compartments which are separated by a medium porosity glass frit. The large compartment (the working electrode compartment) and the smaller compartment (the auxiliary electrode compartment) have a volume capacity of 35 and 22 mL respectively.



**Figure 7. Electrochemical Solution Cell**

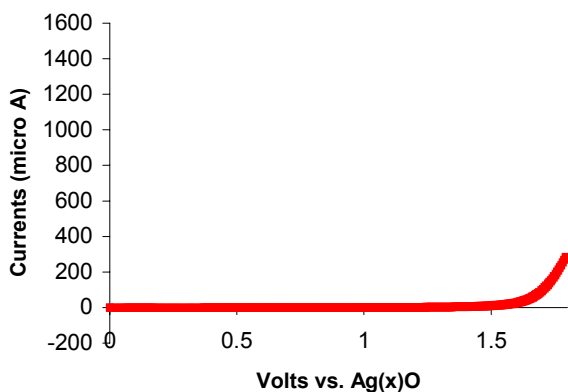
The working electrode and auxiliary electrode have the dimensions of 1 cm x 2.5 cm and 5 cm x 5 cm respectively. The instrumental configuration is shown in Figure 8. The working electrode and auxiliary compartments were filled with a solution of 1 M LiClO<sub>4</sub> (5.3200 g), 100 mM 2-nitropropane (44.90  $\mu$ L), and 100 mM NaOH (0.2200 g) in methanol, 28 mL and 15 mL respectively. Over the course of the electrolysis, the current was recorded and the potential was held at 1.0 Volt vs. Ag/Ag<sub>x</sub>O to completely oxidized 2-nitropropane. The yield of the reaction was 32%.



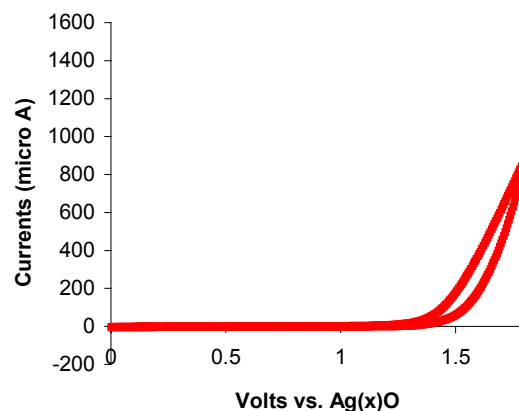
**Figure 8. Electrolytic and Voltammogram Instrumentation**

### Electrochemical Oxidation of HMNAZ

The background voltammogram of the GC electrode in methanol containing only 0.2 M LiClO<sub>4</sub> is shown in Figure 9. The background curve is featureless on this current scale, indicating no significant interfering reactions are occurring up to potentials of ~1.6V. The increase in current at 1.6 V is probably due to H<sub>2</sub>O oxidation, a kinetically slow process at GC electrodes. Addition of 100 mM HMNAz to the CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub> resulted in very little change to the voltammetric response as shown in Figure 10, indicating that HMNAz is electrochemically inactive.

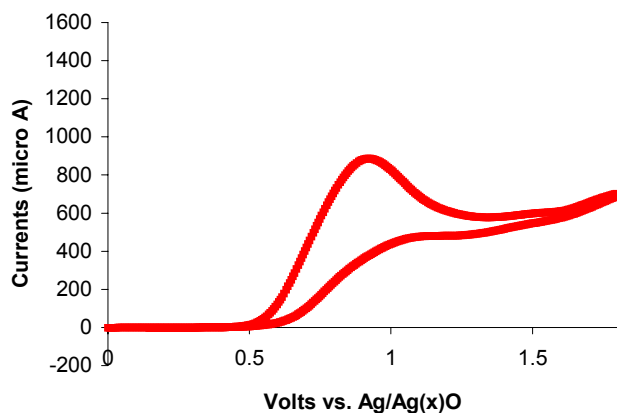


**Figure 9. Voltammogram of Glassy Carbon (GC) Electrode in CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>**

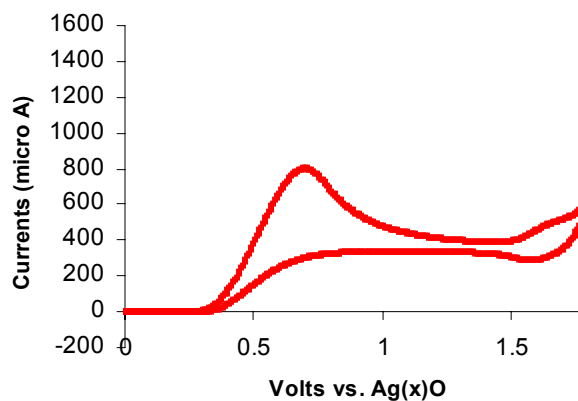


**Figure 10. Voltammogram of Glassy Carbon (GC) Electrode in CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>/100mM HMNAz**

The addition of 110 mM triethylamine (TEA) to the CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>, to deprotonate the hydroxyl group resulted in a large wave shown in Figure 11. A peak potential at ca. 0.90 V was observed, which corresponded to the oxidation of TEA at the GC electrodes (equation 2).



**Figure 11. Voltammogram of Glassy Carbon (GC) Electrode in CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>/110mM TEA**

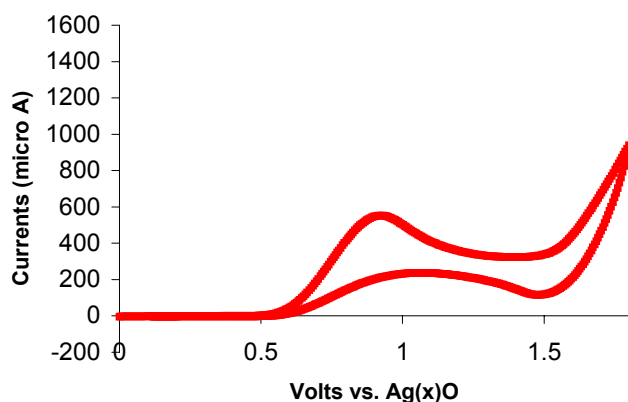


**Figure 12. Voltammogram of Glassy Carbon (GC) Electrode in CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>/110mM NaNO<sub>2</sub>**

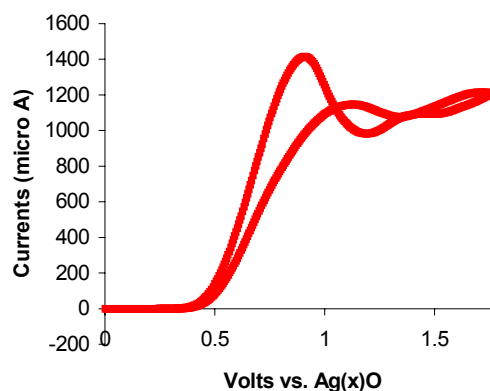
The same experiments were repeated after the addition of 110 mM NaNO<sub>2</sub> to the CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>. Figure 12 shows the voltammetric response recorded in a CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub> solution containing 110 mM NaNO<sub>2</sub>. A peak potential at ca. 0.70 V was observed, which corresponded to the oxidation of NO<sub>2</sub><sup>-</sup> at the GC electrode.



The addition of 110 mM TEA and 110 mM NaNO<sub>2</sub> to the CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub> resulted in a large wave shown in Figure 13. A peak potential at ca. 0.90 V was observed corresponded to the oxidation of both TEA and NO<sub>2</sub><sup>-</sup> at the GC electrode. The addition of 100 mM HMNAz and 110 mM NaNO<sub>2</sub> to the CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub> resulted in a large wave shown in Figure 14. A peak potential at ca. 0.90 V was observed, corresponded to the oxidation of NO<sub>2</sub><sup>-</sup> at the GC electrode.

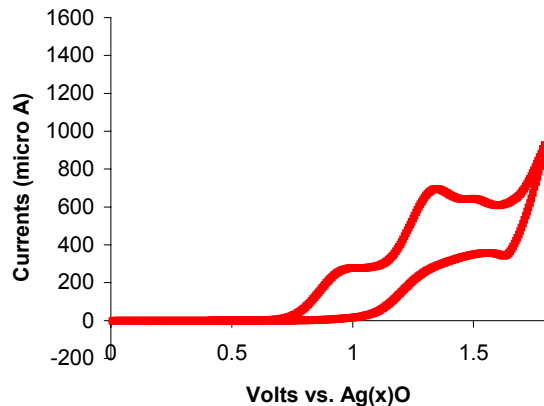


**Figure 13. Voltammogram of Glassy Carbon (GC) Electrode in CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>/110mM TEA/110mM NaNO<sub>2</sub>**

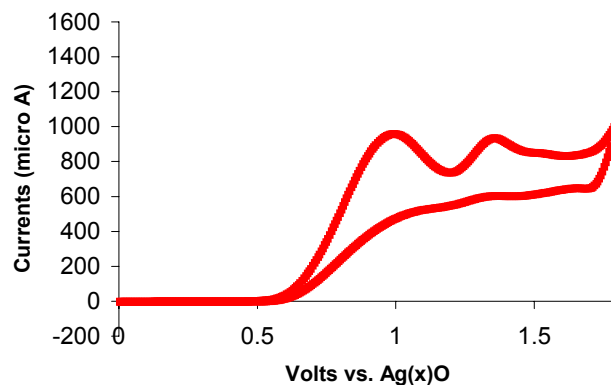


**Figure 14. Voltammogram of Glassy Carbon (GC) Electrode in CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>/100mM HMNAz/110mM NaNO<sub>2</sub>**

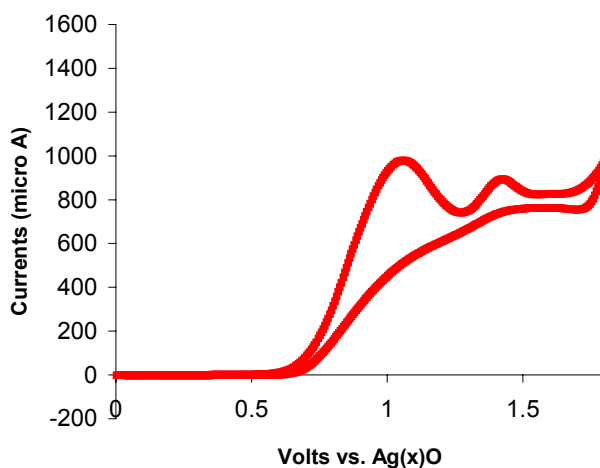
The addition of 110 mM TEA and 100 mM HMNAz to the CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>, resulted in a large wave shown in Figure 15. Two large peak potentials at ca. 0.90 V and 1.30 V were observed, corresponded to the oxidation of excess TEA and probably the oxidation of deprotonated HMNAz at the GC electrode. Addition of 0.1 M HMNAz to the CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>/ 110 mM TEA and 110 mM NaNO<sub>2</sub> resulted in the appearance of two oxidation waves which had the same potential peaks as the addition of 110 mM TEA and 100 mM HMNAz to the CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub> solution. However, the height of the first wave at 0.90 V was different. This may be due to the excess of NaNO<sub>2</sub>. We assigned the second wave to the oxidation of deprotonated HMNAz. In addition, when TEA was replaced with NaOH, the volammetric response shown in Figure 16 was the same as Figure 17.



**Figure 15. Voltammogram of Glassy Carbon (GC) Electrode in CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>/100mM HMNAz/110mM TEA**

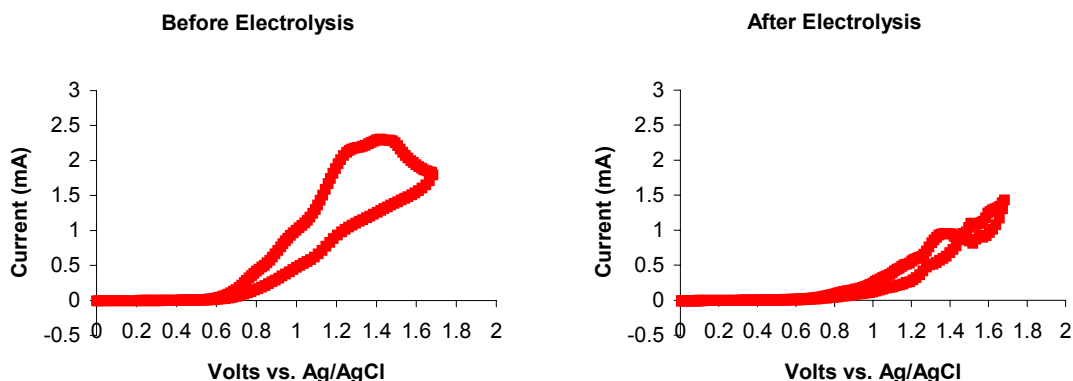


**Figure 16. Voltammogram of Glassy Carbon (GC) Electrode in CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>/100mM HMNAz/110mM TEA/110 mM NaNO<sub>2</sub>**



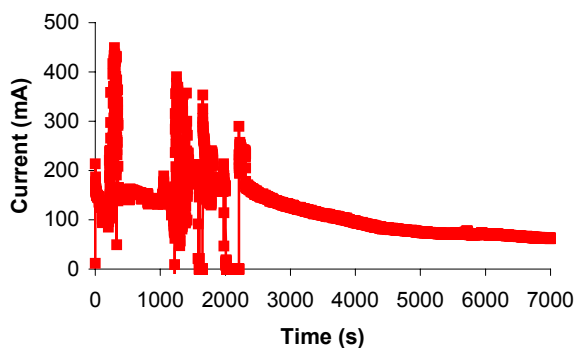
**Figure 17. Voltammogram of Glassy Carbon (GC) Electrode in CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>/100mM HMNAz/110mM NaOH/110 mM NaNO<sub>2</sub>**

In another experiment, three waves were observed during the electrolysis of HMNAZ at 0.9 V, 1.30 V and 1.45 V (Figure 18). These waves were attributed to the oxidation of  $\text{NO}_2^-$ ;  $\text{OH}^-$  and deprotonated HMNAZ respectively.



**Figure 18. Voltammograms at the Glassy Carbon (GC) Electrode before and after Electrolysis of HMNAZ solution**

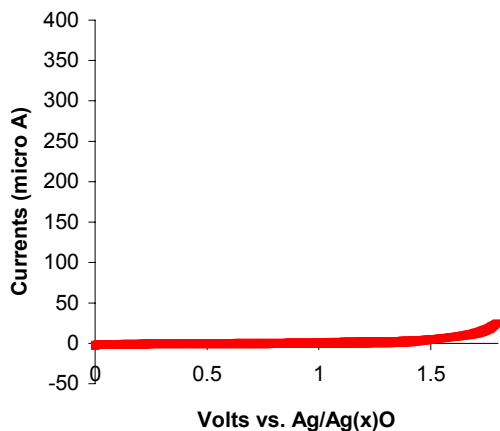
Over the course of the electrolysis reaction, the color of the solution changed from pale yellow to darker yellow with a total charge of 812 Coulombs. The electrolysis was stopped when there was no change in the current (Figure 19). Figure 19 shows that the current displayed significant noise during electrolysis. This was due to a change in the stirring rate. The magnetic stir bar was bumping the working electrode, which affected the nitrogen flow. Unexpectedly, the current reached a steady state value of 65 milliamps (mA) instead of zero (Figure 19). DNAZ was isolated from the reaction mixture in 48% yield and was characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.



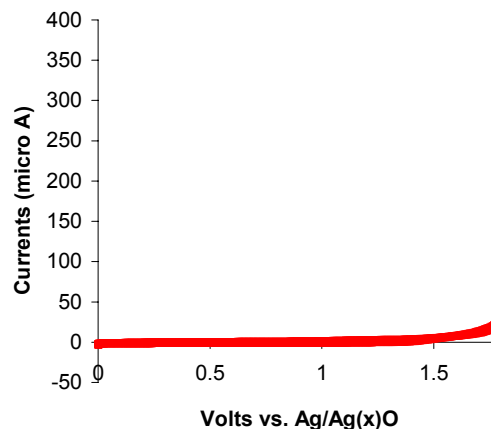
**Figure 19. Electrolysis Reaction of HMNAZ Solution**

### Electrochemical Oxidation of TNT

The background voltammogram of the GC electrode in methanol containing only 0.2 M  $\text{Bu}_4\text{NBF}_4$  was shown in Figure 20. The background curve was featureless on this current scale, indicating no significant interfering reactions were occurring up to potentials of  $\sim 1.5$  V. The increase in current at 1.5 V was probably due to  $\text{H}_2\text{O}$  oxidation, a kinetically slow process at the GC electrodes. Addition of 50 mM TNT to the  $\text{CH}_3\text{OH}/0.2$  M  $\text{Bu}_4\text{NBF}_4$  resulted in very little change to the voltammetric response, indicating that TNT was electrochemically inactive, Figure 21.

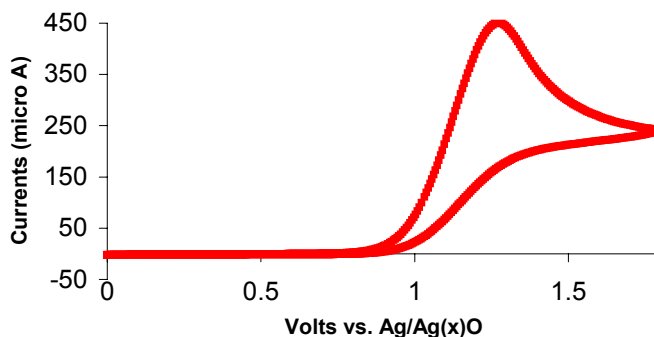


**Figure 20. Voltammogram of Glassy Carbon (GC) Electrode  $\text{CH}_3\text{OH}/0.2$  M  $\text{Bu}_4\text{NBF}_4$**



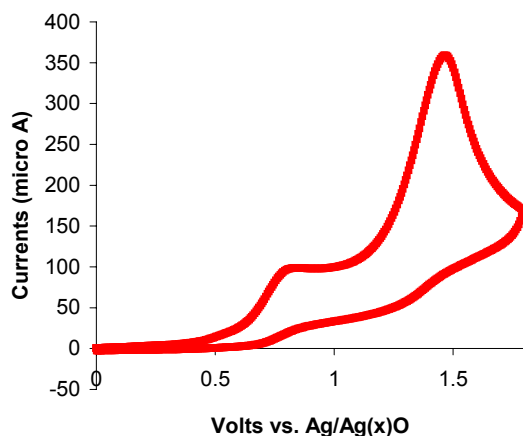
**Figure 21. Voltammogram of Glassy Carbon (GC) Electrode 50 mM TNT/ $\text{CH}_3\text{OH}/0.2$  M  $\text{Bu}_4\text{NBF}_4$**

The above experiments were repeated after the addition of 55 mM NaOH to the solution, to deprotonate the methyl group. Figure 22 shows the voltammetric response recorded in a  $\text{CH}_3\text{OH}/0.2$  M  $\text{Bu}_4\text{NBF}_4$  solution containing 55 mM NaOH. A peak potential at ca. 1.35 V was observed, corresponded to the oxidation of  $\text{OH}^-$  at the GC electrode (equation 1).



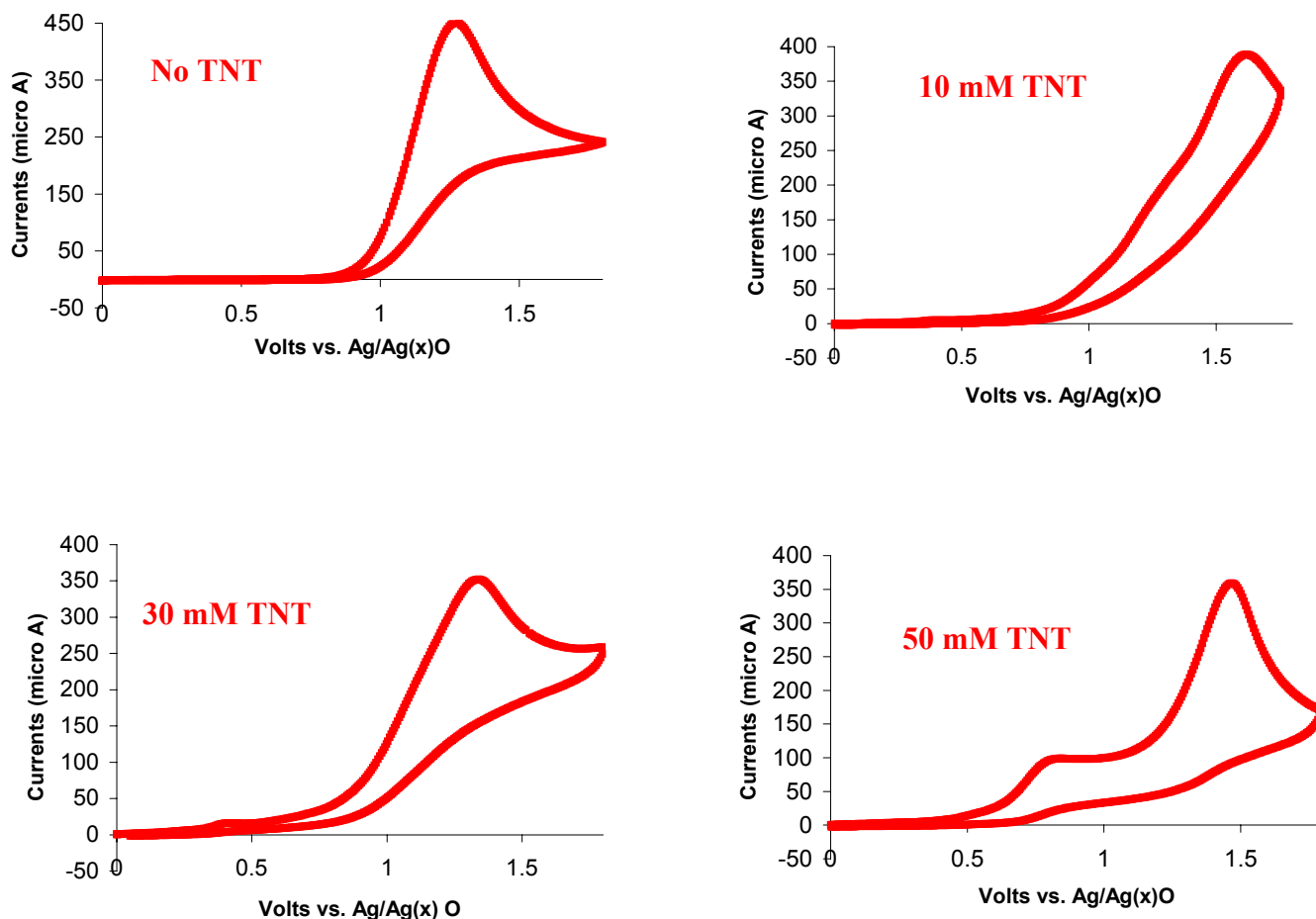
**Figure 22. Voltammogram of Glassy Carbon (GC) Electrode 50 mM TNT/ $\text{CH}_3\text{OH}/0.2$  M  $\text{Bu}_4\text{NBF}_4/55$  mM NaOH**

The standard redox potential for this reaction was 0.401 V, which is consistent with an onset current at 0.7 V (note: slow electron-transfer kinetics introduces a significant over potential for this reaction). Addition of 100 mM TNT to the basic solution ( $\text{CH}_3\text{OH}/0.2 \text{ M Bu}_4\text{NBF}_4/55 \text{ mM NaOH}$ ) resulted in the appearance of a new oxidation wave with a peak potential at ca. 0.80 V as shown in Figure 23. We assigned this wave to the oxidation of the deprotonated TNT.



**Figure 23. Voltammogram of Glassy Carbon (GC) Electrode 100 mM TNT/  $\text{CH}_3\text{OH}/0.2 \text{ M Bu}_4\text{NBF}_4/55 \text{ mM NaOH}$**

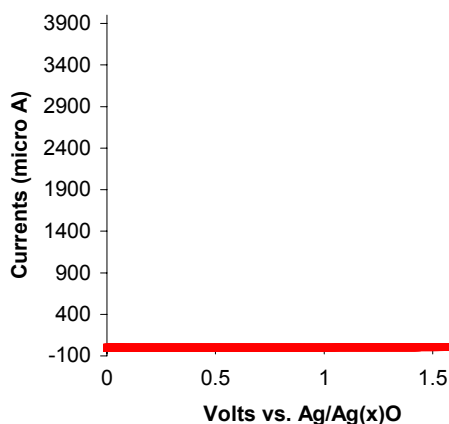
The dependence of the voltammetric response on the concentration of TNT was investigated to provide further evidence for this reaction assignment. Figure 24, the voltammograms for 0, 10, 30 and 50 mM solutions (each containing 0.1 M NaOH). Figure 24 demonstrated that the peak potential at ca. 0.80 V increased with increasing TNT concentration, suggesting that this wave was due to the oxidation of deprotonated TNT.



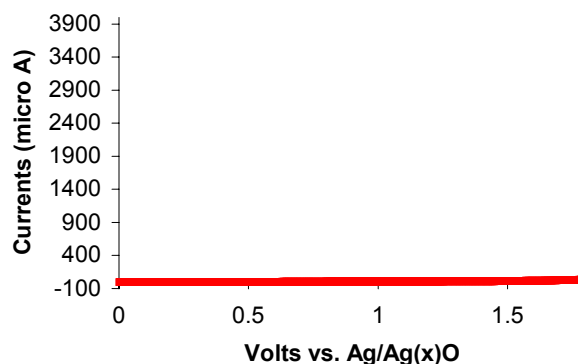
**Figure 24. Dependence of Voltammetric Response on the Concentration of TNT**

#### **Electrochemical Oxidation of Phloroglucinol**

The background voltammogram of the GC electrode in methanol containing only 0.2 M LiClO<sub>4</sub> is shown in Figure 25. The background curve was featureless on this current scale, indicating there were no significant reactions occurring up to potentials of ~1.6 V. The increase in current at 1.6 V was probably due to H<sub>2</sub>O oxidation, a kinetically slow process at the GC electrodes. Addition of 100 mM phloroglucinol to the CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub> resulted in very little change to the voltammetric response as shown in Figure 26, indicating that phloroglucinol was electrochemically inactive.

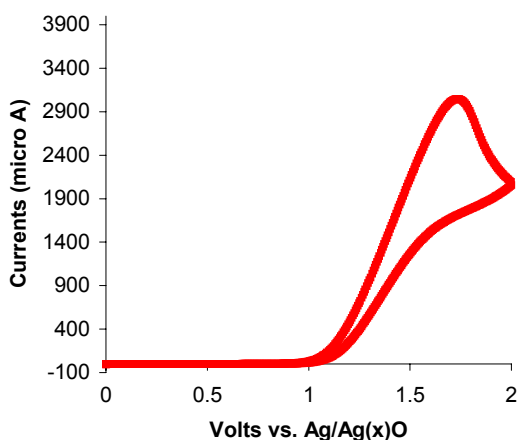


**Figure 25. Voltammogram of Glassy Carbon (GC) Electrode  $\text{CH}_3\text{OH}/0.2 \text{ M LiClO}_4$**

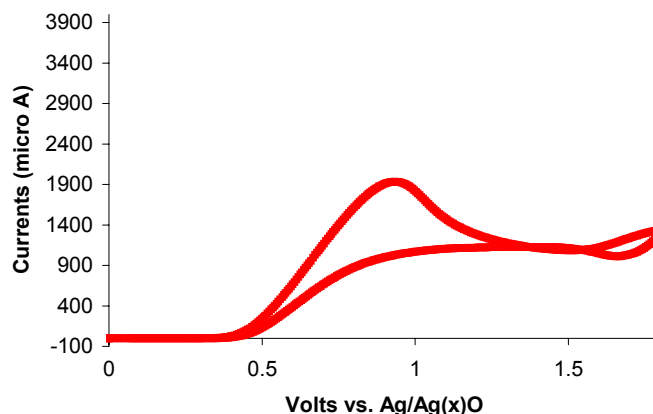


**Figure 26. Voltammogram of Glassy Carbon (GC) Electrode 100 mM Phloroglucinol/ $\text{CH}_3\text{OH}/0.2 \text{ M LiClO}_4$**

The addition of 330 mM NaOH to  $\text{CH}_3\text{OH}/0.2 \text{ M LiClO}_4$ , which resulted in a large wave as shown in Figure 27. A large wave with peak potential at ca. 1.80 V was observed, corresponded to the oxidation of  $\text{OH}^-$  directly at the GC electrode (equation 3). The same experiments were repeated after the addition of 330 mM  $\text{NaNO}_2$  to the  $\text{CH}_3\text{OH}/0.2 \text{ M LiClO}_4$ . Figure 28 shows the voltammetric response recorded in a  $\text{CH}_3\text{OH}/0.2 \text{ M LiClO}_4$  solution containing 330 mM  $\text{NaNO}_2$ . A large wave with peak potential at ca. 0.90 V was observed, corresponding to the oxidation of  $\text{NO}_2^-$  at the GC electrode (equation 2).

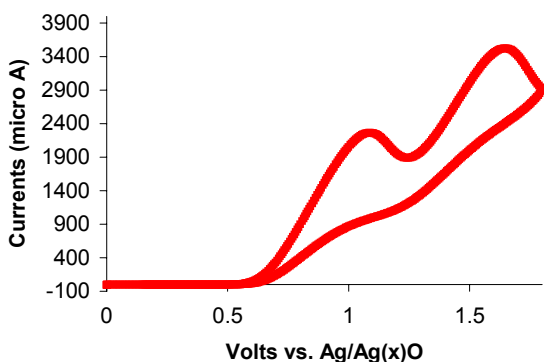


**Figure 27. Voltammogram of Glassy Carbon (GC) Electrode 330 mM NaOH/ $\text{CH}_3\text{OH}/0.2 \text{ M LiClO}_4$**

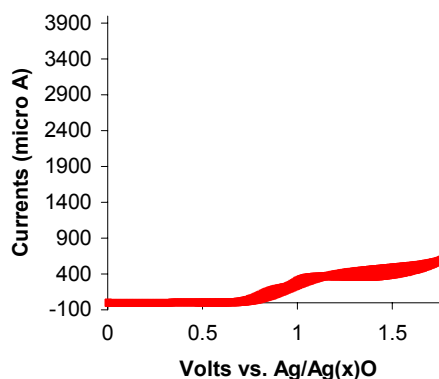


**Figure 28. Voltammogram of Glassy Carbon (GC) Electrode 330 mM  $\text{NaNO}_2$ /330 mM NaOH/ $\text{CH}_3\text{OH}/0.2 \text{ M LiClO}_4$**

The addition of 330 mM NaOH and 330 mM NaNO<sub>2</sub> to the CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub> resulted two large waves as shown in Figure 29. Two large waves with peak potentials at ca. 1.00 V and 1.6 V were observed, corresponding to the oxidation of both OH<sup>-</sup> and NO<sub>2</sub><sup>-</sup> directly at the GC electrode respectively. Addition of 100 mM phloroglucinol to the CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>/ 330 mM NaOH and 330 mM NaNO<sub>2</sub> resulted in no oxidation waves as shown in Figure 30. This indicated that the oxidation of phloroglucinol was not feasible under our reaction conditions.



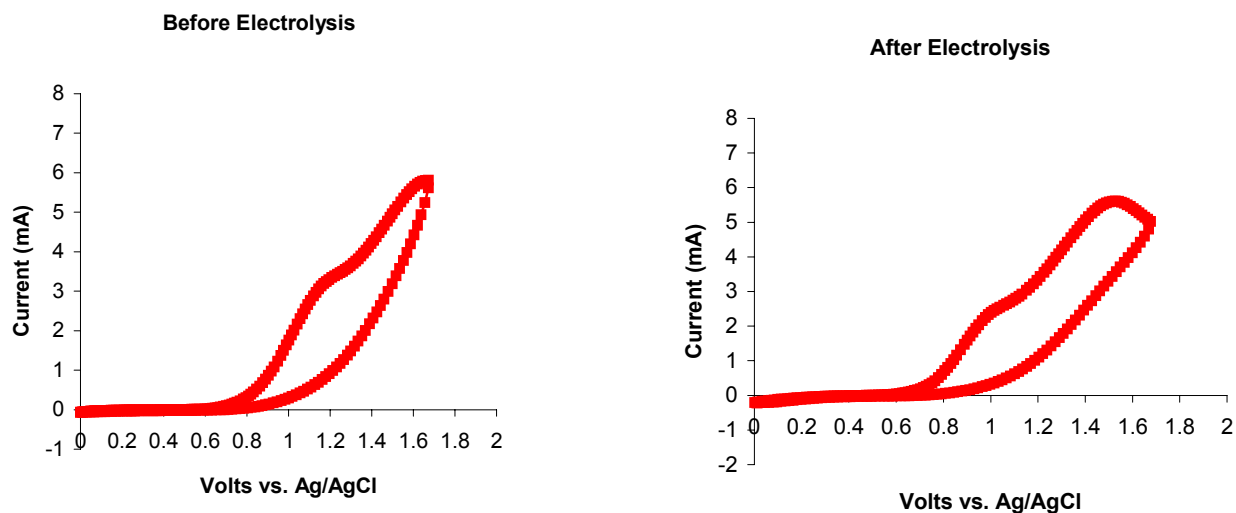
**Figure 29. Voltammogram of Glassy Carbon (GC) Electrode 330 mM NaNO<sub>2</sub>/330 mM NaOH/CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>**



**Figure 30. Voltammogram of Glassy Carbon (GC) Electrode 100 mM Phloroglucinol/330 mM NaNO<sub>2</sub>/330 mM NaOH/CH<sub>3</sub>OH/0.2 M LiClO<sub>4</sub>**

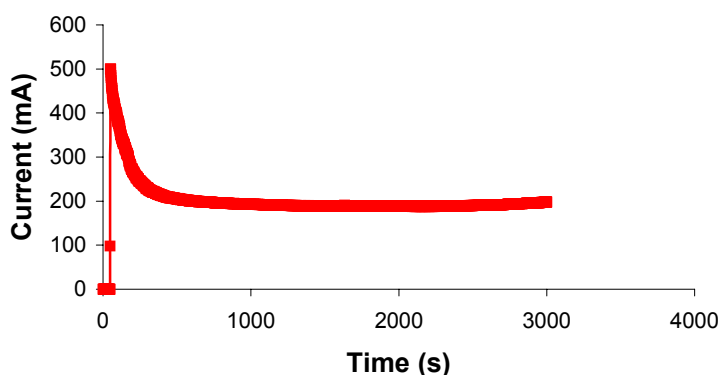
#### **Electrolysis of 2-Nitropropanol (NPOH)**

During the electrolysis of NPOH, a broad wave was observed at 1.10 V (Figure 31) which corresponded to the electrochemical oxidation of both NO<sub>2</sub><sup>-</sup> and deprotonated NPOH. Therefore, an electrode potential of 1.40 V should be sufficient to oxidize all of the deprotonated NPOH.



**Figure 31. Voltammograms at the Glassy Carbon (GC) Electrode Before and After Electrolysis of 2-Nitropropanol (NPOH) solution**

Over the course of the electrolysis reaction, the color of the solution changed from pale yellow to darker yellow with a total charge of 625 Coulombs. The electrolysis was stopped when there was no change in the current (Figure 32). The voltammetric measurement after electrolysis Figure 31 showed two waves at 1.00 V and 1.50 V (which may be attributed to excess  $\text{NO}_2^-$ ). Unexpectedly, the current of the voltammogram after the electrolysis reached a steady state value of 195 milliamperes (mA) instead of zero. Additional experiments will be performed to understand the electrolysis of sodium nitrite and sodium hydroxide and why the reaction yield was not quantitative. DNPOH was isolated from the reaction mixture in 40% yield and was characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.



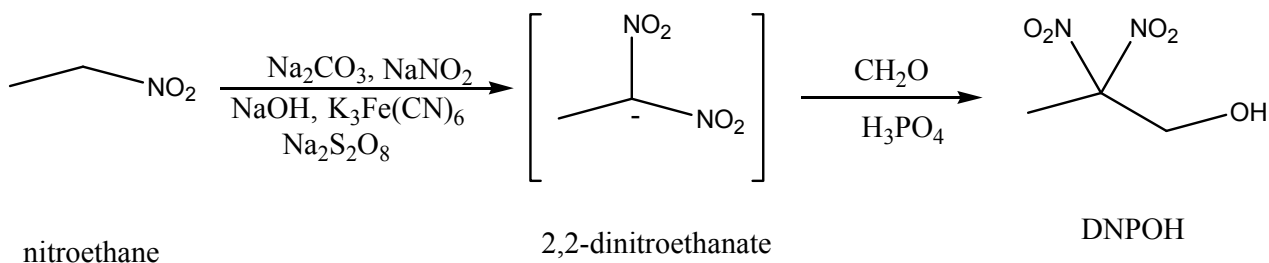
**Figure 32. Electrolysis Reaction of 2-Nitropropanol (NPOH)**

### Economic Feasibility Assessment

To assess the economic feasibility of the electrochemical approach over traditional synthesis, a comparison of the Chemical Synthesis Route and the Electrosynthesis Route to DNPOH was made. The processing economics and the environmental discharge of these two routes to 2,2-dinitropropanol (DNPOH) are compared here.

#### **ATK Thiokol Synthetic Route**

This synthetic route was used at ATK-Thiokol to produce over 100,000 pounds of DNPOH the precursor to BDNPA/F. In this process nitroethane was converted to DNPOH with potassium ferricyanide, sodium persulfate and sodium nitrite in the presence of formaldehyde. The procedure was documented in ATK-Thiokol TR11743 under contract DAAA21-94-D-003 in September of 1999. The overall synthesis is outlined here (Scheme 5):



**Scheme 5. ATK-Thiokol DNPOH Synthesis (Traditional)**

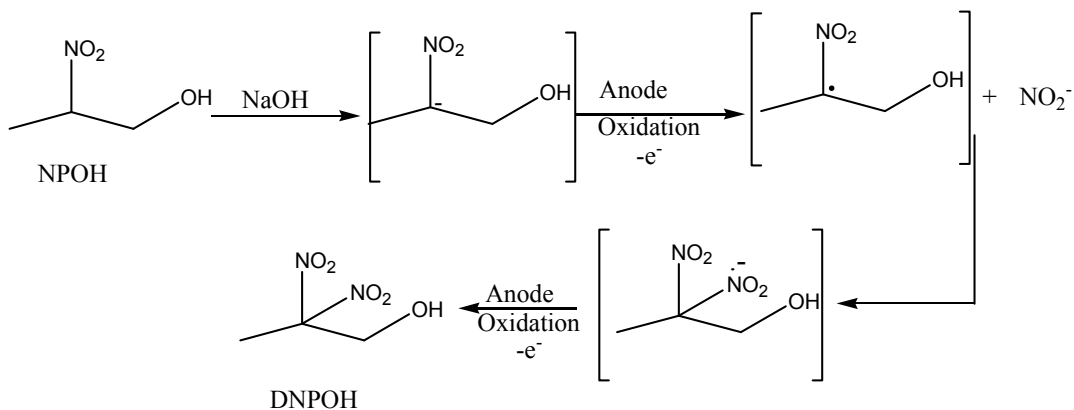
A summary of the quantities of the reagents used to synthesize 79.5 pounds of DNPOH, with a yield of 70 molar percent is shown in Table 1. A large amount of water was dictated by the amount required to keep the byproduct, sodium sulfate in solution. Premature precipitation of the salt caused the process tubes to clog with solids. The water consumption was 25 pounds per pound of DNPOH.

**Table 1. Cost Comparison**

|                                | Cost<br>\$/lb | <u>ATK-Thiokol Process</u> |                     | <u>Electrochemical Process</u> |                     |
|--------------------------------|---------------|----------------------------|---------------------|--------------------------------|---------------------|
|                                |               | Qty                        | Cost                | Qty                            | Cost                |
|                                |               | Used lbs                   | \$/79.5lbs<br>DNPOH | Used lbs                       | \$/79.5lbs<br>DNPOH |
| <b>Reagents</b>                |               |                            |                     |                                |                     |
| Water                          |               | 1838                       |                     | 1070                           |                     |
| Sodium Nitrite                 | \$ 0.46       | 195                        | \$ 89.70            | 195                            | \$ 89.70            |
| Sodium Carbonate               | \$ 0.50       | 53                         | \$ 26.50            | 53                             | \$ 26.50            |
| Nitroethane                    | \$ 3.52       | 53                         | \$ 186.56           | 53                             | \$ 186.56           |
| Potassium Ferricyanide         | \$ 4.20       | 46.6                       | \$ 195.72           |                                |                     |
| Sodium Persulfate              | \$ 1.00       | 169                        | \$ 169.00           |                                |                     |
| Sodium Hydroxide               | \$ 0.60       | 36.5                       | \$ 21.90            | 36.5                           | \$ 21.90            |
| 37% Formaldehyde               | \$ 0.38       | 64                         | \$ 24.32            | 64                             | \$ 24.32            |
| 75% Phosphoric Acid            | \$ 0.23       | 70                         | \$ 16.10            | 70                             | \$ 16.10            |
| <b>Product</b>                 |               |                            |                     | 1541.5                         |                     |
| DNPOH                          |               | 79.5                       |                     | 79.5                           |                     |
| <b>Waste</b>                   |               |                            |                     |                                |                     |
| Water                          |               | 2011                       |                     | 1269                           |                     |
| Sodium Nitrite                 |               | 158                        |                     | 158                            |                     |
| Sodium Bicarbonate             |               | 25                         |                     | 25                             |                     |
| Ethanates                      |               | 17                         |                     | 17                             |                     |
| Potassium Ferricyanide         |               | 46.6                       |                     |                                |                     |
| Sodium Persulfate              |               | 194                        |                     |                                |                     |
| Formaldehyde                   |               | 7.7                        |                     | 7.7                            |                     |
| Sodium phosphate               |               | 65                         |                     | 65                             |                     |
| <b>Total Waste:</b>            |               | 2524                       |                     | 1542                           |                     |
| <b>Waste disposal cost</b>     |               |                            | \$ 75.62            |                                | \$ 46.19            |
| <b>Cost per pound of DNPOH</b> |               |                            | \$ 9.18             |                                | \$ 4.59             |

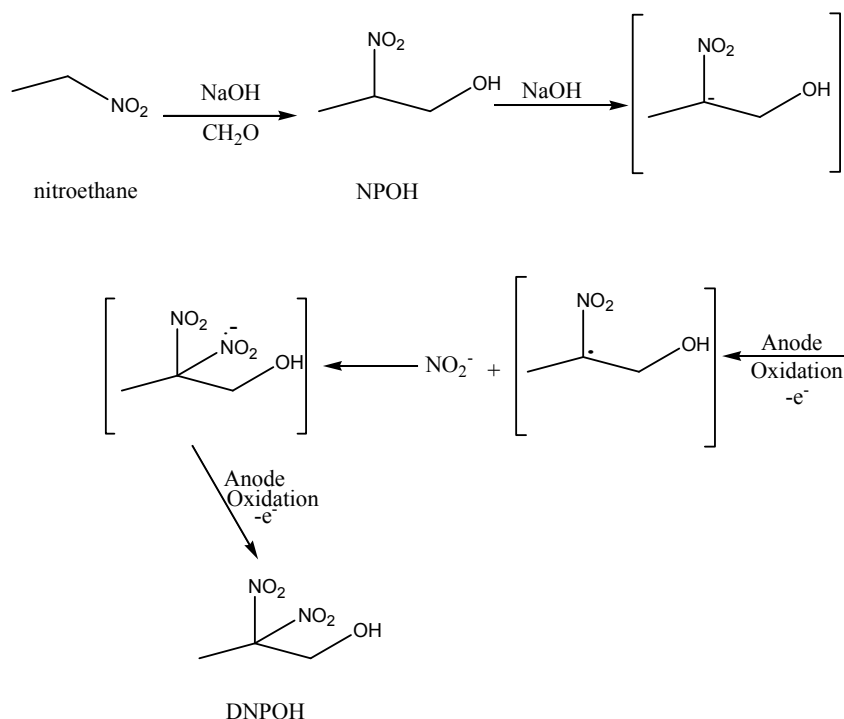
#### **Electrochemical Route**

The electrochemical route as described earlier in this report afforded 40 mol percent of DNPOH (Scheme 6). The significance of the electrochemical nitration was the elimination of the chemical oxidants potassium ferricyanide and sodium persulfate that contributed 27% and 23% respectively to the total material costs for producing DNPOH by the ATK-Thiokol process. The water consumption was reduced proportionately to the decrease in salts consumption to about 16 pounds per pound of DNPOH produced.

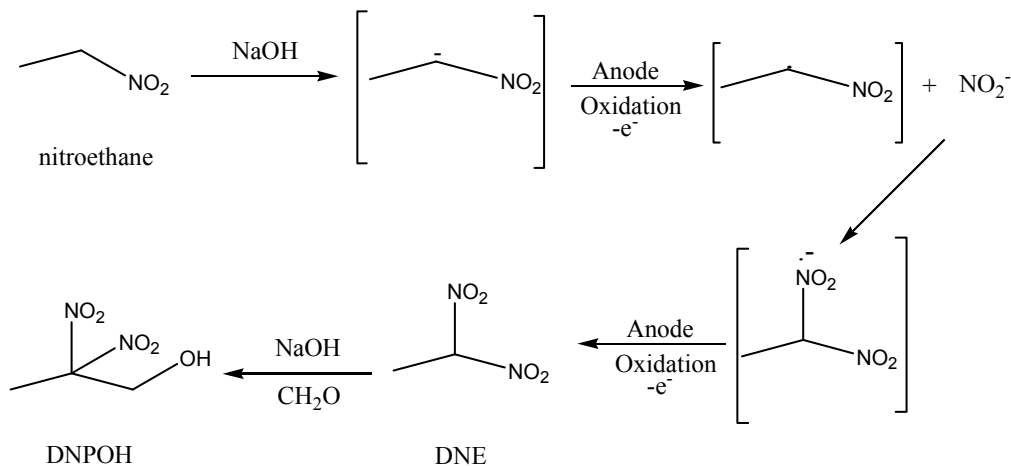


**Scheme 6. Electrosynthesis of DNPOH**

However, 2-nitropropanol is not a commodity material and it would have to be synthesized from nitroethane. The initial evaluation for an improved synthesis is very promising but more lab scale work needs to be done to determine an optimum synthesis and an improved yield from 40% to 70-80% that was obtained by the ATK Thiokol route. These proposed syntheses are outlined below (Schemes 7 or 8).



**Scheme 7. Electrosynthesis of DNPOH**



**Scheme 8. Electrosynthesis of DNPOH**

### TRANSITION PLAN/RECOMMENDATIONS

The evaluation and data obtained within this ‘SEED’ activity have indicated that application of electrochemical processing methods to energetic material manufacturing processes is feasible and could provide a substantial savings to the cost of the energetic commodity. Application of these methods should also significantly reduce the amount of wastes generated in the process. The SEED effort, however, was not able to get deep enough into the study to fully prove out a process for full scale application. A development effort needs to be funded to scale a chemistry to a reasonable size (pound scale?), conduct some indepth optimization work, and refine the economic assessment to include facilitization as well as production costs. A thorough review of safety issues

related to this approach should also be made within this next effort. ATK Thiokol, teaming with other local electrochemical experts such as Idaho National Engineering and Environmental Laboratory (INEEL) or the University of Utah, will have the expertise and facilities to support this continued effort. A proposal for this follow-on effort will be provided upon request. Should the follow-on project prove feasible, ATK has the infrastructure at either the Thiokol facility (in Northern Utah) or the Radford facility (Virginia) to bring this new technology into place at production scale.

## EXPERIMENTAL

Reagent grade methanol (Mallinckrodt) was dried over activated 3 Å molecular sieves. Anhydrous LiClO<sub>4</sub> (Alfa Aesar), NaOH pellets (Mallinckrodt), tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, Aldrich) and tetrabutylammonium tetraborate (TBABF<sub>4</sub>, Aldrich) were used without further purification. Anhydrous LiClO<sub>4</sub> was stored in a beaker at 130°C before use. 2-Nitropropanol (97% NPOH, Aldrich) and 2,4,6-Trinitrotoluene (TNT, ATK-Thiokol) were used without further purification. 1-*tert*-Butyl-3-hydroxymethyl-3-nitroazetidine (HMNAZ, ATK-Thiokol) was dissolved in reagent grade acetone (Mallinckrodt) and was purified by filtering through a plug of silica gel on a glass frit.

Background: 0.5 M LiClO<sub>4</sub> (0.5320 g) in methanol was prepared in a 25 mL volumetric flask. The solution was sonicated over 20 seconds.

### Electrosynthesis of 1-*tert*-Butyl-3,3-Dinitroazetidine (DNAZ)

To a solution of HMNAz (0.94 g, 0.0050 mol) in methanol (5 mL) was added NaOH (0.60 g, 0.015 mol) in methanol (10 mL). The mixture was stirred at room temperature for 45 minutes. The solution was then transferred to a 50 mL volumetric flask. To the mixture was added a solution of LiClO<sub>4</sub> (7.98 g, 0.075 mol) and NaNO<sub>2</sub> (0.38 g, 0.0055 mol) in methanol (30 mL). Methanol was added to make a 50 mL solution. The working electrode and auxiliary electrode compartments of electrochemical cell were filled with 30 mL (0.0030 mol deprotonated HMNAz) and 15 mL of this solution, respectively, and bubbled with a stream of nitrogen for 20 minutes. The electrolysis reaction ran for approximately 2 hours. After the end of the electrolysis, the yellow solution was added to 50 mL distilled water to remove LiClO<sub>4</sub>, excess NaOH and NaNO<sub>2</sub>. Then the mixture was extracted by dichloromethane (3 x 15 mL). The combined organic layer was dried over with anhydrous MgSO<sub>4</sub> for 20 minutes and filtered. The filtrate was then concentrated under vacuo to a pale yellow liquid which slowly crystallized to a solid 290 mg (48% yield). <sup>1</sup>H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO) δ 1.05 (9 H, CH<sub>3</sub>, s); 4.20 (4H, CH<sub>2</sub>, s). <sup>13</sup>C NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO) δ 23 (CH<sub>3</sub>), δ 52.1 (CH<sub>2</sub>); δ 55.8 (C-CH<sub>3</sub>); δ 119.5 (C-NO<sub>2</sub>).

### Electrosynthesis of 2,2-Dinitropropanol (DNPOH)

To a solution of 2-nitropropanol (NPOH) (440 µL, 0.0050 mol) in distilled water (5 mL) was added NaOH (0.30 g, 0.0075 mol) in distilled water (10 mL). The mixture was stirred at room temperature for 45 minutes. The solution was then transferred to a 50 mL

volumetric flask and was added to a solution of LiClO<sub>4</sub> (7.98 g, 0.075 mol) and NaNO<sub>2</sub> (1.38 g, 0.020 mol) in distilled water (30 mL). Distilled water was added to make at 50 mL solution. The working electrode and auxiliary electrode compartments of electrochemical cell were filled with 30 mL and 15 mL solution of (0.0030 mol of deprotonated NPOH), respectively, and bubbled with a stream of nitrogen for 20 minutes. The electrolysis reaction ran for approximately 1 hour. After the electrolysis, the pale yellow solution was extracted with ether (3 x 15 ml). The combined organic layer was dried over anhydrous MgSO<sub>4</sub> for 20 minutes and filtered. The filtrate was then concentrated under vacuo to a yellow liquid which slowly crystallized to a pale yellow solid 180 mg (40 % yield). <sup>1</sup>H NMR (300 MHz, DMSO-D<sub>6</sub>) δ 2.2 (3 H, CH<sub>3</sub>, s); δ 4.3 (2H, O-CH<sub>2</sub>, s). <sup>13</sup>C NMR (300 MHz, DMSO-D<sub>6</sub>) δ 20.3 (CH<sub>3</sub>); δ 64.5 (O-CH<sub>2</sub>); δ 119.0 (C-NO<sub>2</sub>).

### **Electrosynthesis of 2,2',4,4',6,6'-Hexanitrostilbene (HNS)**

In a 50 mL volumetric flask, a solution of 0.2 M TBABF<sub>4</sub> (3.29 g, 0.010 mol), 50 mM TNT (0.57 g, 0.0025 mol) and 110 mM NaOH (0.22 g, 0.0055 mol) in methanol was prepared. The working electrode and auxiliary electrode compartments of electrochemical cell were filled with 30 mL (0.0015 mol deprotonated TNT) and 15 mL of this solution respectively, and bubbled with a stream of nitrogen for 20 minutes. The electrolysis reaction ran for approximately 8 hours. After the electrolysis, the dark brown solution was added with 50 ml distilled water to remove LiClO<sub>4</sub>, excess NaOH and NaNO<sub>2</sub>. Then the mixture was extracted with ether (3 x 15 mL). The combined organic layer was dried over anhydrous MgSO<sub>4</sub> for 20 minutes and filtered. The filtrate was concentrated under vacuo to give a black solid 350 mg. There was no evidence of HNS from <sup>1</sup>H NMR.

### **2-nitropropane**

Background with 2-nitropropane: A solution of 100mM 2-nitropropane (224.6 μL) and 0.5M LiClO<sub>4</sub> (0.5320 g) in methanol was prepared in a 25 mL volumetric flask.

### **Electrochemical Synthesis of 2,3-dinitro-2,3-dimethylbutane**

In a 25 mL volumetric flask, a solution of 0.5M LiClO<sub>4</sub> (0.5320 g), 10 mM 2-nitropropane (22.5 μL) and 100 mM NaOH (0.1000) in methanol was prepared. The same procedure was repeated for 50 mM 2-nitropropane (112.3 μL) and 100 mM 2-nitropropane (224.6 μL). In a 50 ml volumetric flask, a solution of 1 M LiClO<sub>4</sub> (5.3200 g), 100 mM 2-nitropropane (44.90 μL), and 100 mM NaOH (0.2200 g) in methanol was prepared. The solution was bubbled with nitrogen for 20 minutes. The working electrode and auxiliary compartments were filled with solution 28 mL and 15 mL respectively. The potential was held at 1.0 Volt vs. Ag/Ag<sub>x</sub>O to completely oxidized the deprotonated 2-nitropropane. The solution of the working electrode compartment was stirred with a magnetic stirrer under nitrogen for 2.8 hours. The solvent was removed under vacuum, which resulted in a white solid. The solid was washed with 8 mL of cold water to remove the LiClO<sub>4</sub> and excess NaOH. The solid was filtered and air-dry overnight gave 80 mg (32% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.7 (12 H, CH<sub>3</sub>, s); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 23 (CH<sub>3</sub>), δ 91 (C-NO<sub>2</sub>).

### **Electrochemical Oxidation of HMNAZ, TNT, and Phlorogucinol**

A polished glassy carbon (GC) electrode was used in all experiments. The reference and auxiliary electrodes were Ag/Ag<sub>x</sub>O wire electrode and Pt gauze 52 mesh electrode, respectively. The dimension of the auxiliary electrode is 1 cm x 2.5 cm. Voltammogram measurements were run at two different times: before the electrolysis and after the electrolysis. All voltammograms were measured over the range 0.00 V to 1.30 V vs. Ag/Ag<sub>x</sub>O, and are plotted on the same current and potential scale for direct comparison. The solutions were bubbled with nitrogen for 20 minutes.

Reagent grade methanol and acetonitrile (Mallinckrodt) were dried over activated 3 Å molecular sieves. Anhydrous LiClO<sub>4</sub> (Alfa Aesar), triethylamine (TEA) (EM Science), NaNO<sub>2</sub>, NaOH pellets (Mallinckrodt) and anhydrous tetrabutylammonium tetrafluoroborate (Bu<sub>4</sub>NBF<sub>4</sub>) (Aldrich) were used without further purification. Anhydrous LiClO<sub>4</sub> (Alfa Aesar) was stored in a beaker at 130 °C before use. 2-nitropropane, HMNAz, TNT and phloroglucinol were used without further purification.

#### Electrochemical Oxidation of HMNAz

Background: 0.2 M LiClO<sub>4</sub> (0.5320 g) in methanol was prepared in a 25 mL volumetric flask. The solution was sonicated over 20 seconds.

Background with TEA: A solution of 110 mM TEA (0.1390 mL) and 0.2 M LiClO<sub>4</sub> (0.2128 g) in methanol was prepared in a 10 mL volumetric flask.

Background with NaNO<sub>2</sub>: A solution of 110 mM NaNO<sub>2</sub> (0.0750 g) and 0.2 M LiClO<sub>4</sub> (0.2128 g) in methanol was prepared in a 10 mL volumetric flask.

Background with HMNAz: A solution of 110 mM HMNAz (0.1880 g) and 0.2 M LiClO<sub>4</sub> (0.2128 g) in methanol was prepared in a 10 mL volumetric flask.

Background with TEA and NaNO<sub>2</sub>: A solution of 110 mM NaNO<sub>2</sub> (0.0750 g), 110 mM TEA (0.1390 mL) and 0.2 M LiClO<sub>4</sub> (0.2128 g) in methanol was prepared in a 10 mL volumetric flask.

Background with TEA and HMNAz: A solution of 110 mM TEA (0.1390 mL), 110 mM HMNAz (0.1880 g) and 0.2 M LiClO<sub>4</sub> (0.2128 g) in methanol was prepared in a 10 mL volumetric flask.

Background with HMNAz and NaNO<sub>2</sub>: A solution of 110 mM HMNAz (0.1880 g), 110 mM NaNO<sub>2</sub> (0.0750 g) and 0.2 M LiClO<sub>4</sub> (0.2128 g) in methanol was prepared in a 10 mL volumetric flask.

Electrochemical oxidation of HMNAz: In a 10 mL volumetric flask, a solution of 0.2 M LiClO<sub>4</sub> (0.2128 g) 110 mM NaNO<sub>2</sub> (0.0750 g), 110 mM TEA (0.1390 mL) and 100 mM HMNAz (0.1880 g) in methanol was prepared.

### Electrochemical Synthesis of DNAz

To 50 mL volumetric flask, 0.005M HMNAz (0.9400 g) and 0.0055M NaOH (0.2200 g) were dissolved in 40 mL methanol. The solution was sonicated for 30 seconds and then stirred. 0.0055M NaNO<sub>2</sub> (0.3795 g) and 0.05M LiClO<sub>4</sub> (5.0320 g) were added to the solution and the solution was sonicated for 30 seconds and then stirred. The potential was held at 1.0 Volt vs. Ag/Ag<sub>x</sub>O to completely oxidized the deprotonated HMNAz. The solution of the working electrode compartment was stirred with a magnetic stirrer under nitrogen for 15 hours. The solvent was removed under vacuum, which resulted in a yellow oil. The solid was washed with 8 mL of cold water to remove the LiClO<sub>4</sub> and excess NaOH. The solid was filtered and air-dry overnight gave 25 mg (8 % yield). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>): δ 1.0 (9 H, CH<sub>3</sub>, s), δ 4.2 (4 H, CH<sub>2</sub>, s); <sup>13</sup>C NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>): δ 29 (CH<sub>3</sub>), δ 50 (CH<sub>2</sub>), δ 53 (C-CH<sub>3</sub>). FTIR: 1570 and 1368 cm<sup>-1</sup> (NO<sub>2</sub> stretching) and 2969 cm<sup>-1</sup> (CH stretching).

### Electrochemical Oxidation of TNT

Background: 0.2 M Bu<sub>4</sub>NBF<sub>4</sub> (0.6586 g) in methanol was prepared in a 10 mL volumetric flask. The solution was sonicated over 20 seconds

Background with NaOH: A solution of 55 mM NaOH (0.0220 g) and 0.2 M Bu<sub>4</sub>NBF<sub>4</sub> (0.6586 g) in methanol was prepared in a 10 mL volumetric flask.

Background with TNT: A solution of 50 mM TNT (0.1136 g) and 0.2 M Bu<sub>4</sub>NBF<sub>4</sub> (0.6586 g) in methanol was prepared in a 10 mL volumetric flask.

Electrochemical oxidation of TNT: In a 10 mL volumetric flask, a solution of 0.2 Bu<sub>4</sub>NBF<sub>4</sub> (0.6586 g), 55 mM NaOH (0.0220 g) and 50 mM TNT (0.1136 g) in methanol was prepared.

### Electrochemical Oxidation of Phloroglucinol

Background: Background: 0.2 M LiClO<sub>4</sub> (0.5320 g) in methanol was prepared in a 25 mL Volumetric flask. The solution was sonicated over 20 seconds.

Background with NaOH: A solution of 330 mM NaOH (0.1320 g) and 0.2 M 0.2 M LiClO<sub>4</sub> (0.2128 g) in methanol was prepared in a 10 mL volumetric flask.

Background with NaNO<sub>2</sub>: A solution of 330 mM NaNO<sub>2</sub> (0.2277 g) and 0.2 M LiClO<sub>4</sub> (0.2128 g) in methanol was prepared in a 10 mL volumetric flask.

Background with phloroglucinol: A solution of 100 mM phloroglucinol (0.1612 g) and 0.2 M 0.2 M LiClO<sub>4</sub> (0.2128 g) in methanol was prepared in a 10 mL volumetric flask.

Background with NaOH: A solution of 330 mM NaOH (0.1320 g), of 330 mM NaNO<sub>2</sub> (0.2277 g) and 0.2 M 0.2 M LiClO<sub>4</sub> (0.2128 g) in methanol was prepared in a 10 mL volumetric flask.

Electrochemical oxidation of phloroglucinol: In a 10 mL volumetric flask, a solution of 330 mM NaOH (0.1320 g), of 330 mM NaNO<sub>2</sub> (0.2277 g), 0.2 M 0.2 M LiClO<sub>4</sub> (0.2128

g) and 100 mM phloroglucinol (0.1612 g) in methanol was prepared in a 10 mL volumetric flask.

## **APPENDIX**

Note: There are no publications submitted to date on this new technology application.