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ORIGINAL PAPER

Electrochemical synthesis of 2,2-dinitropropanol

Tedd E. Lister · Robert V. Fox

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Abstract This paper describes electrochemical approaches to the synthesis of 2,2-dinitropropanol (DNPOH) and discusses the potential for pilot-plant scale synthesis. In this work, the anode of the electrochemical cell replaces the chemical oxidants used in the conventional synthesis for the purpose of reducing secondary waste and the consequent disposal cost. The electrosynthesis reactions described in this work use the common starting material, nitroethane (NE). The synthesis of the end-product DNPOH involves two steps: (1) electrochemical oxidative nitration (addition of a geminal NO_2 group); and, (2) condensation with formaldehyde. Electrochemical oxidation of NE was first attempted by direct oxidation on a Pt electrode surface resulting in low yield and significant generation of undesirable by-product. Alternatively, two different mediators were employed resulting in a dramatic improvement of yield for the oxidative nitration step. The two different mediators used, Ag^+/Ag^0 and $Fe(CN)_6^{-3/-4}$, were derived from the chemical oxidants known to perform the oxidative nitration. The $Fe(CN)_6^{-3/-4}$ mediator demonstrated the best promise for scale-up and industrial production due to the lower cost of the mediator and the solubility of the mediator lending it to greater ease-of-use in conventional electrochemical cell designs.

Keywords Oxidative nitration · Electrolysis · Plasticizer · Nitroparaffin · Mediator · Energetic material

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T. E. Lister (✉) · R. V. Fox
Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415, USA
e-mail: tedd.lister@inl.gov

1 Introduction

The compound, 2,2-dinitropropanol (DNPOH), is used in the synthesis of nitroplasticizer compounds such as bis(dinitropropyl)-acetal (BDNPA) [1]. Conventional manufacture of DNPOH involves two chemical reactions starting from nitroethane (NE): (i) an oxidative nitration; and, (ii) condensation with formaldehyde. These two different reactions can be performed in either order [2]. Figure 1 shows these two reaction pathways. The oxidative nitration step uses chemical oxidant(s) to perform a two-electron oxidation in basic sodium nitrite solution resulting in the addition of a geminal nitro group to NE. Figure 2 shows the established reaction pathway starting with the anion of NE (nitroethanate ion) [3]. The initial electron transfer creates a radical from the nitroethanate ion (Fig. 2, part 1). Addition of NO_2^- to this radical generates a dinitro-intermediate (Fig. 2, part 2) that is oxidized to the 1,1-dinitroethanate ion (Fig. 2, part 3). The second reaction, condensation of the anion of 1,1-dinitroethane (1,1-DNE) with formaldehyde, is a well established reaction having yields exceeding 95% for 1,1-DNE to DNPOH, and somewhat lower yield for reaction of NE to 1-nitropropanol (NPOH) [2].

Common chemical oxidants used to drive the oxidative nitration reaction have been Ag^+ [4] and later $Fe(CN)_6^{-3}$ [3]. Due to the issues of cost, a secondary oxidant, $Na_2S_2O_8$, was employed [5]. The $Na_2S_2O_8$ regenerates spent $Fe(CN)_6^{-4}$ by oxidation back to the active $Fe(CN)_6^{-3}$ state; thus keeping active catalytic amounts of $Fe(CN)_6^{-3}$ available for reaction. The replacement of the chemical oxidants with an anode has the possibility of removing the need for chemical oxidants and reducing process and disposal costs.

Attempts have been made in the past to perform nitration reactions on nitroalkanes using electrode surfaces. The

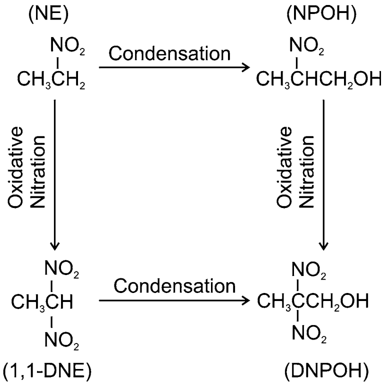

Fig. 1 Two routes to the synthesis of DNPOH from NE

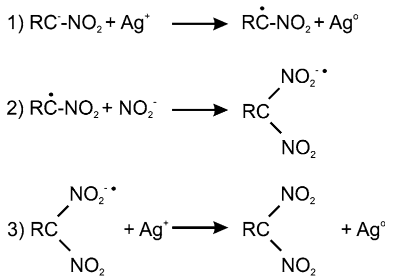

Fig. 2 Proposed mechanism for the oxidative nitration reaction [3]

first attempt involved a direct oxidative nitration on a Pt anode of 2-nitropropane to 2,2-dinitropropane albeit with low yield [6]. That work was reported about 10 years before the chemical synthesis method was reported [4]. Reaction mechanisms were not proposed in either of those works. Later, the use of a Ag metal electrode was shown to produce 1,1-DNE in excellent yield [7]. In that work, the Ag^+ oxidant was generated by corrosion of a silver anode. A silver powder bed electrode was proposed to avoid loss of Ag. Attempts by the same researchers using other electrodes, including Pt and graphite, resulted in low yields and an abundance of ethylnitrolic acid by-product. More recently, work on the oxidative addition of several anions to nitroalkanes was reported [8]. This included the synthesis of 1,1-DNE from NE with a reported yield of 35%. In that investigation the researchers speculated that the yield was limited by the reaction of the products with polynitroalkyl radicals at the given reaction conditions. Additionally, the product was not stable due to reaction with by-products under the given reaction conditions.

The focus of this work is on replacement of the conventional chemical oxidants with an electrochemical technique for oxidative nitration of NE to 1,1-DNE. Initial efforts investigated the direct electrochemical reaction of NE on a Pt electrode. Poor yield was observed confirming previously reported results [7, 8]. The use of mediator couples Ag^+/Ag^0 or $Fe(CN)_6^{-3/-4}$ improved 1,1-DNE yield dramatically and allowed the electrochemical reaction to run at much lower cell potentials. It is anticipated that the reaction pathway for the mediated electrochemical reaction investigated in this work is identical to the reaction paths studied previously [3, 4], with the electrode serving as a regenerator of the oxidant species. Product yield and reaction efficiency were determined in both batch and continuous-flow cells to evaluate each configuration for future pilot-plant development.

2 Experimental

2.1 Electrochemical setup

A Solartron Model 1287A potentiostat (Solartron Analytical, Farnborough, Hampshire, UK) operated using CorrWare software package (Scribner and Associates, Southern Pines, NC, USA) was used to perform all electrolysis and cyclic voltammetry experiments. The cyclic voltammetry cell was a 25 mL four-necked flask. A Pt microelectrode (Bioanalytical Systems Inc., West Lafayette, IN, USA) with a diameter of 1.6 mm was used for all cyclic voltammetry experiments. The Pt electrode was polished with 0.05 µm alumina polish and sonicated in nanopure water prior to use.

The batch electrolysis cell was a three-compartment type with porous frits separating each compartment. Anode and cathode compartments were approximately the same volume (35 mL) whereas the reference compartment was smaller. The entire cell volume was not always utilized. The solution was stirred using a Teflon coated stir bar. A platinum mesh electrode (assembled in house) with dimensions of approximately 3.1 cm by 2.7 cm was used as an anode. The mesh (52 mesh, 0.1 mm wire) was folded over and spot welded to double the surface area. The estimated surface area was calculated to be 42.9 cm^2. A similar Pt mesh cathode was utilized. Electrodes were cleaned by soaking in 50% nitric acid solution before use. Gel type Ag/AgCl reference electrodes were employed (Bioanalytical Systems Inc.). The anode compartment was stirred during the reaction using a magnetic stir bar.

The silver bed electrolysis cell was comprised of a commercially available 40 mL fine-frit Buchner funnel (Thermo Fisher Scientific Inc., Waltham, MA, USA). The silver bed anode was formed using 4–7 µm diameter Ag powder (Alfa Aesar, Ward Hill, MA, USA). A platinum mesh feeder electrode (52 mesh, 0.1 mm wire) was inserted at the bottom of the Buchner funnel with approximately 2 g of Ag powder covering the Pt feeder electrode. The cathode compartment was tube-shaped with a fine porosity frit at the bottom facing the Ag bed. A platinum flag electrode was used as the cathode. A Ag/AgCl reference electrode (Bioanalytical Systems Inc.) was utilized directly in the anode solution.

2.2 Solution makeup

NaOH or KOH (Fisher, Fair Lawn, NJ, USA) was combined with a fraction of the total nanopure water volume ($\sim$10–20%) and stirred until dissolved. Nitroethane (>99%, Alpha Aesar, Ward Hill, MA, USA) was added slowly and stirred for at least 30 min to form the nitroethanate anion. The remaining water and $NaNO_2$ (Fisher) or KNO_2 (Fisher) was added and the solution stirred until dissolved. This solution was used in the anode compartment. When used, potassium ferrocyanide (Alpha Aesar) was added just prior to initiating the electrolysis. The cathode and reference compartments contained 0.5 M NaOH or KOH.

2.3 Electrolysis and production of 1,1-DNE and 2,2-DNPOH

The electrolysis was performed in both potentiostatic and galvanostatic control. Following the reaction, the product solution containing the 1,1-dinitroethanate ion was removed from the anode compartment after completing the electrolysis reaction. To produce DNPOH, the pH of the anode solution was amended to $\text{pH} > 10$ (if necessary), and an excess amount (two moles formaldehyde to one mole of 1,1-DNE) of 37% formaldehyde (Sigma-Aldrich, St. Louis, MO, USA) was added. After reaction, the solution was neutralized to pH 4–5 with 1 M H_3PO_4 and DNPOH was extracted into ethyl acetate (Acros Organics, Morris Plains, NJ, USA) for GC-MS and NMR analysis.

2.4 GC-MS, GC, and NMR analysis of products

Ethyl acetate extracts were analyzed by GC-MS, GC, and NMR. GC-MS analysis was performed using a Shimadzu model GCMS-QP2010 (Shimadzu Scientific Instruments, Columbia, MD, USA). The column used was a Restek (Restek Corporation, Bellefonte, PA, USA) XTI-5 (crossbonded 5% diphenyl–95% dimethyl polysiloxane) 30 m × 0.25 mm ID × 0.25 μm. 2,2-dinitro-1-propanol (95%, Sigma-Aldrich), 2-nitro-1-propanol ($\geq$97%, Sigma-Aldrich), nitroethane (99.5%, Sigma-Aldrich) and acetic acid (Sigma-Aldrich) were used for preparation of standards.

NMR data (1H and 13C{1H}) were acquired on a Bruker DMX 300WB (Bruker BioSciences Corporation, Billerica, MA, USA) spectrometer with a magnetic field strength of 7.04 Tesla corresponding to operating frequencies of 300.13 MHz (1H) and 75.48 MHz (13C). The NMR spectra were referenced internally utilizing an appropriate deuterated solvent. Deuterium oxide, diethyl ether-d-10, chloroform-d, and methylene chloride-d-2 (Cambridge Isotope Laboratories, Andover, MA, USA) were used as received.

3 Results and discussion

3.1 Direct oxidative nitration of NE

Direct oxidation of NE was investigated on Pt surfaces. Figure 3 shows cyclic voltammetry performed on solutions with and without nitrite addition. In the absence of nitrite, two oxidation waves were observed by cyclic voltammetry at 1.2 V and 1.55 V versus Ag/AgCl. In the presence of nitrite, the entire oxidative area grows and a small hysteresis loop is formed on the reverse sweep. The cathodic sweep was reversed at the initiation of H_2 evolution as reproducible curves could not be achieved at more positive switching potentials. Use of a more positive switching potential (i.e., 0 V) resulted in an anodic shift in the oxidation waves and decreasing current with each sweep. This is thought to be an effect of the Pt oxide film growing with the number of sweeps although it was not investigated further. H_2 evolution results in an oxide free surface which refreshes the surface activity. The oxidation of NO_2^- is expected on Pt surfaces and is sensitive to oxide film growth [9, 10]. This reaction could lead to problems in current efficiency and NO_2^- consumption for reactions requiring more positive potentials. Fig 4.

The electrolysis of NE was attempted both at constant potential and constant current. With the anode held at 1.6 V versus Ag/AgCl the current decreased very rapidly indicating a decrease in kinetics with significant NE remaining in solution. Very low product yield was observed and most of the NE remained. These observations are in agreement with the cyclic voltammetry observations

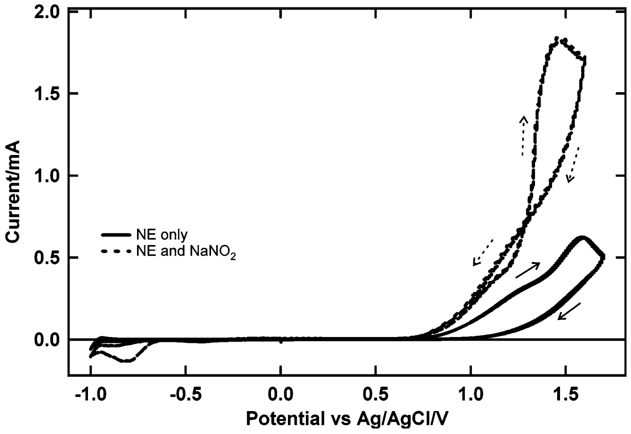

Fig. 3 Cyclic voltammetry of a Pt electrode in a solution of 0.1 M NE + 0.15 M NaOH with and without addition of 0.4 M $NaNO_2$

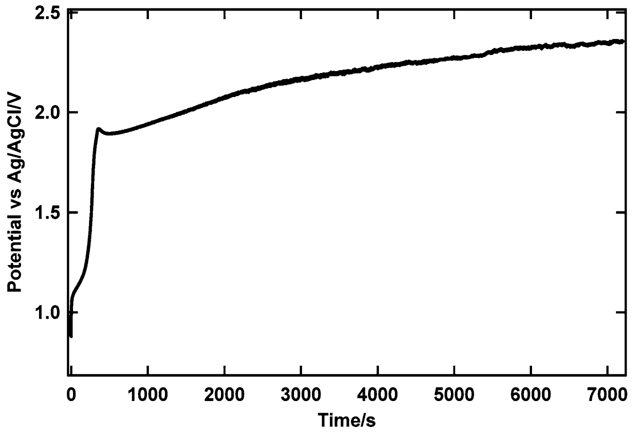

Fig. 4 Bulk electrolysis of a NE solution performed with a constant current of 0.5 A. The solution composition was 0.5 M NE + 0.55 M NaOH + 1 M $NaNO_2$. The anode solution volume was 35 mL

of decreased reactivity with cycling due to oxide film growth. It was concluded that a more significant driving force was needed to sustain the reactivity of the electrode. When the electrolysis was performed using constant current (0.5 A) the potential quickly rose above 1.5 V within 5 min and slowly increased afterwards to over 2.3 V. In addition to oxidation of NE, it is expected that NO_2^- and OH^- (O_2 evolution) oxidation reactions also occur at the anode. An amber color was observed in solution after about 15 min of electrolysis indicative of ethylnitrolic acid (CH_3CHNO_2NOH) formation [11]. Generation of ethylnitrolic acid was observed previously in the electrolysis of NE on Pt anodes [7, 8]. Ethylnitrolic acid is a known photolysis product of 1,1-DNE [12]. A decrease in pH during the electrolysis was also observed. The color was observed to reversibly change with pH, from deep amber to yellow as the pH was lowered with the amber color returning with the addition of NaOH.

Analysis of product by GC-MS confirmed production of 1,1-DNE. In addition, significant amounts of acetic acid were observed. It was observed that solution concentrations of 1,1-DNE decreased and acetic acid concentrations increased if left overnight in the electrolysis solution. This degradation reaction was not investigated further but has been described in electrolysis reactions previously [7, 8]. Acetic acid was the final degradation product of the photolysis of 1,1-DNE via degradation of ethylnitrolic acid [12].

To determine DNPOH yield, the condensation of 1,1-DNE with formaldehyde was performed on the basic ($pH > 10$) electrolysis solution, yielding DNPOH. This reaction was found to be relatively insensitive to conditions, but excess formaldehyde was added to promote complete reaction (stoichiometric ratios over 2:1 assuming 100% yield in oxidative nitration). The product was extracted and analyzed by GC-MS. The highest yield achieved was 15% (of theoretical) for direct oxidative nitration of NE to 1,1-DNE on Pt surfaces followed by condensation with formaldehyde to form DNPOH.

3.2 Mediator-based electrolysis

Attempts to form 1,1-DNE directly on a Pt electrode showed very little promise, which is in agreement with previous work [7, 8]. The issue appears to involve the mechanism of the reaction. Oxidative nitration reactions have been shown to be sensitive to the oxidant, possibly due to formation of a complex which enables electron transfer [4]. The two oxidants that are known to work well for this reaction are Ag^+ and $Fe(CN)_6^{-3}$ [3, 4]. Without formation of the complex, the energy barrier for this reaction requires higher electrochemical potentials, which in turn gives rise to undesirable side reactions.

3.2.1 *Ag^+/Ag^0 mediated electrolysis*

The use of Ag^+ as a mediator in the oxidative nitration of NE was described by Wright and Levering [7]. No instance of continued work or process use in a commercial manner has been found in the literature. In this process, a silver metal electrode is essentially corroded forming Ag^+ ions, which act as an oxidant the same as $AgNO_3$ is used in the chemical reaction [4]. The Ag^0 produced during the oxidative nitration reaction forms very small metal particles. A continuous-flow cell utilizing a gravity feed Ag powder bed electrode was described previously [7]. Figure 5 shows a diagram of the Ag powder bed electrode as used in this work described herein. Ag^+ ions are generated by corrosion of Ag from the particle bed with particles of Ag reforming on the Ag bed after reaction with NE in solution to form 1,1-DNE. Thus, Ag is not consumed and the oxidant is fully replaced by a power supply and electrodes. In the industrial chemical process, $AgNO_3$ was regenerated from the metal via reaction with nitric acid [2]. Investigation of the Ag bed electrode for the oxidative nitration of NE is further described below.

The Ag bed electrode in this work was operated using both constant current and constant potential modes. The Ag bed electrode was successful at reducing the electrode potential and DNPOH yield was improved dramatically versus the results obtained when performing oxidative nitration of NE on Pt. It was however, very difficult to keep the cell at optimum conditions leading to very erratic plots with either constant current or constant potential operation. Matching the flow rate and the current (reaction rate) through the cell proved difficult. As the solution flow through the filter outpaced the reaction rate, the cell was

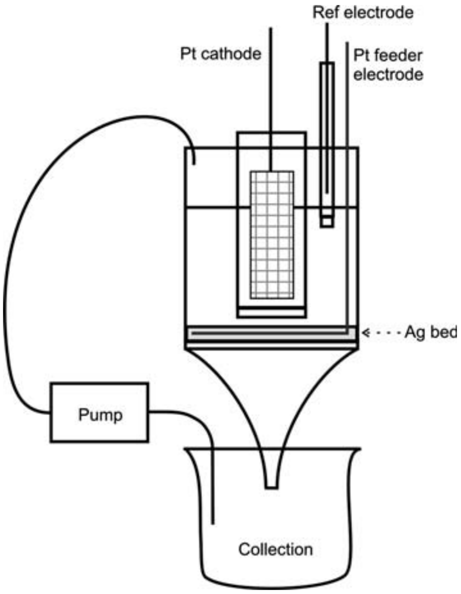

Fig. 5 Diagram of Ag powder bed electrode

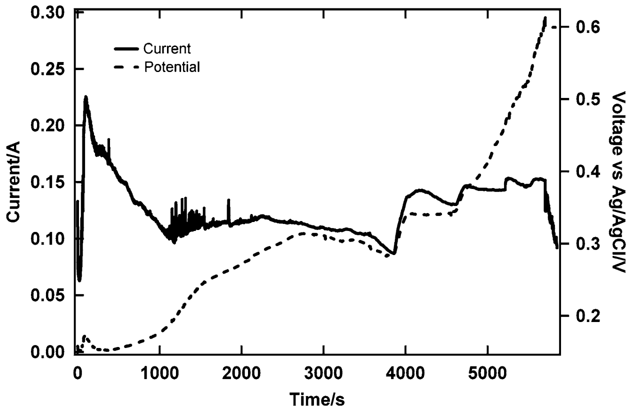

Fig. 6 Bulk electrolysis of a NE solution using the Ag bed electrode. The potential set point was 0.6 V with the measured potential plotted. The solution composition was 0.8 M NE + 0.85 M NaOH + 1.6 M $NaNO_2$. The solution (10 mL) was continuously pumped from the collection flask back to the top of the cell. After the reaction was complete the cell was rinsed with additional 0.5 M NaOH solution to remove remaining product

operated by recirculation of the solution from the collection flask back to the top of the cell so that the solution could be completely reacted. Thus, the cell operated essentially in a batch recirculation mode. More balanced flow and reaction rates should be possible in a more developed system. There were also issues with stability of the Ag bed electrode, where blooming (fine particle formation) occurred, particularly in constant current operation. Those events were correlated with potential excursions above 1 V in constant current operation. Those events led to Ag precipitate formation in the filter exit and collection flask. Thus, best operation could be achieved using a constant potential which would prevent such excursions. A plot of the current and potential versus time for potentiostatic electrolysis at 0.6 V is shown in Fig. 6. As can be seen, the voltage cannot be driven to the set value of 0.6 V due to the limited voltage output (30 V) of the potentiostat. This is an impedance issue for the Ag bed electrode paired with the low voltage output device. This might be remedied by modification of the Ag bed configuration to achieve better electrical contact, or by using a higher voltage power source (less desirable).

The batch electrolysis shown in Fig. 6, after condensation with formaldehyde to form DNPOH, yielded 57.6% molar yield and 75% current efficiency. Those values are in agreement with results previously obtained for the Ag bed electrode [7]. It is thought that this reaction is best suited for a continuous-reaction as the dissolution-reaction and precipitation cycle for Ag might be problematic when the organic concentration is decreased. One could envision the Ag^+ ions diffusing further from the electrode to react at lower starting material concentration. In this case the precipitation for Ag metal may change and form different size particles. Even under the best conditions there were signs of Ag passing through the frit and condensing on the exit tube of the funnel, or in the collection flask. This suggests that a Ag recovery system might be needed for an industrial-scale process. Ag recovery systems are efficient but add to the overall cost of the process and would result is some Ag losses. Problems with Ag loss (about 1%) were described for reactions using $AgNO_3$ as the oxidant [2]. Given that Ag losses were an important cost issue for chemical synthesis viability [2], the $Fe(CN)_6^{-3/-4}$ mediator was investigated.

3.2.2 *$Fe(CN)_6^{-3/-4}$ mediated electrolysis*

$Fe(CN)_6^{-3}$ is another oxidant known to perform well in oxidative nitration reactions. Since the $Fe(CN)_6^{-3/-4}$ couple is a reversible reaction, and has facile electrochemical kinetics, it should be amenable to a mediated process using an electrode. Chemical processes which are currently used to synthesize DNPOH employ a secondary oxidant (sodium persulfate) to regenerate a catalytic amount of $Fe(CN)_6^{-3}$, leading to the conclusion that an electrochemical process was promising. The solubility of the $Fe(CN)_6^{-3/-4}$ mediator has advantages in the simplicity of the reaction and is amenable to standard electrolysis cells. Since the cost of $Fe(CN)_6^{-3}$ is much lower than Ag, losses in the reaction scheme would be much less of an issue. As will be shown below, the $Fe(CN)_6^{-3/-4}$ mediator provided some promising bench-scale results.

Initial experiments were performed using a batch-cell process in the same electrolysis cell used for the direct oxidation experiments. Solutions were prepared with either

Na or K salts (hydroxide and nitrite). The use of potassium salts was ultimately utilized to take advantage of the limited solubility of the K-salt of 1,1-DNE [2]. While the reaction worked well for either cation, the use of K salts coupled with chilling of the cell in an ice bath produced the best results for overall product yield. Figure 7 shows an electrolysis run in K salts performed at 0.6 V for slightly over 2 h using 20 mL of solution. There is a sharp drop in current at 23.7 min (1,427 s) due to precipitate formation of 1,1-DNE product within the anode compartment. The precipitate was yellow in color and formed on surfaces including the electrode which likely resulted in the current drop observed in Fig. 7. The reaction continued at a slower rate with slightly over 2/3 of the theoretical charge being passed before the reaction was stopped. Unlike the Ag powder bed electrode, the potential of 0.6 V was maintained throughout the reaction. Stirring was increased at 4,458 s with very little increase in current. After reaction with excess formaldehyde, a yield of 62% DNPOH was obtained which provided a value of 90% current efficiency. Precipitation of the intermediate product likely improves yield, as the 1,1-DNE product is removed from the solution and prevents further side reaction. Removal of 1,1-DNE product also improves the equilibrium for the reaction. Using a batch cell, the problem with precipitation is that the electrode is coated, decreasing the effective electrode area and reaction rate. In a continuous-loop, the precipitate can be formed in a chilled container separate from the electrolysis cell and thus can be effectively removed from the system without electrode coating.

The continuous-loop concept was tested using the same batch-cell with the anode solution continuously circulated to a separate chilled container (where precipitation of the product occurs) and back to the cell. Figure 8 shows a diagram of the continuously circulated batch-cell configuration which utilizes the same H-cell used in previous work. Solution was removed to a separate chilled container and return back to the cell using small peristaltic pumps. The reaction was performed for 6.79 h at 0.6 V with an initial solution volume of 60 mL, with 5 mL additions of a more concentrated solution (1.6 M NE + 1.7 M KOH + 1.6 M KNO_2) made to the cell where indicated on Fig. 9. The additions increased the solution volume during the test and made balancing the anode and cathode solutions in the H-cell difficult, and some disturbances in the cell are present other than those from solution addition. The anode solution was circulated to the crystallization cell using peristaltic pumps with a flow rate of 4.6 mL/min. The crystallization container was held near 0 °C using a chiller

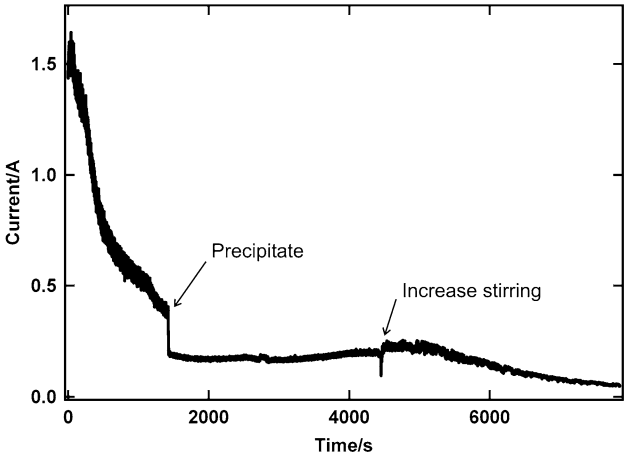

Fig. 7 Bulk electrolysis mediated by $Fe(CN)_6^{-3/-4}$ at 0.6 V. The point where precipitate formed and where solution-stirring rate was increased is noted. The anode solution volume was 20 mL with the following composition: 0.8 M NE + 0.85 M KOH + 3.2 M KNO_2 + 0.16 M $K_4Fe(CN)_6$. The cathode and reference electrode solutions used 0.5 M KOH. The total charge was 2,114.6 C

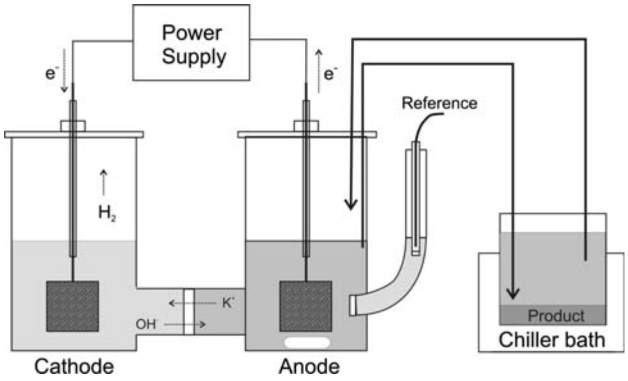

Fig. 8 Diagram of the continuous loop cell employing a separate container for precipitation of the K-salt of 1,1-DNE

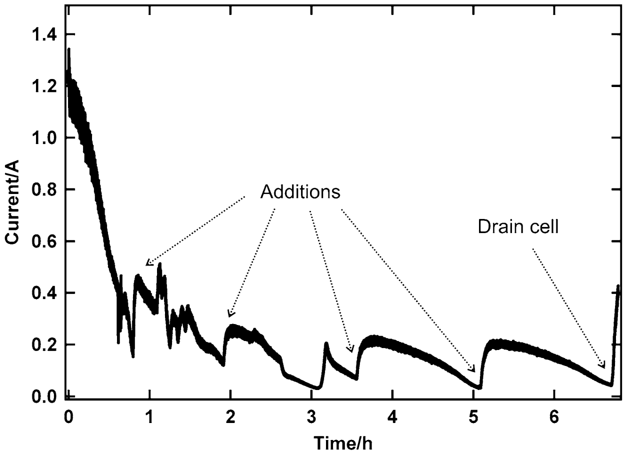

Fig. 9 Current versus time for continuous electrolysis experiment performed at 0.6 V. The initial anode solution composition was 0.8 M NE + 0.85 M KOH + 3.2 M KNO_2 + 0.16 M $K_4Fe(CN)_6$. Solution additions are noted, where 5 mL of the following solution were added: 1.6 M NE, 1.7 M KOH, and 1.6 M KNO_2. Two peristaltic pumps were used to circulate solution to a separate container in a chilled bath (0°C)

bath. The product precipitated in the secondary container placed in an ice bath, forming long needles of bright yellow 1,1-DNE K-salt. Note that the 1,1-DNE K-salt should be kept moist as it has been reported as shock sensitive when dry [2]. This sensitivity was confirmed in recent tests by ATK Launch Systems. After the electrolysis was completed, the precipitate and the spent solution from the electrolysis cell were reacted with excess formaldehyde above pH 10 to produce DNPOH. The total product yield of DNPOH was 57% and the current efficiency was calculated to be 91%. Note that the current increased when the solution was drained (solution from the circulation loop was not returned to the cell) from the cell while still under electrolysis. This is likely from the cathode solution increasing the pH of the anode solution as it flowed into the anode to balance the fluid levels. Maintaining a higher pH is required to maintain the active deprotonated form of the nitroethanate ion. With solution addition, the current was observed to increase indicating that the reaction was not shutting down during the reaction and that the original $Fe(CN)_6^{-3/-4}$ remains active (although diluted by the additions). During the electrolysis, the pH of the solution drops as detected by measurement with pH paper. This is due to the removal of the nitroethanate anion via product formation and subsequent precipitation of the product. In a process environment this can be accounted for by the OH^- created by the counter electrode (H_2 evolution). The solution would be reconstituted by using this OH^- to create the nitroethanate anion, ideally without significant water addition to avoid mediator dilution.

4 Conclusions

The oxidative nitration of NE, a crucial step in production of 2,2-dinitro-1-propanol (DNPOH), was performed using both direct oxidation and mediated electrochemical reactions. To determine total yield of DNPOH, the intermediate product, 1,1-dinitroethane (1,1-DNE) was reacted with formaldehyde in a condensation reaction. The direct oxidation on Pt surfaces was shown to have problems with undesirable by-products and poor overall yield in agreement with previous literature observations. The side reactions appear to occur at the high cell potentials required to drive current for the reaction. Attempts at using mediators to perform the reaction resulted in much lower potentials and much greater product yields with minimal undesired by-product. The two mediators investigated, Ag^+/Ag^0 and $Fe(CN)_6^{-3/-4}$, were chosen due to previous use of the oxidant form in nitration reactions. The Ag^+/Ag^0 mediator required a powder bed electrode that was difficult to operate at ideal conditions. Excellent yields of DNPOH product were achieved using the Ag^+/Ag^0 mediator. The best results were obtained using the $Fe(CN)_6^{-3/-4}$ mediator. Because this mediator is soluble, no special cell requirements were needed. The use of potassium salts of the starting materials enabled an effective separation method for the K-salt of 1,1-DNE. The $Fe(CN)_6^{-3/-4}$ mediator appeared most conducive to industrial implementation. Future studies are planned to investigate pilot-plant scale reaction.

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