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# Electrochemical Synthesis of Adiponitrile from the Renewable Raw Material Glutamic Acid

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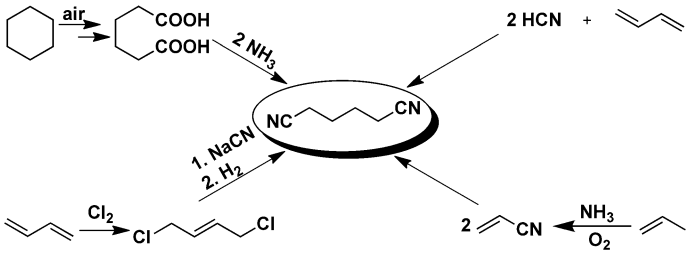
Adiponitrile, the precursor of hexamethylenediamine, is an important bulk chemical,[1] and used for the production of the popular polymer nylon 6.6. In 2005, the global production volume of adiponitrile amounted to about 1.55 million tonnes.[2] Because of its industrial value many methods have been developed for its synthesis. In an early industrial route, adiponitrile is made from adipic acid through dehydration of adipic diamide. More recently, adiponitrile has also been produced from butadiene through chlorination/cyanation or direct cyanation. In addition, adiponitrile can be made through the electrolytic hydrodimerization of acrylonitrile (Scheme 1).[3] Notably, all of these industrial routes for adiponitrile synthesis

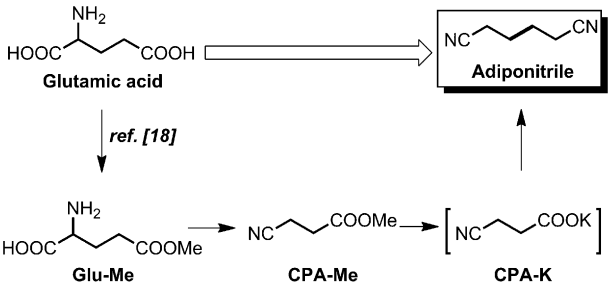



**Scheme 1.** Petroleum-based routes towards adiponitrile.

are based on petroleum resources. They all required external nitrogen sources (i.e., $NH_3$, NaCN, or HCN). However, diminishing fossil fuel resources and increasing environmental concerns have emphasized the need to use renewable raw materials as educts in the fuel and chemical industries.[4] Accordingly, researchers have shown considerable interest in the transformation of biomass into transportation fuels.[5] The conversion of biomass platform molecules into bulk chemicals is also gaining increasing attention.[6] In this context, the production of adiponitrile from renewable materials presents an interesting challenge.

Herein, we demonstrate a biobased synthesis of adiponitrile from glutamic acid (a renewable compound) by using electrochemical methods under mild conditions. The protocol involves (1) the conversion of glutamic acid into glutamic acid 5-methyl ester (Glu-Me), (2) electro-oxidative decarboxylation of glutamic acid 5-methyl ester (Glu-Me) to 3-cyanopropanoic acid methyl ester (CPA-Me), and (3) a one-pot electrochemical synthesis of adiponitrile via Kolbe coupling of potassium 3-cyanopropanoate (CPA-K) generated in situ from 3-cyanopropanoic acid methyl ester (CPA-Me) (Scheme 2).

Electrochemistry has emerged as a powerful tool for numerous industrial-scale transformations.[7] The Kolbe reaction is an important synthetic tool for carbon–carbon bond formation in organic synthesis, on both laboratorial and industrial scales.[8] For example, sebacic acid, an important raw material for polymeric plasticizers, can be obtained from adipic acid via Kolbe coupling. This process has been used on an industrial scale by Asahi Chemical.[9] Also, amino acids constitute alternative sources of nitrogen for nitrogen-containing bulk chemicals.[10] Glutamic acid is considered the most-abundant non-essential amino acid in plant proteins,[11] and in addition has been identified as one of the top 12 biomass-derived platform molecules that can be converted into a variety of value-added chemicals.[12] It can be obtained from the waste streams of dried distillers grains with solubles (DDGS) associated with bioethanol production from wheat and maize.[11] Glutamic acid can also be produced by microbial fermentation.[13] By 2020, the production of glutamic acid as a cheap biobased feedstock is estimated to reach ca. 20 million tonnes per year.[11] Recently, Scott and co-




**Scheme 2.** Biomass-based adiponitrile synthesis from glutamic acid.

workers have reported a series of papers on the production of chemicals from glutamic acid, including γ-aminobutyric acid,[14] acrylonitrile,[11] N-methylpyrrolidone,[15] N-vinylpyrrolidone, and succinonitrile.[16] Our study is inspired by the use of electrochemical methods in industrial synthesis as well as Scott's recent work on the transformation of glutamic acid into value-added compounds. Our study not only shows an alternative route for the synthesis of adiponitrile from glutamic acid based on electrochemical methods, but also gives an additional example of the use of electrochemical techniques in the transformation of biomass into chemicals.[17]

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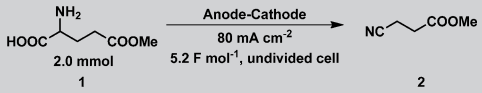
A facile procedure for the conversion of glutamic acid into glutamic acid 5-methyl ester (Glu-Me) was previously reported by Baldwin and co-workers.[18] Hence, we investigated the electrochemical synthesis of adiponitrile starting from (Glu-Me). In order to make 3-cyanopropanoic acid methyl ester (CPA-Me) from Glu-Me, Scott and co-workers recently demonstrated oxidative decarboxylation of Glu-Me by using sodium hypochlorite in the presence of a catalytic amount of sodium bromide.[16] However, the need for stoichiometric amounts of sodium hypochlorite is considered a drawback of this method.[16,19] Electrochemical methods generally enable transformations to occur under mild conditions without the use of strong, hazardous chemical reagents.[20] Thus, oxidative decarboxylation without the use of sodium hypochlorite may be achieved by the application of electro-organic synthesis techniques.

Our work started with the electro-oxidative decarboxylation of Glu-Me **1** to CPA-Me **2**. We initially chose platinum and graphite as anode and cathode, respectively. Notably, bromide salts have served both as the supporting electrolyte and as mediator in anodic oxidations.[21] Treatment of Glu-Me **1** with sodium bromide at a current density of 80 mA cm$^{-2}$ in MeOH at room temperature led to electro-oxidative decarboxylation, providing CPA-Me **2** in 33% yield (Table 1, entry 1). Optimization of the solvents revealed that a mixture of MeOH/$H_2O$ in a 4:1 ratio (*v*/*v*) was a better solvent, increasing the yield of CPA-Me **2** to 60% (entries 2–9). Next, we examined other bromide salts, and found that the use of salts including LiBr·$H_2O$, KBr, $Me_4NBr$, $Et_4NBr$, and $Bu_4NBr$ could also effect the reaction, but the yields of CPA-Me **2** remained low (entries 10–14). Also, when other halide salts such as NaCl or NaI were employed, the yields of the desired CPA-Me **2** were only 19% and 16%, respectively (entries 15 and 16). When platinum was used as cathode instead of graphite, the yield of CPA-Me **2** increased dramatically (entries 17 and 19–21). To our delight, when the reaction was conducted at 0 °C, the desired product CPA-Me **2** was obtained in 91% yield (entry 18).

**Table 1.** Electro-oxidative decarboxylation of glutamic acid 5-methyl ester to 3-cyanopropanoic acid methyl ester.[a]




| Entry | MX | Anode–cathode | Solvent | Yield[b] [%] |
|---|---|---|---|---|
| 1 | NaBr | Pt–C | MeOH | 33 |
| 2 | NaBr | Pt–C | MeOH/$CH_3CN$ (1:1) | 50 |
| 3[c] | NaBr | Pt–C | MeOH/DMF (1:1) | 20 |
| 4 | NaBr | Pt–C | MeOH/$H_2O$ (1:1) | 55 |
| 5 | NaBr | Pt–C | $CH_3CN$/$H_2O$ (1:1) | 35 |
| 6 | NaBr | Pt–C | MeOH/$H_2O$ (4:1) | 60 |
| 7[d] | NaBr | Pt–C | MeOH/$H_2O$ (4:1) | 36 |
| 8[e] | / | Pt–C | MeOH/$H_2O$ (4:1) | 0 |
| 9 | NaBr | Pt–C | EtOH/$H_2O$ (4:1) | trace |
| 10 | LiBr·$H_2O$ | Pt–C | MeOH/$H_2O$ (4:1) | 42 |
| 11 | KBr | Pt–C | MeOH/$H_2O$ (4:1) | 46 |
| 12 | $Me_4NBr$ | Pt–C | MeOH/$H_2O$ (4:1) | 58 |
| 13 | $Et_4NBr$ | Pt–C | MeOH/$H_2O$ (4:1) | 49 |
| 14 | $Bu_4NBr$ | Pt–C | MeOH/$H_2O$ (4:1) | 36 |
| 15 | NaCl | Pt–C | MeOH/$H_2O$ (4:1) | 19 |
| 16 | NaI | Pt–C | MeOH/$H_2O$ (4:1) | 16 |
| 17 | NaBr | Pt–Pt | MeOH/$H_2O$ (4:1) | 72 |
| **18**[f] | **NaBr** | **Pt–Pt** | **MeOH/$H_2O$ (4:1)** | **91 (76)**[g] |
| 19 | KBr | Pt–Pt | MeOH/$H_2O$ (4:1) | 65 |
| 20 | $Me_4NBr$ | Pt–Pt | MeOH/$H_2O$ (4:1) | 70 |
| 21 | NaBr | Pt–Pt | $CH_3CN$/$H_2O$ (1:1) | 54 |

[a] Reaction conditions: L-glutamic acid 5-methyl ester (2.0 mmol), MX (3.0 mmol) in solvent (10 mL) was electrolyzed at a current density of 80 mA cm$^{-2}$ in an undivided cell at room temperature. The cell voltage was 5–10 V. [b] GC yields were determined with the use of succinonitrile as an internal standard. [c] DMF = *N*,*N*-Dimethylformamide. [d] 20 mmol% NaBr was used. [e] 0.5 mmol $Bu_4NPF_6$ was used as the supporting electrolyte. [f] Reaction was conducted at 0 °C. [g] Current efficiency in parentheses.

With these results in hand, we turned our attention to the electrochemical synthesis of adiponitrile via Kolbe coupling from CPA-Me **2**. First, CPA-Me **2** was converted to CPA-K **3** by saponification (see Supporting Information).[22] Because the current density plays an important role in Kolbe coupling,[23] we next optimized the current density for the electrochemical synthesis of adiponitrile **4** via Kolbe coupling of CPA-K **3**. Initially, the MeOH solution of CPA-K **3** was electrolyzed at current densities of 60, 120, 180, 240, 300, and 360 mA cm$^{-2}$, respectively.[24] The desired product adiponitrile **4** was obtained after 6.7 F mol$^{-1}$ of electricity passed, however, the yields were only 30 to 45%. This can be attributed to the poor solubility of the product forming at the surface of the platinum anode, decreasing the efficiency of the Kolbe coupling. In order to keep the surface of the platinum anode clean, we chose acetone as a co-solvent with MeOH for Kolbe coupling of CPA-K **3**.[25] Indeed, the yield of adiponitrile **4** was effectively improved. As shown in Figure 1, the yield of the desired product **4** was 65% at a current density of 180 mA cm$^{-2}$ with MeOH/acetone (1:1) as solvent at room temperature.

In an attempt to increase the efficiency of the conversion of CPA-Me **2** to adiponitrile **4**, we next tried to combine the saponification reaction and Kolbe coupling in a single step. Treatment of CPA-Me **2** with the corresponding base in MeOH at 60 °C for 30 min caused the full conversion of CPA-Me **2** to CPA-M (M = K, Li, $Me_4N$, etc.). Various conditions for Kolbe coupling of CPA-M were examined to optimize the reaction conditions (Table 2). Furthermore, it was found that the best ratio of MeOH/acetone was 1:1 (*v*/*v*; entries 2–4). The desired product **4** was obtained in inferior yields when using $H_2O$, $CH_3CN$, DME, or HFIP as the co-solvent (entries 5–10). Temperature is not considered a critical variable but may improve transport in electrodecarboxylation. An increase of the temperature usually gives a higher yield in Kolbe couplings.[23] Indeed, when the reaction was carried out at a lower temperature (0 °C), the desired product **4** was obtained in lower yield (entry 11). In contrast, the yield of the desired product **4** increased to 78% at 60 °C (entry 13). We also used a divided cell to reduce the reduction reaction in the undivided cell. Unfortunately the yield of **4** was not increased effectively (entry 12). The organic base $Me_4NOH$ also gave the product **4** in a moderate yield (entry 14).

Finally, we combined all the reactions and tested the full process for the synthesis of adiponitrile from glutamic acid

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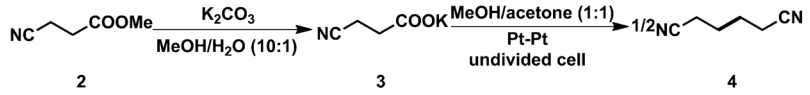


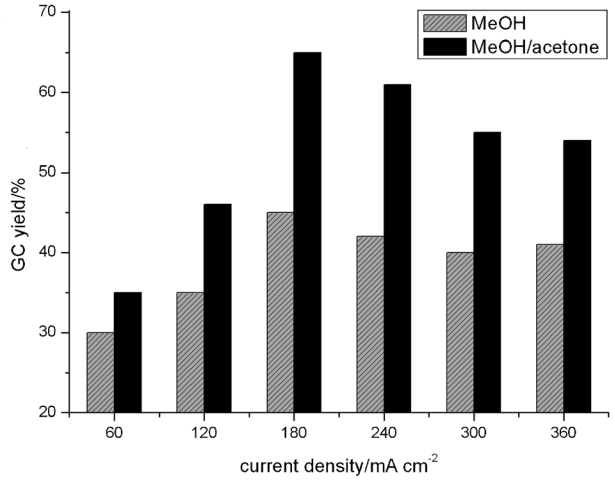
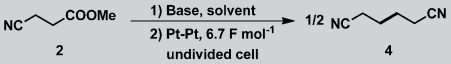




**Figure 1.** Optimization of the current density for Kolbe coupling. GC yields were determined with the use of phthalonitrile as an internal standard.

**Table 2.** One-pot synthesis of adiponitrile via Kolbe coupling of 3-cyanopropanoic acid salts form 3-cyanopropanoic acid methyl ester.[a]




| Entry | Base | Solvent | Yield [%][b] |
|---|---|---|---|
| 1 | KOH | MeOH | 40 |
| 2 | KOH | MeOH/acetone (1:1) | 65 |
| 3 | KOH | MeOH/acetone (4:1) | 55 |
| 4 | KOH | MeOH/acetone (1:4) | 37 |
| 5 | LiOMe | $MeOH/H_2O$ (4:1) | 11 |
| 6 | NaOMe | $MeOH/H_2O$ (4:1) | 15 |
| 7 | KOH | $MeOH/H_2O$ (4:1) | 33 |
| 8 | KOH | $MeOH/CH_3CN$ (1:1) | 42 |
| 9[c] | KOH | MeOH/DME (1:1) | 52 |
| 10[d] | $Me_4NOH$ | MeOH/HFIP (1:1) | 56 |
| 11[e] | KOH | MeOH/acetone (1:1) | 42 |
| 12[f] | KOH | MeOH/acetone (1:1) | 66 |
| **13[g]** | **KOH** | **MeOH/acetone (1:1)** | **78 (29)[h]** |
| 14[g] | $Me_4NOH$ | MeOH/acetone (1:1) | 75 |

[a] Reaction conditions: 3-cyanopropanoic acid methyl ester (2.0 mmol), base (3.0 mmol) in solvent (10 mL) at 60 °C for 30 min yield the corresponding 3-cyanopropanoic acid salts and the mixture was electrolyzed at a current density of 180 mA $cm^{-2}$ in an undivided cell at room temperature. The cell voltage was 7–15 V. [b] GC yields were determined with the use of phthalonitrile as an internal standard. [c] DME = 1,2-dimethoxyethane. [d] HFIP = Hexafluoroisopropanol. [e] Reaction was conducted at 0 °C. [f] H-type divided cell with cation exchange membrane was used, the distance between two platinum electrodes was 8 cm. [g] Reaction was conducted at 60 °C (Close to the boiling point of the solvent), 3.4 F $mol^{-1}$ of electricity passed. [h] Current efficiency in parentheses.

(Figure 2).[24] Although industrial-scale synthesis of adiponitrile is beyond the scope of this Communication, the overall yield of adiponitrile from glutamic acid was found to be 58%.

In summary, we demonstrate electrochemical routes for the synthesis of adiponitrile from the biomass-derived compound glutamic acid by using electro-oxidative decarboxylation and Kolbe coupling reactions. This work serves as another example of the versatility of the substrate glutamic acid in the transformation of biomass into chemicals, and of the use of electrochemical methods to effect such transformations. Further studies on the conversion of biomass into chemicals by electrochemical methods are ongoing in our laboratory.

## Experimental Section

**General experimental procedure for the electro-oxidative decarboxylation:** The electro-oxidative decarboxylation of L-glutamic acid 5-methyl ester (Glu-Me) was carried out in an undivided cell (ca. 20 mL vial) equipped with two platinum electrodes (1.0×1.0 cm). The distance between the electrodes was 5 mm. L-glutamic acid 5-methyl ester (Glu-Me) (2.0 mmol), sodium bromide (3.0 mmol) was placed in an undivided cell. Then MeOH (8.0 mL) and $H_2O$ (2.0 mL) were added with a syringe. A constant current (80 mA $cm^{-2}$, the cell voltage 5–10 V) was passed through the cell at the appointed temperature and the mixture was stirred. After 5.2 F $mol^{-1}$ electricity had passed, the solvents ($MeOH/H_2O$) were removed and then diethyl ether (30 mL) was added to the mixture. The organic layers were washed with water (2×30 mL), then with brine, dried over $MgSO_4$, and filtered. Then the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **2** in 88% yield. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 2.62$ (m, 4H), 3.68 ppm (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 12.87$ 29.67 52.25 118.53 170.55 ppm. HRMS (EI) Calcd for $C_5H_7NO_2$ [*M*]: 113.0477, Found: 113.0476 (Table 1, entry 18).

**General experimental procedure for the one-pot synthesis of adiponitrile:** 3-cyanopropanoic acid methyl ester (CPA-Me) (2.0 mmol), KOH (3.0 mmol), and 5.0 mL MeOH were placed in a 20 mL vial. The mixture was heated at 60 °C for 30 min, yielding the corresponding potassium 3-cyanopropanoate (CPA-K) (GC analysis showed full conversion). After the reaction, another 5.0 mL acetone as the co-solvent was added by a syringe. Then two platinum electrodes (1.0×1.0 cm) were equipped in the cell with a 180 mA constant current applied and the mixture was stirred at 60 °C. The distance between the electrodes was 5 mm. After 3.4 F $mol^{-1}$ electricity had passed, the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **4** in 74% yield. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.77$ (m, 4H), 2.38 ppm (m, 4H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 16.52$ (2C) 24.17 (2C) 118.85 ppm (2C). HRMS (EI) Calcd for $C_6H_9N_2$ [*M*+H]: 109.0766, Found: 109.0770 (Table 2, entry 13).

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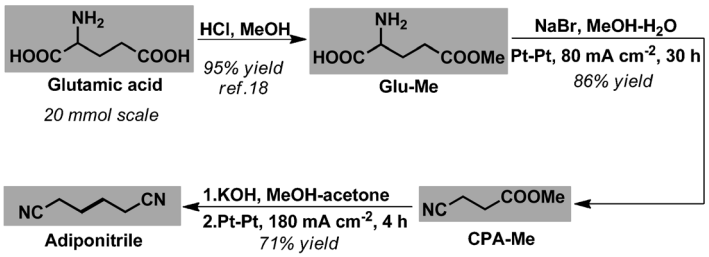


**Figure 2.** Full process for synthesis of adiponitrile.

## *Acknowledgements*

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**Keywords:** biomass · electrochemistry · nitrogen · renewable resources · sustainable chemistry

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