Supporting information

**Gamma-Aminobutyric Acid-Functionalized Naphthalene Diimide for Aqueous Organic Flow Batteries**

Mahsa Shahsavan *, Cedrik Wiberg * and Pekka Peljo *

* Research Group of Battery Materials and Technologies, Department of Mechanical and Materials Engineering, Faculty of Technology, University of Turku, 20014 Turku, Finland

* Corresponding author: pekka.peljo@utu.fi

**Synthesis of GABA-NDI**

For synthesizing GABA-NDI, 40 g of 1,4,5,8-naphthalenetetracarboxylicacid dianhydride (TCI) and 30.76 g of gamma-aminobutyric acid (Sigma Aldrich) were added to a 250 ml round-bottom flask. 100 ml of DMSO (VWR) was added, and the temperature was raised to 100 °C under stirring – the mixture started as a suspension but dissolved as the temperature increased. The solution turned first green, then black, and after two hours, the reaction mixture was poured into deionized water resulting in brown precipitation, which was the product. The product was filtered and washed with generous amounts of water before leaving to dry under a vacuum at 35 °C overnight (yield: 91%). The reaction is shown in Figure S1-a.

*Elemental analysis for GABA-NDI: Calculated [C 60.28, H 4.14, N 6.39]- Found [C 59.97, H 4.15, N 5.82]*

*Figure S1-b: $^1$H NMR (500 MHz, DMSO) δ 12.034 (s, 2H), 8.667 (s, 4H), 4.132-4.105 (t, J = 6.9258, 4H), 2.362-2.333 (t, J=7.324, 4H), 1.955-1.898 (quint, 4H).*

![Reaction diagram](attachment:image.png)
Figure S1- a) GABA-NDI synthesis procedure. b) 1H NMR spectra after the synthesis of GABA-NDI in DMSO

**Cyclic Voltammetry (CV)**

A glassy carbon working electrode (3 mm in diameter, BASI) was polished with alumina (0.05 μm, Buehler) and sonicated for one minute before each experiment. An Ag/AgCl reference electrode (3 M KCl, Redox.me) with the potential of 212 mV vs. SHE was used with a platinum wire as a counter electrode. Voltammograms at scan rates of 20, 50, 75, 100, 250, and 500 mV/s were collected with a 90% iR-correction by positive feedback. A Gamry Reference 600 potentiostat was used for CV measurements, and all measurements were done in triplicate.

**Rotating Disk Electrode (RDE)**

A glassy carbon working electrode (5 mm in diameter, Metrohm) was polished with alumina (0.05 μm, Buehler) and sonicated for one minute before each experiment. An Ag/AgCl reference electrode (3 M KCl, Redox.me) with the potential of 212 mV vs. SHE was used as a reference electrode with a platinum wire as a counter electrode. Voltammograms were collected with a 90% iR-correction by positive feedback at the rotation rates of 400, 900, 1600, 2500, and 3600 rpm and the scan rate of 5 mV/s. An Autolab RDE motor and Gamry Reference 600 potentiostat were used for RDE measurements, and measurements were done in triplicate. The viscosity measurement is done with the AMETEK Brookfield DVE viscosity meter.

**Flow battery measurements**

A flow battery cell made in-house with flat flow fields and 5 cm² carbon felt electrodes was used for the cycling test. The carbon felts were 4.6 mm in thickness and were used without pre-treatment and compressed to 3 mm. The membrane was soaked in the used supporting electrolyte for one day before assembling the battery. A peristaltic pump (Chonry BT600M) was calibrated with Masterflex C-Flex tubing (Cole-Parmer) with a flow rate of 60 ml/min. The two glovebox batteries were placed in the glovebox purged with nitrogen (MBRAUN). After circulating the battery with electrolytes for an hour, the ohmic resistance at the open circuit potential was determined using impedance spectroscopy with a BioLogic SP-300 potentiostat. For battery measurements, a LANHE Battery tester 400 W was used. Deionized water was used to prepare the electrolytes, and the electrolytes for the glovebox batteries were degassed.
and purged with nitrogen before being cycled. In the air and unbuffered batteries, 1 M ammonium chloride and in the buffered battery, 1 M ammonium chloride and 0.5 M ammonium phosphate were used as supporting electrolytes. Before cycling the air battery and unbuffered battery, the pH on the negative electrolyte was adjusted to 8.5 by adding ammonia to the electrolyte. When making the supporting electrolyte for the buffered battery, the pH was adjusted to 8.5 by adding ammonia. The pH on the positive electrolyte was 6.5 in the unbuffered battery and the air battery, and it was 8.5 in the buffered battery. An excess of positive electrolyte was used to ensure that the negative electrolyte was the limiting side. Charge and discharge cut-offs were 1.25 V and 0.15 V, respectively. However, the chosen cut-offs were corrected by the ohmic resistance for cycling at each current density for the flow battery measurements based on the resistance measured by impedance spectroscopy. The procedure for cycling the two glovebox batteries was as follows: Firstly, three activation cycles at 60 mA/cm$^2$ were applied. Then, each battery was cycled for three galvanostatic charging/discharging cycles at varying current densities from 20, 40, 60, 80, and 100 mA/cm$^2$. Finally, to investigate the stability of the system, a larger number of galvanostatic charging/discharging at 60 mA/cm$^2$ were performed. The air battery was only cycled at 60 mA/cm$^2$.

**Electrochemistry of GABA-NDI**

![Figure S2: Scan rate normalized CVs of 5 mM GABA-NDI in 1 M NH$_4$Cl](image)
Figure S3- RDE of 1 mM GABA-NDi in 1 M NH₄Cl at different rotation rates

Table S1- First and second reduction currents from RDE voltammograms of 5 mM GABA-NDi in 1 M NH₄Cl

| 1ˢᵗ reduction current (µA) | 2ⁿᵈ reduction current (µA) | 1ˢᵗ/2ⁿᵈ  |
|---------------------------|-----------------------------|----------|
| -40.06                    | -27.18                      | 1.47     |
| -63.24                    | -39.43                      | 1.60     |
| -90.59                    | -50.41                      | 1.80     |
| -123.13                   | 60.33                       | 2.04     |
| -162.05                   | 68.98                       | 2.35     |
**Analysis of ion-exchanged ammonium ferrocyanide**

**Table S2- Elemental analysis of ammonium ferrocyanide**

|           | C    | H    | N     |
|-----------|------|------|-------|
| Calculated| 17.57| 7.37 | 34.15 |
| Found in sample 1 | 24.50 | 4.06 | 36.38 |
| Found in sample 2 | 20.02 | 2.60 | 25.54 |

**Table S3- ICP analysis of ammonium ferrocyanide**

|                         | Fe (mg/l) | Na (mg/l) |
|-------------------------|-----------|-----------|
| Found in sample 1 (0.4133 g) | 492.6     | 379.0     |
| Found in sample 2 (0.3987 g) | 426.4     | 466.4     |

**Table S4- Amount of sodium and ammonium in the ammonium ferrocyanide samples**

|                         | Na %   | NH₄ %  |
|-------------------------|--------|--------|
| Found in sample 1 (0.4133 g) | 46.83  | 53.17  |
| Found in sample 2 (0.3987 g)     | 66.58  | 33.42  |
Figure S5- CV of 5 mM of different ferrocyanide salts: \( \text{K}_4\text{Fe(CN)}_6 \) in 1 M KCl, \( \text{Na}_4\text{Fe(CN)}_6 \) in 1 M NaCl, \( \text{(NH}_4\text{)}_4\text{Fe(CN)}_6 \) in 1 M NH\(_4\)Cl at 100 mV/s

**Cycling results**

Figure S6- CVs of 5mM GABA-NDI and 5 mM ammonium ferrocyanide in 1 M NH\(_4\)Cl and the average voltage between them
Figure S7- Charging and discharging curves of the buffered battery (negative electrolyte: 13 mL of 200 mM GABA-NDi in buffer solution, positive electrolyte: 30 mL of 200 mM ammonium ferrocyanide in buffer solution)

Figure S8- Charging and discharging curves of the unbuffered battery (negative electrolyte: 10 mL of 200 mM GABA-NDi in 1 M NH₄Cl, positive electrolyte: 30 mL of 200 mM ammonium ferrocyanide in 1 M NH₄Cl)
Figure S9- Voltage-time plots for the unbuffered battery from cycle 273 to 276; a slight voltage depression can be seen at the beginning of each curve.

Figure S10- Continuation of cycling of the air battery in the glovebox for 1000 cycles (negative electrolyte: 10 mL of 200 mM GABA-NDI in 1 M NH₄Cl, positive electrolyte: 30 mL of 200 mM ammonium ferrocyanide in 1 M NH₄Cl). Cycle 590 is the cycle where 10 mL of 200 mM ammonium ferrocyanide in the supporting electrolyte is added to the positive electrolyte.
Due to the net transfer of water to the positive side, DI water was added to the negative side to check if the capacity could be retrieved, but as it can be seen, there is a continuous water transport to the positive side, which results in the capacity fade.

**Post-mortem analysis**

| pH on negative electrolyte before cycling | pH on negative electrolyte after cycling | pH on positive electrolyte before cycling | pH on positive electrolyte after cycling |
|------------------------------------------|-----------------------------------------|------------------------------------------|------------------------------------------|
| buffered battery                         | 8.5                                    | 7.7                                      | 8.5                                      |
| unbuffered battery                       | 8.5                                    | 7.5                                      | 6.5                                      |

To prove if the pH-drop in the batteries was due to the evaporation of ammonia, the supporting electrolytes used in our batteries were placed in the glovebox antechamber. After degassing the solutions for three times, as was done for the battery electrolytes, the pH was measured again. The pH drop in all the solutions indicates that ammonia evaporates from the solution during the degassing. Moreover, ammonia can continuously evaporate from the solution during the cycling to reach the equilibrium at lower pHs.

| pH on supporting electrolyte before degassing | pH on supporting electrolyte after degassing |
|----------------------------------------------|----------------------------------------------|
| buffered supporting electrolyte              | 8.55                                         | 8.26                                         |
| NH₄Cl+NH₃                                    | 8.51                                         | 8.21                                         |
| NH₄Cl                                        | 5.01                                         | 4.95                                         |
Figure S12 - Carbon felt after a) buffered battery, b) unbuffered battery

Figure S13 - CVs of the GABA-NDi after cycling at 100 mV/s (concentrations are unknown)
Figure S14- Full range CVs on negative electrolyte after cycling of the batteries at 100 mV/s (concentrations are unknown)

Figure S15- Full range CVs on the positive electrolyte after cycling of the batteries at 100 mV/s (concentrations are unknown)
$^1$H NMR results on GABA-NDI show the appearance of a new peak at around 2.7 ppm that may be a result of decomposition. However, the peak integral is very small compared to the GABA-NDI main peaks and since the capacity loss is very small in the batteries, the decomposition mechanism cannot be identified.
Figure S16. $^1$H NMR spectra of GABA-NDI in 10% D$_2$O a) before cycling in the battery. b) after cycling in the buffered battery. c) after cycling in the unbuffered battery. d) after cycling in the air battery.

$^1$H NMR on precipitated material on the carbon felt in D$_2$O

$^1$H NMR results on precipitated material on the carbon felt shows exactly the same peaks as the GABA-NDI and therefore the percipitated materials is GABA-NDI.
Measuring the solubility of GABA-NDI:

For measuring the solubility of GABA-NDI in DI water, $^1$H NMR with internal standard (2.4 mM 3-(trimethylsilyl)propionic-2,2,3,3 acid sodium salt D4 (TSP-d4), δ 0.00 (s, 9H),) was used. First, a saturated solution of GABA-NDI in DI water was made. Then it was diluted 10 times and the NMR spectrum was obtained. Finally, by taking one of GABA-NDI peak integrals in the aliphatic region into account, a solubility of 587 mM could be calculated for GABA-NDI in DI water.

Calculations are as follow:

TSP-d4 peak located at δ 0.00 (s, 9H) with an integral of 9.192 is equal to 2.4 mM of protons and the GABA-NDI peak located at δ 1.955-1.898 (quint, 4H) has an integral of 100 so the integral represents 234.99 mM of protons. As each GABA-NDI molecule has four aromatic protons, the concentration of the diluted GABA-NDI would be 58.75 mM and therefore concentration of the saturated solution is 587 mM.
Electrochemical and physical properties of different NDI derivatives:

Table S7- Properties of negatively charged NDI derivatives

| Compound          | First Reduction Potential (V vs. SHE) | Second Reduction Potential (V vs. SHE) | Solubility                                      | Ref   |
|-------------------|---------------------------------------|----------------------------------------|-------------------------------------------------|-------|
| K²-BNDI           | -0.2                                  | -0.47                                  | in DI water: 167 mM in 1 M KCl: 30 mM            | 17    |
| Na²-BNDI          | -0.2                                  | -0.47                                  | in DI water: ~ 210 mM in 1 M NaCl: ~ 40 mM       | 17    |
| GABA-NDI          | -0.12                                 | -0.43                                  | in DI water: 587 mM in 1 M NH₄Cl: 250 mM         | This work |

Performance of different NDI-based flow batteries:

Table S8- Flow battery performance of NDI molecules

| Negative electrolyte, concentration | Positive electrolyte, concentration | Supporting electrolyte, membrane | Cycling time (days)a | Average capacity utilization (%) | Average energy efficiency (%) | Ref |
|-------------------------------------|-------------------------------------|----------------------------------|----------------------|---------------------------------|-------------------------------|-----|
| K²-BNDI, 25 mM                     | 4-OH-TEMPPO, 100 mM                 | 1 M KCl, AEM                     | 1.25                 | ~ 75                            | ~ 80 at 10 mA/cm²             | 17  |
| Na²-BNDI, 40 mM                    | 4-OH-TEMPPO, 160 mM                 | 1 M NaCl, AEM                    | 4.1                  | ~ 52.5                          | -                             | 17  |
| 2H-NDI, 50 mM                      | BTMAP-Fc, 50 mM                     | 1 M NH₄Cl + 0.5 M ammonium phosphate, AEM | 3.9            | ~ 89                            | ~ 82 at 10 mA/cm²             | 9   |
| 2H-NDI, 500 mM                     | BTMAP-Fc, 500 mM                    | 1 M NH₄Cl + 0.5 M ammonium phosphate, AEM | 8.8             | ~ 82.5                          | ~ 62 at 25 mA/cm²             | 9   |
| 2DMA-NDI, 50 mM                    | BTMAP-Fc, 50 mM                     | 1 M KCl + 0.5 M potassium phosphate, AEM | 1.47             | ~ 82.5                          | ~ 90 at 10 mA/cm²             | 9   |
| 2DMA-NDI, 500 mM                   | BTMAP-Fc, 500 mM                    | 1 M NH₄Cl + 0.5 M ammonium phosphate, AEM | 4.06             | ~ 91                            | ~ 93.5 at 10 mA/cm²           | 9   |
| GABA-NDI, 200 mM                   | (NH₄)₄Fe(CN)₆, 200 mM               | 1 M NH₄Cl, CEM                   | 9                    | ~ 97                            | 80 at 60 mA/cm²               | This work |
| GABA-NDI, 200 mM                   | (NH₄)₄Fe(CN)₆, 200 mM               | 1 M NH₄Cl + 0.5 M ammonium phosphate, CEM | 8.2             | ~ 92                            | 79 at 60 mA/cm²               | This work |

a: Cycling times are calculated based on the data presented in the reference 9 (Figure 5 and 6) and reference 17 (Figure 4,5,6,8).