Electronic Supplementary Information for

Electrochemical Nitrogen Reduction to Ammonia under Mild Conditions Enabled by a Polymer Gel Electrolyte

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Materials and Methods

Catalyst Synthesis

The catalysts were synthesized by alcohol reduction method, in which Pt or Ir is reduced on the surface of carbon Vulcan XC-72 (100%, obtained as a sample from Cabot).[1] 0.5 g of Carbon Vulcan XC-72 was dispersed in 200 mL of ethylene glycol (99% Purity, Purchased from Fisher Scientific) in a 500 mL round bottom flask by agitation for 2 hours in a Branson 2800 Ultrasonic Bath, after which a solution of metal salt in ethylene glycol was added to the dispersion. The metal salt was either $IrCl_3{\cdot}3H_2O$ (53-56% Ir, Purchased from Acros Organics) for the Ir catalyst synthesis, or $H_2PtCl_6{\cdot}6H_2O$ (99.9% Purity, Purchased from Alfa Aesar) for the Pt catalyst synthesis. The Pt catalyst was prepared to 50 wt% metal on carbon, the Ir catalyst to 35%. For the Pt catalyst, 7.6 mL of 1 M KOH (Purchased from Fisher Scientific, certified 0.995-1.005 N) solution was added to balance the acidity of the salt for every 1 g of Pt salt in the solution. After stirring for 30 minutes using a magnetic stir bar, the mixture was heated to 180 °C. The temperature was maintained using a temperature controller, and stirring was continued for 16 hours, after which heat was reduced and the catalyst was allowed to cool to room temperature. The catalyst was recovered from the ethylene glycol suspension using vacuum filtration with a polyamide membrane filter with a 0.2 µm pore size (Purchased from Sartorius) followed by washing with H_2O. Washing was done by agitating the catalyst in deionized (DI) H_2O, followed by centrifuging for 45 minutes at 5000 rpm using a Thermo Scientific Sorvall Legend X1 Centrifuge, after which the water was drained and the process repeated two more times to fully remove the ethylene glycol. The catalyst was then dried at 110 °C and -0.08 MPa gage pressure. The catalyst was next characterized by transmission electron microscopy (TEM) shown in the main body of the report, and energy dispersive X-ray spectroscopy (EDX), which is shown in figure S3. A JEM JEOL-2100F high resolution transmission electron microscope (HRTEM) operated at 200 kV was used for imaging. In order to characterize the materials, AMETEK EDAX was applied by using TEAMTM EDS Analysis System for TEM. The average size of the Ir nanoparticles based on the TEM images is approximately 2.3 nm in diameter, and the average size of the Pt nanoparticles is approximately 5.3 nm in diameter.

Electrode Preparation

The catalyst ink for spraying was made by depositing 0.4 g of the catalyst produced on carbon support in 65 g of isopropanol (Laboratory grade, purchased from Fisher). Next 0.1 g of the ionomer FAA-3 (purchased from Fumatech), which had been dissolved in methanol (99.9% purchased from Fisher) to form a 10 wt% solution, was added to the ink mixture (in other words, 1g was added of the 10 wt% solution). This resulted in a ratio of catalyst and support to ionomer which was 4:1. Finally the ionomer and catalyst were dispersed in the isopropanol by agitating in the ultrasonic bath for 1 hour, followed by mixing using an IKA T18 D S1 ultrasonic horn at 9000 rpm for 15 minutes, this cycle of agitation bath followed by mixing in the horn was repeated until there was no sediment remaining in the mixture, indicating that the ink was fully dispersed. Whenever the ink was to be used again it was re-dispersed in the same way. The ink was sprayed on the microporous layer (MPL) of the gaseous diffusion electrode (GDE) material while the material was held at approximately 90 °C on a hot plate and was sprayed using a master brand airbrush model G22.

Electrochemical Setup

The electrochemical cell setup used was a Scribner Associates liquid fuel cell test fixture using electrodes with a 5 cm^2 surface area. The Celgard® 3401 polypropylene porous separator was obtained as a sample from Celgard. Both the N_2 and H_2 gasses were 5.0 ultra high purity, purchased from Praxair. KOH used to make the electrolyte was made from pellets purchased from Fisher scientific (purity ≥ 85%) the polyacrylic acid homopolymer was obtained as a sample from Lubrizol of Carbopol Ultrez 30. The electrolyte was prepared by combining 10 mL of 6 M KOH solution with 0.58 g of the homopolymer Ultrez 30 and mixing. This was done slowly, with approximately a third of the polymer powder being added to the KOH solution at a time before mixing. After all of the polymer had been added, the electrolyte was allowed to set for several hours until it was visibly homogeneous, at which point it was centrifuged at 4000 rpm for 1 minute to remove any air bubbles leaving a transparent homogeneous gel. 6 M KOH was used because KOH shows the highest ionic conductivity at that concentration The GDE material used for the anode was CeTech carbon cloth with a MPL on one side, and was purchased from Fuelcellstore.com, the material for the cathode was Freudenberg carbon paper H23C6 which is a GDE with an MPL and a hydrophobic treatment also purchased from Fuelcellstore.com. Potential for the experiments was controlled using an Arbin Instruments BT-2000.

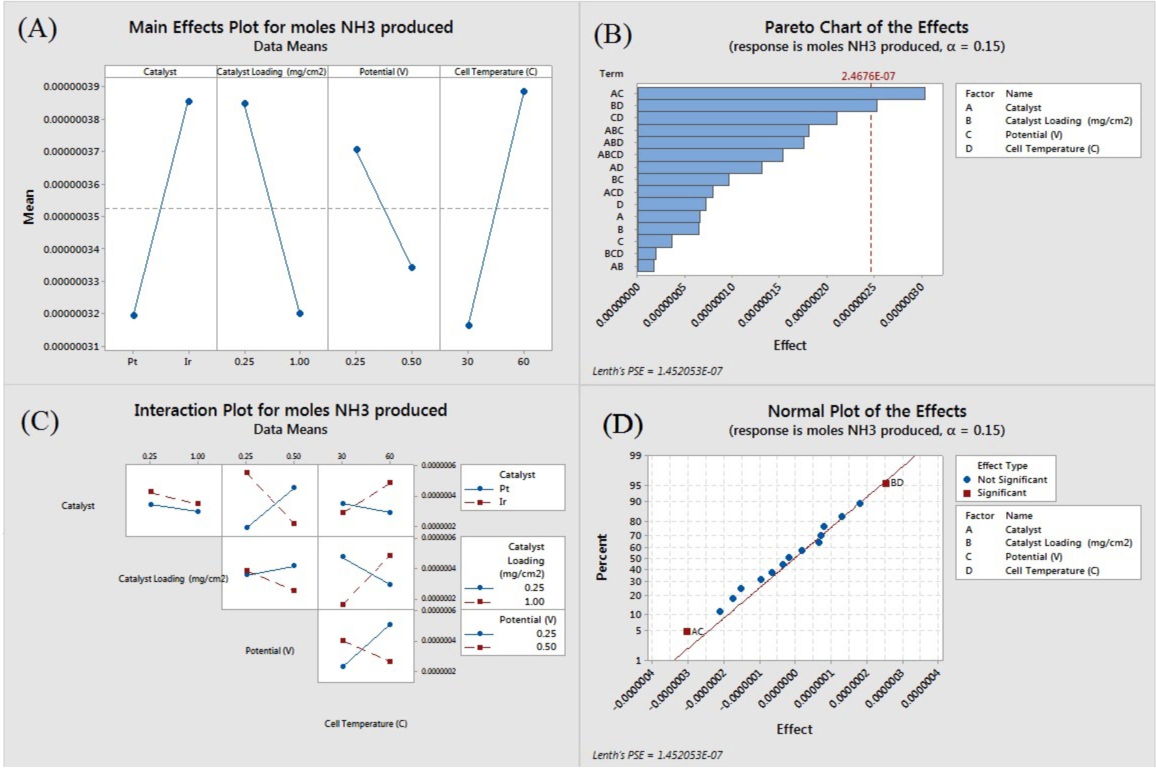
Ammonia Determination

Ammonia was captured in an acid trap using dilute sulfuric acid (66° baumé, purchased from Fisher Scientific) and was detected via a reaction with excess phenol (99%, purchased from Acros Organics) and sodium hypochlorite (99%, purchased from Fisher Scientific) catalyzed by sodium nitroferricyanide (Reagent grade, Purchased from Ricca Chemical Company) which forms indophenol and exhibits a blue coloration .[2] The indicator solutions prepared for the test were 10 g/L phenol and 0.05 g/L for indicator solution 1, and 5 g/L NaOH ($\geq$99% purchased from Fisher) and 0.42 g/L for NaOCl for indicator solution 2. The test was performed by mixing 500 µL of the sample with 125 µL of a pH 7.15 buffer made from KOH and KH_2PO_4 (99% purchased from Fisher) in a small container. Next 500 µL of indicator solution 1 and 500 µL of indicator solution 2 were added in quick succession to the test sample, the sample was capped, and shaken by hand to mix the sample solution. The solution color developed over 30 minutes, at which point it was tested to determine the indophenol concentration in the solution. The concentration of the indophenol is directly related to the concentration of ammonia in the sample, and was quantified by UV-Vis spectroscopy via a broad absorbance peak at 630 nm[2]. A Hewlett Packard 8452A Diode Array Spectrophotometer was used to collect the UV-Vis absorbance spectra. The calibration curve for the ammonia concentration is shown in Figure S4**.**

Statistical Analysis

The experiment was designed to test four different parameters for their effect on the ammonia synthesis; catalyst, catalyst loading, temperature, and potential. Using Minitab 17 (v.17.3.1) factorial design was done for 2^4 experiments performed in random order to analyze the effect of these four parameters on the reaction. In order to test the effect of catalyst experiments were run with Ir and Pt for comparison, for temperature two temperatures of 30 and 60 °C were used, potentials of 250 and 500 mV were used, and catalyst loadings of ~0.25 and ~1.0 mg/cm^2 were used. Higher temperatures could not be tested with this cell due to the ionomer not being stable at high temperatures The uncertainties associated with the values given in Table 1 are a result of the uncertainty in the measurements of the volume of the acid traps, combined with the standard deviations obtained for three UV-Vis measurements for each acid trap. Because the minimum error associated with these values was 5% and most were higher, the confidence level used for the analysis was 85%. The result of the statistical analysis is shown in Figures S1 and S2.

Supporting Figures



Statistical Analysis of the Effects of the Parameters on the Production Rate of NH_3

Fig. S1. Statistical analysis of the impact and significance of the catalyst, catalyst loading, potential and cell temperature on the production of NH_3 performed in Minitab 17. Analysis shows the (A) Main effects plot (B) Pareto chart (C) Interaction Plot and (D) Normal plot for the production of NH_3. While none of the individual factors are significant according to the analysis, combinations of different factors can be significant, and general trends can still be observed.

Statistical Analysis of the Effects of the Parameters on the Effective Current Density

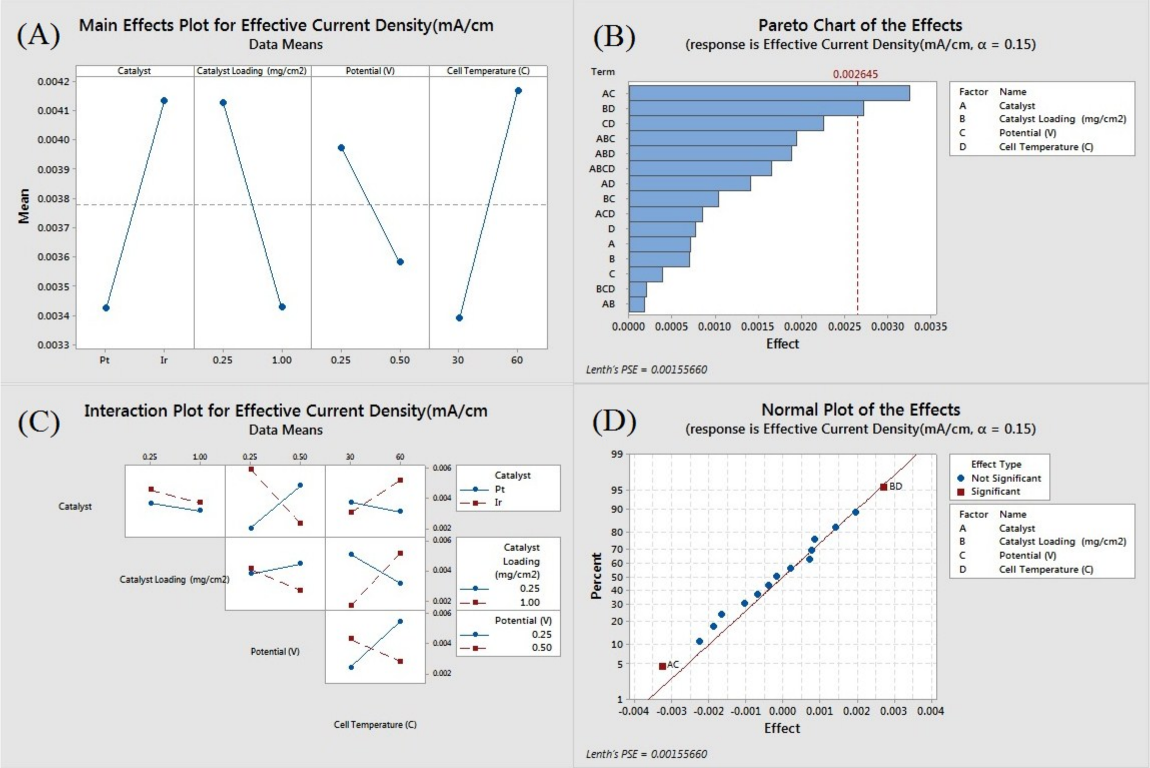


Fig S2. Statistical analysis of the impact and significance of the catalyst, catalyst loading, potential and cell temperature on the effective current density performed in Minitab 17. Analysis shows the (A) Main effects plot (B) Pareto chart (C) Interaction Plot and (D) Normal plot for the effective current density. While none of the individual factors are significant according to the analysis, combinations of different factors can be significant, and general trends can still be observed.

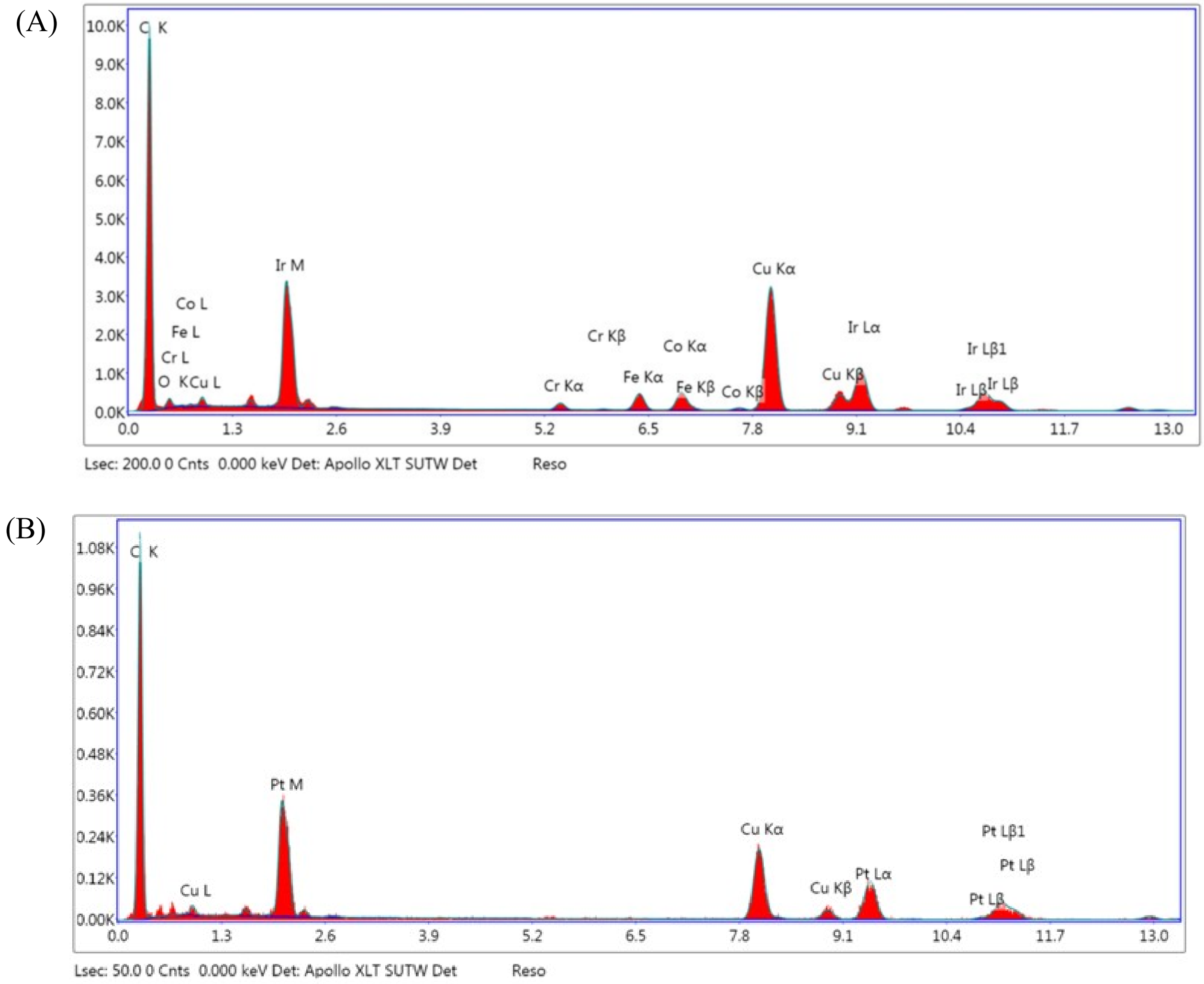


Fig. S3 Energy Dispersive Spectroscopy of the electrocatalyst used at the cathode for (A) Ir and (B) Pt on carbon support. The copper signal is due to the copper grid on which the sample was taken. Pt and Ir signals show that catalyst was successfully reduced onto the carbon support.

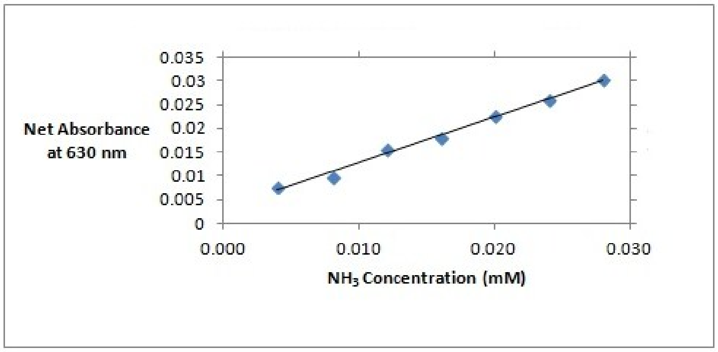


Fig S4. Absorbance as a Function of NH_3 Concentration. Calibration curve used to calculate result NH_3 concentration from the UV-Vis absorbance value obtained when testing a sample. The curve showed a clear linear relationship between observed absorbance at 630 nm and NH_3 concentration as expected. Calibration curve was obtained using standard solutions prepared from sulfuric acid and ammonium sulfate (99.95%, purchased from Alfa Aesar).

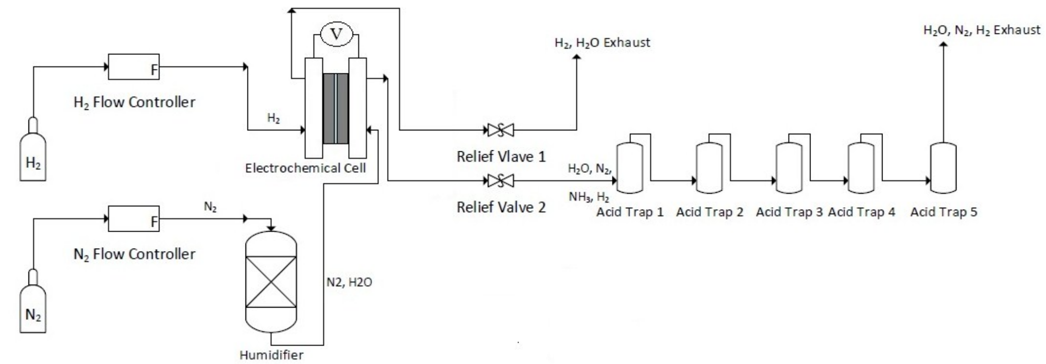


Fig S5. Process flow diagram for the ammonia synthesis setup. Pressure in the system is maintained using relief valves; flow rate is set using flow controllers. Cathode exhaust is passed through 5 acid traps successively in order to ensure capture of all ammonia.

1. Kim, D. W.; Lee, J. M.; Oh, C.; Kim, D. S.; Oh, S. G., A novel preparation route for platinum-poly styrene heterogeneous nanocomposite particles using alcohol-reduction method. *Journal of Colloid and Interface Science* **2006,** *297* (1), 365-369.
2. Chaney, A. L.; Marbach, E. P., Modified Reagents for Determination of Urea and Ammonia. *Clinical Chemistry* **1962,** *8* (2), 130-132.