

Supporting Information

A Carbon-Supported Copper Complex of 3,5-Diamino-1,2,4-triazole as a Cathode Catalyst for Alkaline Fuel Cell Applications

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Catalyst Preparation and Verification: The Cu-tri/C was prepared as described previously.¹ The integrity of the commercial Pt/C (50 wt% Pt on Vulcan carbon, E-Tek) and Ag/C (60 wt% Ag on Vulcan carbon, E-Tek) catalysts used, for comparison with the novel Cu-tri/C, were verified via cyclic voltammetry (CV). The CVs of Pt/C and Ag/C are shown in Figure S1a and Figure S1b. Studies were performed on a glassy carbon electrode (0.196 cm²) in 0.1 M HClO₄ (70%, ULTREX II Ultrapure Reagent, J.T. Baker) under an Ar atmosphere. Catalyst inks containing carbon-supported catalysts (1.0 mg mL⁻¹) and Nafion solution (4 μL mL⁻¹ 5 wt%, Aldrich) were prepared in water and sonicated for 10 minutes. A 20 μL drop was deposited onto a glassy carbon electrode (polished with 0.05 μ alumina and sonicated in water) and was dried under a stream of Ar. Electrochemical measurements were performed using a CHI 760C bipotentiostat (CH Instruments), a Pt gauze counter electrode, and a “no-leak” Ag/AgCl reference electrode (Cypress Systems). The reference electrode was calibrated to the RHE scale by saturating the cell with H₂ and measuring the open circuit potential at a Pt working electrode.

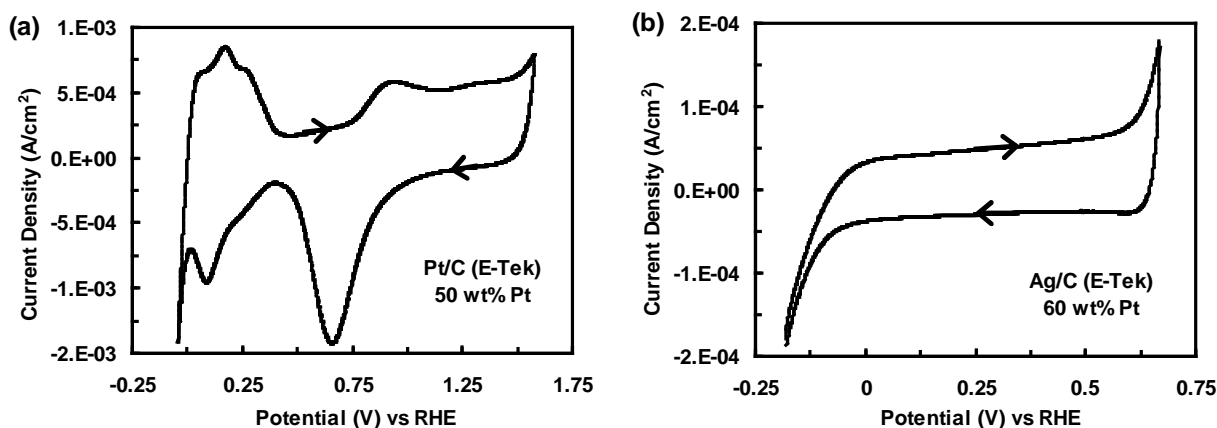


Figure S1. CV of 50 wt % Pt/C (a) and 60 wt % Ag/C (b) on a GC electrode in 0.1 M HClO₄ under Ar atmosphere with a 100 mV/s sweep rate.

Gas Diffusion Electrode (GDE) Preparation: Commercial Pt/C and in-house synthesized Cu-tri/C (3.76 wt% Cu on carbon black) were used as cathode catalysts. For all studies, Pt/C was used as the anode catalyst. Catalyst inks were prepared by mixing a total of 8 mg of Pt/C or 16 mg of Cu-tri/C and a desired amount of Nafion (5 wt% solution, Solution Technology) in a 30:1 ratio (catalyst : Nafion) with 200 μ L of Millipore water and 200 μ L of isopropyl alcohol. The catalyst inks were sonicated (Branson 3510) overnight and were hand-painted on the hydrophobized side of a carbon cloth gas diffusion layer (GDL, BASF) to create a GDE. The geometric surface area was 4 cm². Thus, the final cathode loadings were 2 mg Pt/C /cm² (1 mg Pt /cm²) and 0.067 mg Nafion /cm² or 4 mg Cu-tri/C /cm² (0.15 mg Cu /cm²) and 0.134 mg Nafion /cm². The final Pt/C anode loading was identical to that of the Pt/C cathode.

The GDE preparation procedure of the Ag/C cathode and Pt/C anode used in Figure 2c is detailed in a previous publication.² The catalyst ink was prepared by mixing a total of 26.8 mg of Ag/C or 8 mg of Pt/C and a desired amount of polytetrafluoroethylene (PTFE, Aldrich) powder with 200 μ L of Millipore water and 200 μ L of isopropyl alcohol. The weight percentage of PTFE to the total weight of the PTFE / catalyst mixture within the catalyst ink was 40 wt%. The catalyst inks were sonicated and then hand-painted onto the hydrophobized carbon side of a Toray carbon paper GDL (EFCG “S” type electrode, E-Tek) to create a GDE. The GDEs were sintered under a N₂ atmosphere at 330 °C for 20 min in a preheated tube furnace (Lindberg/Blue) followed by hot pressing at a pressure of 340 psi (~2344 kPa) and a temperature of 120 °C. The geometric surface area was 4 cm². Thus, the final cathode and anode loadings were 6.7 mg Ag/C /cm² (4 mg Ag /cm²) and 4.47 mg PTFE /cm² and 2 mg Pt/C /cm² (1 mg Pt /cm²) and 1.33 mg PTFE /cm², respectively.

Microfluidic Fuel Cell Assembly: Two GDEs, anode and cathode, were placed on opposite sides of a 0.15-cm thick polymethylmethacrylate (PMMA) sheet, such that the catalyst-coated sides interfaced with the 3-cm long and 0.33-cm wide precision-machined window. The window has an inlet and outlet on either side such that the alkaline electrolyte flows between the GDEs. Two 1-mm thick graphite windows served as current collectors. The hydrogen (H₂) and oxygen (O₂) gas flow chambers (5 cm (L) x 1 cm (W) x 0.5 cm (H)) were precision-machined into polycarbonate sheets. The multilayered assembly was held together using binder clips (Highmark). Detailed fuel cell schematics may be found in the following references.²⁻⁴

Microfluidic Fuel Cell Testing: Fuel cell experiments were conducted using a potentiostat (Autolab PGSTAT-30, EcoChemie) at room temperature with H₂ and O₂ gases (laboratory grade, S.J. Smith), each at a flow rate of 50 sccm. Electrolyte flow rate held at 0.6 mL/min using a syringe pump (Harvard Apparatus). Potassium hydroxide (KOH, Mallinckrodt, 88%, balance of H₂O) was used as the electrolyte. Fuel cell polarization curves were obtained by steady-state chronoamperometric measurements at different cell potentials. The exposed geometric electrode surface area (1 cm²) was used to calculate the current and power densities. After the exiting the fuel cell, the electrolyte stream collects in a beaker with a reference electrode (Ag/AgCl in saturated NaCl, BASi). Anode and cathode polarization losses are independently measured by attaching two multimeters (Fluke) to the reference electrode and to the anode and cathode current collectors, respectively.⁵ No potential drop is observed along the plastic tubing (Cole Parmer, 1.57 mm ID) connecting the microfluidic fuel cell and the reference electrode.

Prior to fuel cell testing, each PTFE-based GDE was acclimated via CVs in 0.5 M H₂SO₄ from 0.05 - 1.15 V vs. DHE to remove excess PTFE from the catalyst surface and improve wetting. Furthermore, the Ag/C cathode was activated in the fuel cell by holding the potentiostat at 150 mA/cm² galvanostatically or 0.3 V potentiostatically for at least 20 min to reduce any Ag oxides present on the electrode surface.² As shown in Figure S2 for an alkaline microfluidic H₂/O₂ fuel cell operated with Pt/C electrodes (both anode and cathode), the choice of GDE preparation, either with Nafion or PTFE, does not have a significant impact on fuel cell performance except at very high current densities. This difference at mass transport limiting conditions between Nafion- and PTFE-based electrodes is most likely due to the hot-pressing of the PTFE-based GDEs which reduces porosity. We perform detailed analysis of the impact of hot-pressing on electrode performance in an upcoming publication.⁶

The Ag/C cathode data used in Figure 2c, is obtained in an alkaline microfluidic H₂/O₂ fuel cell with a 0.2-cm thick PMMA channel and an alkaline electrolyte flow rate of 0.3 mL/min.²

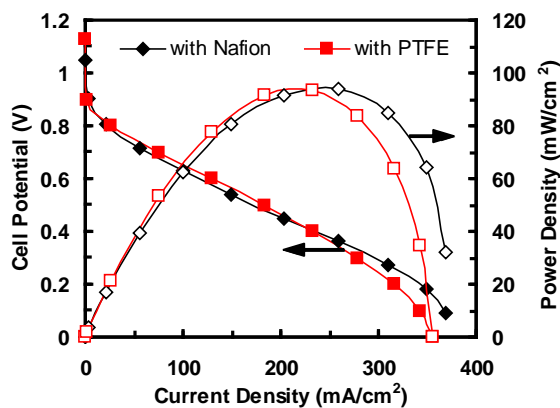


Figure S2. Polarization and power density curves for an alkaline microfluidic H₂/O₂ fuel cell operated with Nafion- or PTFE-based Pt/C electrodes. Experiments were performed at RT, H₂/O₂ flows were 50 sccm each, [KOH] was 1 M and electrolyte flow rate was 0.3 mL/min.

To account for the differences in electrode-to-electrode distance, the fuel cell comparisons are performed after an IR-correction based on the electrolyte resistance. These values were calculated as $0.92 \Omega\text{-cm}^2$ and $0.69 \Omega\text{-cm}^2$ for the 0.2 cm and 0.15 cm gaps¹, respectively.⁷ Furthermore, both configurations showed minimal sensitivity to increased flow rates, between 0.3 and 0.6 mL/min, thus general *qualitative* comparisons are possible.^{2-4,6}

Accelerated Cu-tri/C Cathode Aging: In addition, the cyclic studies shown in Figure 3, electrode aging studies were performed by holding the cathode at 0.535 V vs. RHE for a 24 hr period in the presence of O₂ (Figure S3). Figure S3a shows the chronoamperometric response of the cathode during the 24 hr. potential hold. Over the 24 hr period, the cathode performance drops ~45%. Most of these performance losses occur in the first 14 hrs of operation. In Figure S3b, CVs of oxygen reduction performance are obtained at 0, 14 and 24 hrs. These intermittent voltammograms also show that the majority of the performance losses are observed between 0 and 14 hrs. The durability characteristics are similar to those observed for the aging via cyclic studies (shown in Figure 3). This may suggest the presence of multiple degradation regimes with an initial region of rapid losses before plateauing into a region of slower losses. Further durability analyses are required to better understand, and hopefully mitigate, these adverse processes.

All cathode durability studies were performed in a single compartment 3-electrode electrochemical cell using O₂-saturated 1 M KOH (Fisher) electrolyte with an O₂ atmosphere above the solution. The GDE used as the working electrode was immersed in the electrolyte to a

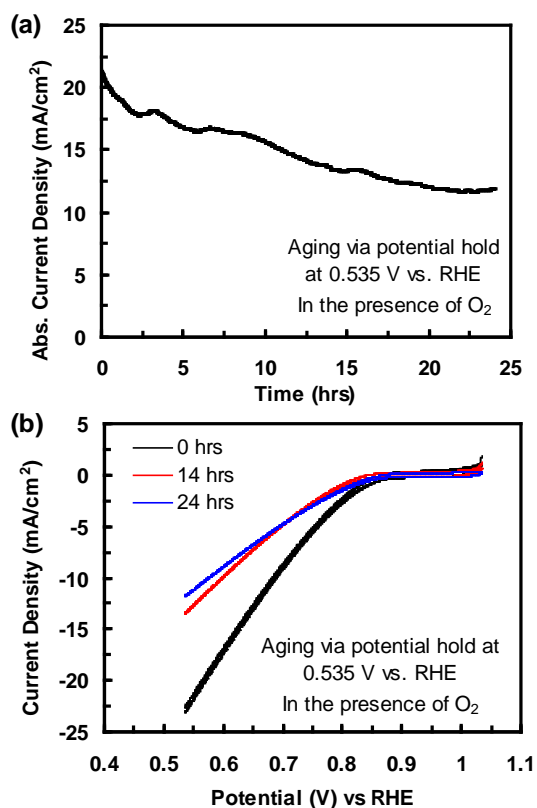


Figure S3. Cu-tri/C cathode aging via potential hold at 0.535 V vs. RHE. **(a)** The cathode chronoamperometric response (in absolute current density) as a function of constant potential aging. **(b)** Cyclic voltammograms are taken at 0, 14 and 24 hrs between 0.535 and 1.035 V vs. RHE at a 5 mV/s scan rate. Studies are performed in a 3-electrode cell in an O₂-saturated 1 M KOH at RT. The cathode loading is 4 mg Cu-tri/C /cm² and the electrode surface area is 4 cm² (geometric).

¹Note that this order of these thicknesses has been accidentally reversed in the JACS SI.

sufficient depth to wet all of the applied catalyst. A graphite rod served as a counter electrode and the reference electrode was a “no leak” Ag/AgCl electrode (Cypress). The working electrode was replaced with Pt at the end of an aging experiment, the cell was saturated with H₂, and the open circuit potential was recorded and used to calibrate the reference electrode to the RHE scale.

Complete Reference: The complete citation of reference #3 in the communication is:

R. Borup; J. Meyers; B. Pivovar; Y.S. Kim; R. Mukundan; N. Garland; D. Myers; M. Wilson; F. Garzon; D. Wood; P. Zelenay; K. More; K. Stroh; T. Zawodzinski; J. Boncella; J.E. McGrath; M. Inaba; K. Miyatake; M. Hori; K. Ota; Z. Ogumi; S. Miyata; A. Nishikata; Z. Siroma; Y. Uchimoto; K. Yasuda; K.I. Kimijima; N. Iwashita *Chemical Reviews* **2007**, *107*, 3904-3951.

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- (3) R.S. Jayashree; M. Mitchell; D. Natarajan; L.J. Markoski; P.J.A. Kenis *Langmuir* **2007**, *23*, 6871-6874.
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- (6) F.R. Brushett; M.S. Naughton; J.W.D. Ng; L.L. Yin; P.J.A. Kenis *in preparation*.
- (7) G. Prentice *Electrochemical engineering principles*; Prentice Hall: Englewood Cliffs, 1991.