

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

Fikile R. Brushett,[†] Matthew S. Thorum,[‡] Nicholas S. Lioutas,[†] Matthew S. Naughton,[†] Claire Tornow,[‡] Huei-Ru "Molly" Jhong,[†] Andrew A. Gewirth,^{*,‡} and Paul J. A. Kenis^{*,†}

Department of Chemical & Biomolecular Engineering and Department of Chemistry, University of Illinois at Urbana–Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

Received June 1, 2010; E-mail: agewirth@illinois.edu; kenis@illinois.edu

Abstract: The performance of a novel carbon-supported copper complex of 3,5-diamino-1,2,4-triazole (Cu-tri/C) is investigated as a cathode material using an alkaline microfluidic H₂/O₂ fuel cell. The absolute Cu-tri/C cathode performance is comparable to that of a Pt/C cathode. Furthermore, at a commercially relevant potential, the measured mass activity of an unoptimized Cu-tri/C-based cathode was significantly greater than that of similar Pt/C- and Ag/C-based cathodes. Accelerated cathode durability studies suggested multiple degradation regimes at various time scales. Further enhancements in performance and durability may be realized by optimizing catalyst and electrode preparation procedures.

Fuel cell-based systems hold promise as alternative power sources for a range of applications due to their high efficiency, high energy density, and low emissions.¹ For low-temperature applications, acidic polymer electrolyte membrane-based fuel cells (PEMFCs) are considered most promising.² Widespread market penetration of these PEMFCs has yet to be realized mainly due to high costs (platinum (Pt) catalysts, Nafion membranes), insufficient durability, and system limitations.³ A key challenge is the oxygen reduction reaction (ORR) on the cathode.⁴ Sluggish kinetics and high overpotentials associated with the ORR necessitate substantial loadings of expensive precious metal catalysts to achieve adequate performance.⁴ Thus, reducing or eliminating Pt content in fuel cell cathodes, without sacrificing performance and durability, is a critical step toward improving the commercial viability of fuel cell technologies.

Alternative Pt-free ORR catalysts include pyrolyzed Fe(Co)/N/C systems,^{5,6} ruthenium-based chalcogenides,⁷ cobalt-polypyrrole composites,⁸ and enzymes, but none have shown the necessary combination of activity and stability to replace Pt catalysts in acidic fuel cells.⁹ In contrast ORR kinetics are often more facile and materials are more stable under alkaline conditions.¹⁰ For example, recent electrochemical studies by Meng et al. showed that Fe/N/C catalysts exhibited enhanced activity and stability under alkaline conditions (pH = 13) compared to acidic conditions (pH = 1).¹¹ Similarly, synthetic Cu^{II} complexes coordinated with bridging azole-type ligands could be a viable choice as an alkaline fuel cell catalyst.¹² Recently we developed a novel method of directly preparing insoluble Cu complexes on carbon black C supports and showed that a carbon-supported Cu complex of 3,5-diamino-1,2,4-triazole (Cu-tri/C) exhibits moderate ORR activity under acidic conditions but high activity under alkaline conditions.⁹

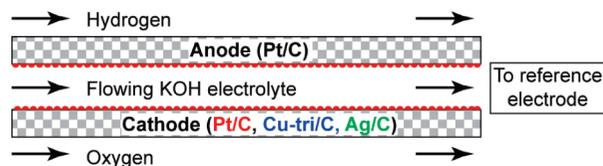


Figure 1. Schematic of microfluidic H₂/O₂ fuel cell with flowing alkaline electrolyte sandwiched by catalyst-coated gas diffusion electrodes.

Building on the promising ORR performance of Cu-tri/C in a three-electrode cell especially under alkaline conditions,¹² we now characterize the performance and durability of the Cu-tri/C catalyst when integrated in an actual electrode for alkaline fuel cell (AFC) applications. Previously, Gasteiger et al. have studied the key factors related to the integration of catalysts into electrodes for PEMFCs.¹ Here, we investigate electrode performance using a previously developed alkaline microfluidic H₂/O₂ fuel cell (Figure 1).^{13,14} Instead of a polymeric membrane between the two electrodes, this cell has a flowing electrolyte stream which enables independent control over electrolyte parameters (i.e., pH) and allows for the *in situ* analyses of individual electrode performance via a reference electrode. Thus, this platform is convenient for studying the performance and durability of novel catalysts integrated in gas diffusion electrodes (GDEs), closely resembling the way in which they will be employed in fuel cells.

Figure 2 compares the cathode performance of the Cu-tri/C catalyst with known ORR catalysts, Pt/C and Ag/C, in a microfluidic H₂/O₂ fuel cell with a flowing electrolyte of 1 M KOH (pH ~14). The total cathode loadings were 4 mg Cu-tri/C/cm² (3.76 wt % Cu, in-house synthesized¹²), 2 mg Pt/C/cm² (50 wt % Pt, E-Tek), and 6.7 mg Ag/C/cm² (60 wt % Ag, E-Tek). Thus the cathode metal loadings are 0.1504 mg Cu/cm², 1 mg Pt/cm², and 4 mg Ag/cm². For all fuel cell studies, the anode loading was 2 mg Pt/C/cm² (again, 50 wt % Pt so 1 mg Pt/cm²). Because the catalysts are integrated into GDEs, their performance will be limited by cell design (e.g., cell resistance) and thus lower than that of catalysts in a three-electrode cell. However, this configuration enables the direct comparison of different cathode catalysts in actual electrodes under realistic fuel cell operating conditions. Details on the GDE preparation, fuel cell assembly, and testing procedures may be found in the Supporting Information (SI).

Figure 2a shows representative polarization and power density curves of an alkaline microfluidic H₂/O₂ fuel cell operated with either a Pt/C or Cu-tri/C cathode which demonstrated peak power densities of 97.8 ± 8.1 and 74.4 ± 2.7 mW/cm², respectively. The difference in performance can be mainly attributed to the lower open circuit potential of the fuel cell operated with the Cu-tri/C cathode, 0.96 ± 0.01 V, as compared to the Pt/C cathode, 1.06 ± 0.02 V. Figure 2b shows corresponding anode and cathode

[†] Department of Chemical & Biomolecular Engineering.

[‡] Department of Chemistry.

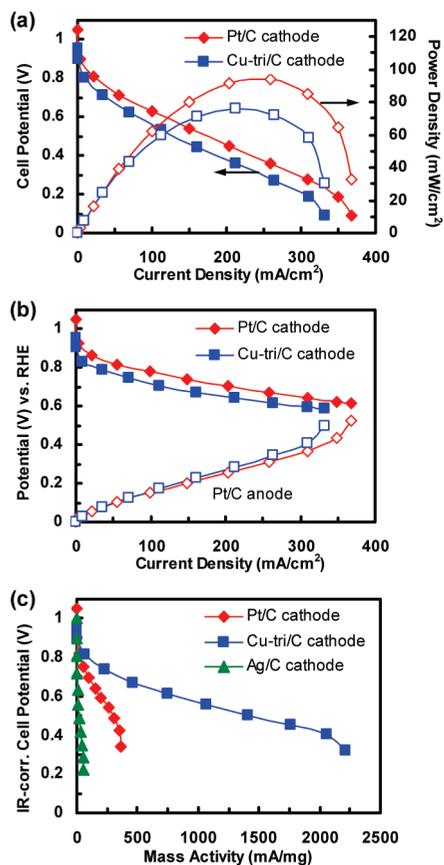


Figure 2. (a) Polarization and power density curves for a microfluidic H₂/O₂ fuel cell with different cathode catalysts (GDE). (b) Corresponding individual electrode polarization curves. (c) IR-corrected polarization curves as a function of cathode catalyst metal content (Pt, Cu, and Ag). In all studies a Pt/C anode was used. Experiments are performed at room temperature using flowing 1 M KOH and 50 sccm H₂/O₂ flows.

polarization curves for the representative fuel cell data shown in Figure 2a. The individual electrode and overall fuel cell performance are similar to those reported in literature.¹⁵ The lower performance of the cell operated with the Cu-tri/C cathode can be attributed to a reduced onset potential, which is 103 ± 26 mV lower than that of the Pt/C cathode. However, absolute cathode performance may be enhanced by increasing the Cu-tri/C loading, which is inexpensive compared to Pt/C. Indeed, on a per metal basis, the Cu-tri/C cathode dramatically outperforms both the Pt/C cathode and the Ag/C cathode as shown by the IR-corrected polarization curves as a function of mass activity (mA/mg). Ag/C cathode data are from previously reported studies in an alkaline microfluidic H₂/O₂ fuel cell.¹³ The mass activity enhancement is especially pronounced at lower potentials (0.5–0.7 V) and higher current densities where commercial fuel cell-based systems would most likely operate. The mass activities of a fuel cell operated with Cu-tri/C, Pt/C, and Ag/C cathodes are 746 mA/mg (at 0.61 V_{IR-corr.}), 149 mA/mg (at 0.64 V_{IR-corr.}), and 9.5 mA/mg (at 0.63 V_{IR-corr.}), respectively. While the electrodes have not been systematically optimized for mass-specific activity, these values highlight the potential of the Cu-tri/C as a cathode material for AFCs.

To the best of our knowledge, this is the first report of a synthetic multi-Cu complex as a cathode material for AFC applications. Promisingly, the Cu-tri/C cathode performance, which has yet to be optimized, is comparable with that of a Pt/C cathode. Presently, directly comparing the Cu-tri/C performance to that of other Pt-free catalysts is difficult as these studies are performed either in an

electrochemical cell^{6,11,16} or embedded in a GDE within an operating acidic PEMFC.^{5,8}

The peak power density was only 6.4 mW/cm² when we tested the Cu-tri/C cathode in the same fuel cell under acidic conditions (0.5 M H₂SO₄). This 11-fold performance drop by shifting from an alkaline to acidic operating environment can be attributed to reduced Cu-tri/C activity, in agreement with prior results.¹²

The long-term stability of the Cu-tri/C cathode was studied employing accelerated durability testing in a three-electrode cell. In Figure 3, the Cu-tri/C cathode was aged in O₂-saturated 1 M KOH by potential cycling between 0.535 and 1.035 V vs RHE. These aging conditions were chosen to simulate the conditions experienced by a cathode within an operating AFC. The ORR activity of the Cu-tri/C cathode degrades substantially over 6000 cycles. As the insert in Figure 3 shows, the initial rates appear more rapid while the later rates appear slower. This may indicate multiple degradation regimes over various time scales, but further analysis is required. Similar trends were observed when the Cu-tri/C cathode aging studies were performed via a potential hold at 0.535 V vs RHE (see SI).

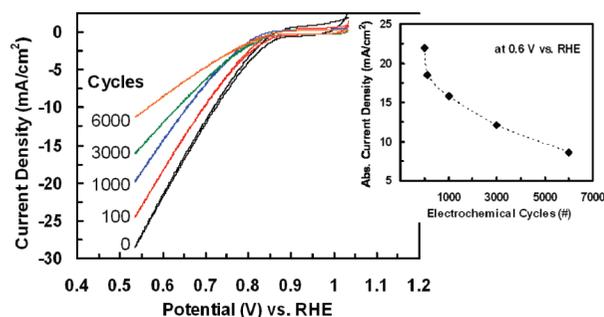


Figure 3. Cu-tri/C cathode (GDE) aging as a function of electrochemical cycles between 0.535 and 1.035 V vs RHE at a 5 mV/s scan rate in a three-electrode cell in O₂-saturated 1 M KOH at room temperature. Insert: absolute current density at 0.6 V vs RHE as a function of cycles. Cathode loading: 4 mg Cu-tri/C/cm²; geometric electrode surface area: 4 cm².

For AFC applications, biomimetic Cu-tri/C cathodes appear to be a promising alternative to Pt/C cathodes. Furthermore, the performance and, in particular, the durability of these cathodes may be enhanced via optimizing synthesis procedures such as increasing Cu site density, tailoring ligand design, and varying the support materials, as well as via improving GDE preparation methods such as optimizing catalyst loading, particle distribution, and catalyst-to-binder ratios. For example, increasing Cu site densities on the carbon black may enable enhanced absolute cathode performance while maintaining, or even lowering, cathode material loadings. In addition, tailoring ligand design may enhance acidic ORR activity and increase the viability of Cu-tri/C as a cathode material for acidic PEMFCs.

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Supporting Information Available: Preparation of catalysts and electrodes, cell assembly, testing procedures, and complete ref 3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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