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In-situ measurement of ethanol tolerance in an operating fuel cell

Matt S. Naughton^a, Claire E. Tornow^b, Yolanda Bonita^a,
Huei-Ru “Molly” Jhong^a, Fikile R. Brushett^a, Andrew A. Gewirth^b,
Paul J.A. Kenis^{a,*}

^aDepartment of Chemical & Biomolecular Engineering, University of Illinois at Urbana-Champaign, 600 S. Matthews Ave, Urbana, IL 61801, USA

^bDepartment of Chemistry, University of Illinois at Urbana-Champaign, 600 S. Matthews Ave, Urbana, IL 61801, USA

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ABSTRACT

Ethanol is seen as an attractive option as a fuel for direct ethanol fuel cells and as a source for on-demand production of hydrogen in portable applications. While the effect of ethanol on *in-situ* electrode behavior has been studied previously, these efforts have mostly been limited to qualitative analysis. In alkaline fuel cells, several cathode catalysts, including Pt, Cu triazole, and Ag can be used. Here, we apply a methodology using a microfluidic fuel cell to analyze *in-situ* the performance of these cathodes as well as Pt anodes in the presence of ethanol and acetic acid, a common side product from ethanol oxidation. For a given concentration of ethanol (or acetic acid), the best cathode catalyst can be determined and the kinetic losses due to the presence of ethanol (or acetic acid) can be quantified. These experiments also yield information about power density losses from the presence of contaminants such as ethanol or acetic acid in an alkaline fuel cell. The methodology demonstrated in these experiments will enable *in-situ* screening of new cathodes with respect to contaminant tolerance and determining optimal operational conditions for alkaline ethanol fuel cells.

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1. Introduction

Direct ethanol fuel cells are emerging as promising power sources due to the availability of bioethanol [1,2]. Ethanol is a liquid at ambient conditions, is relatively non-toxic, and has a high theoretical energy density of 8.0 kWh/kg [3,4]. Furthermore, fuel cells are inherently more efficient than, for example, combustion-based power generation processes [5]. The use of carbon-based fuels in alkaline fuel cells has historically been limited by carbonate formation from CO₂, which has prevented long-term operation in alkaline media [5–7].

More recently, alkaline membrane-based fuel cells have emerged to counteract the problem of carbonate formation [1,4,8,9]. Full electro-oxidation of ethanol still remains a challenge.

In a fuel cell, ethanol can fully oxidize to carbon dioxide, producing 12 electrons, or partially oxidize to acetaldehyde or acetic acid, producing two or four electrons respectively along with water [4,10]. Common ethanol oxidation catalysts are based on Pt in acidic or alkaline media or Pd in alkaline media, but novel catalysts based on other metals are still being developed [11–14]. The commonly used PtRu and PtSn anode

* Corresponding author. Tel.: +1 217 265 0523; fax: +1 217 333 5052.

E-mail address: kenis@illinois.edu (P.J.A. Kenis).

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catalysts are relatively unselective for full oxidation, producing less than 11% CO₂ [4,15]. For example, an alkaline fuel cell with a PtSn anode was >90% selective for the formation of acetic acid when operated at a current density of 20 mA/cm², while the same configuration operated at 60 mA/cm² produced acetic acid as well as acetaldehyde in significant amounts [4]. Thus, analysis of ethanol tolerance should also include an analysis of acetic acid tolerance.

While much research has focused on improved anode catalysis for ethanol fuel cells, ethanol-tolerant cathode catalysts are also a key to maximizing direct ethanol fuel cell performance and efficiency [11]. Ethanol crossover from the anode can cause mixed potentials at the cathode, reducing cathode performance and fuel utilization. This problem is aggravated with higher ethanol concentrations, even though those concentrations may be necessary for better anode kinetics. As a result, cathode catalysts that exhibit selectivity towards the oxygen reduction reaction (ORR) and are unaffected by the presence of ethanol or its degradation products are essential for high-performance direct ethanol fuel cells.

Prior work to analyze cathode performance in the presence of ethanol has largely been limited to *ex-situ* rotating disk electrode (RDE) experiments, which do not accurately replicate fuel cell operating conditions [16]. For example, work by Jiang et al. showed that the onset potential for Pt/C in O₂-saturated 0.1 M NaOH dropped by approximately 0.07 V in the presence of 0.05 M EtOH [17]. While this result illustrates the sensitivity of Pt to ethanol poisoning, the solubility of O₂ in pure water is only 1.25 mM, which is far lower than the 40 mM supply from convected O₂ or the 8 mM supply of O₂ from convected air, and indicates an unfavorable ethanol to O₂ molar ratio of 40 [18]. Additionally, an alkaline membrane or liquid fuel cell would typically contain a hydroxyl concentration of 1 M or greater (pH ≥ 14), instead of the pH 13 found in these RDE experiments. While membrane-based systems intrinsically operate under fuel cell conditions, precise manipulation of the electrolyte is considerably more difficult than it is in liquid electrolyte-based systems, and the lack of a reference electrode in a membrane-based system hampers differentiation between anode and cathode effects.

Similarly, ethanol tolerance of electrodes is also important for hydrogen fuel cells that receive their H₂ feed from the reforming of ethanol. Ethanol is a means to store hydrogen in the liquid phase, but contamination of the hydrogen fuel feed with ethanol and byproducts such as acetic acid have prevented system implementation to date [19–22]. In addition, the loss in performance due to ethanol and acetic acid contamination within an operating H₂ fuel cell has not been quantified.

Here, we use a microfluidic hydrogen-oxygen (H₂/O₂) fuel cell with a flowing alkaline electrolyte stream [23–25] to characterize and quantify the effect of ethanol contaminant on Pt [4], Ag [7], and Cu triazole [26] electrodes. Although these catalysts have been tested in various fuel cell setups, they have not been compared to each other in the presence of ethanol. Determination of cathode performance *in-situ*, in an actual fuel cell, is a more accurate means to determine relative performance and discover which catalyst performs better under realistic operating conditions. The use of a hydrogen fuel cell here, instead of a direct ethanol fuel cell, allows us to achieve higher current densities at the cathode while at the

same time we can control the amount of ethanol, as a contaminant, in the cell. Here we use a microfluidic fuel cell with a reference electrode [27] in combination with an analytical method that we developed previously [28] to quantify single electrode behavior within an operating fuel cell, specifically the effects of ethanol and acetic acid contamination on cathodes and anodes. Using this method, we determine whether the expensive Pt catalyst or the non-noble metal alternative Ag is superior for a given ethanol contaminations and we demonstrate the ability to screen new cathode catalysts by quantifying the effect of ethanol on Cu triazole. We also discuss the importance of the ethanol to oxygen molar ratio when determining ethanol tolerance.

2. Experimental section

2.1. Gas diffusion electrode preparation

For Pt and Ag, commercially available Pt/C (50% mass on Vulcan carbon, E-Tek) or Ag/C (60% mass on Vulcan carbon, E-Tek) were used as electrode catalysts. For Cu triazole, the catalyst was prepared using the procedure developed by Thorum et al., except that centrifugation was used instead of suction filtration [29]. In brief, CuSO₄ (Aldrich) was sonicated with Vulcan XC-72 in water; a solution of 3,5-diamino-1,2,4-triazole (Aldrich) was then added dropwise and the solution was again sonicated. The catalyst was centrifuged to remove the supernatant and dried under vacuum at 90 °C [29]. The copper loading of the Cu triazole/C was determined by elemental analysis using an ELAN DRCe ICP-MS (Dynamic Reaction Cell Inductively Coupled Plasma-Mass Spectrometer) (Perkin Elmer SCIEX) to be 2.84 wt%, which is lower than the previously used Cu loading of 3.76 wt%. The N:Cu ratio was 4.91:1, which matches the N:Cu ratio of 5:1 calculated from the crystal structure. A 30:1 ratio of catalyst to Nafion was used as the catalyst binder such that catalyst inks were prepared by mixing a total of 8.0 mg of Pt/C or 27 mg of Ag/C and 6.13 μL or 20.4 μL of 5 wt% Nafion solution (DuPont), respectively [24,26]. 200 μL of DI water and 200 μL of isopropyl alcohol (Fisher Scientific) were added as carrier solvents. The catalyst inks were sonicated (Branson 3510) for 1 h to obtain a uniform mixture, which was then hand-painted onto 4 cm² of the hydrophobized carbon side of a carbon paper gas diffusion layer (35 BC, SGL carbon group) to create a gas diffusion electrode (GDE). The final catalyst loading was 1 mg/cm² of Pt (50% mass Pt) for the anode and 1 mg/cm² of Pt (50% mass Pt), 4 mg/cm² of Ag (60% mass Ag), or 4 mg/cm² of Cu triazole/C for the cathode.

2.2. Fuel cell assembly and testing

To assemble the fuel cell, shown in Fig. 1, the cathode (Pt/C or Ag/C) and the anode (Pt/C) were placed on the opposite sides of a 0.1-cm or 0.2-cm thick polymethylmethacrylate (PMMA) window, such that the catalyst-coated GDE sides face the 3-cm long and 0.33-cm wide window machined in PMMA [24]. The microfluidic chamber volume was 0.2 ml. The window has one inlet and one outlet from the side for the electrolyte flow, aqueous solutions of potassium hydroxide (KOH,

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