Tailoring electrode hydrophobicity to improve anode performance in alkaline media

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HIGHLIGHTS

- Backing layers may be permeable to catalyst solvent.
- 20 wt% PTFE optimal for alkaline anode.
- High hydrophobicity limits anode performance.
- Hydrophobic anion-conducting binder inferior to Nafion.
- PtRu potentially very good anode catalyst.

ARTICLE INFO

ABSTRACT

Limitations in anode performance have been a major obstacle to widespread alkaline fuel cell usage. In contrast to water management in acidic cathodes, water management in alkaline anodes has not received a lot of attention. Here, we use a methodology based on individual electrode plots to analyze and improve anode performance, especially by changing the hydrophobicity. Specifically, we determine the role of hydrophobicity as it affects performance for backing layers, catalyst layers, and catalyst binders. We use both individual electrode plots and recirculating experiments to determine the optimal PTFE loading was 20 wt% in alkaline media. We investigated PTFE and Fumion binders, determining that their use yields higher overpotentials than when using Nafion in alkaline media. Furthermore, we determined that Nafion alternatives for application in alkaline media would require significant hydrophilicity and anion-conductivity to result in good fuel cell performance.

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1. Introduction

Alkaline fuel cells are showing substantial promise as power sources due to superior cathode kinetics and improved stability of non-noble metal catalysts in alkaline media [1–5]. While adverse effects of carbon dioxide reacting with hydroxide have historically been perceived to substantially limit alkaline fuel cell performance, more recent developments have demonstrated that the effect of carbonate formation can be mitigated by using soda lime scrubbing [6], a membrane without free cations [7], or a flowing electrolyte with a large electrolyte volume [8]. Performance limitations of alkaline fuel cells at higher current densities then stem more from anode limitations, as the anode is the electrode where water formation occurs [9].

Previously, the role of hydrophobicity on performance of the cathode in acidic fuel cells has been examined [10]. These cathodes are prone to flooding issues analogous to an alkaline anode. A study by Li et al. examined the effect of silicone oil on cathode performance [11]. Zhang et al. investigated the role of PTFE in the cathode backing layer [12]. Fairweather et al. determined that PTFE wet-proofing at less than 20 wt% did not cause a substantial loss in electrode porosity [13]. While these studies yielded information about the cathode in acidic media, their results did not discuss applicability to alkaline media.

We have previously developed a microfluidic hydrogen-oxygen (H_2/O_2) fuel cell with a flowing alkaline electrolyte stream [14]. This cell has the versatility of a three electrode cell within an operating fuel cell. More recently, we have developed a method to analyze individual electrodes by plotting their overpotential versus a

reference electrode. We have used this method to determine the effects of electrolyte contamination and cathode catalysts on performance [8,9], but we have not focused on using this methodology to improve anodes.

In this work, we use the aforementioned microfluidic H_2/O_2 fuel cell to characterize the effect of hydrophobicity of the electrode on anode performance. Specifically, we tune the hydrophobicity both in the backing layer and in the catalyst layer of an electrode to obtain optimal performance. The effect of PTFE loading is investigated both for polarization curves of single electrodes as well as for 4.5 h whole-cell experiments using a recirculating electrolyte. Furthermore, we activated and tested alternate binders to determine their effects on electrode performance.

2. Experimental

2.1. Gas diffusion electrode preparation

Commercially available Pt/C (50% mass on Vulcan carbon, Alfa Aesar) was used as cathode and anode catalyst. For one trial, PtRu/C (50% Pt mass, 25% Ru mass on Vulcan carbon, Alfa Aesar) was used as the anode catalyst in place of Pt/C. Unless otherwise stated, 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 PtRu/C) and 6.13 μL of 5 wt% Nafion solution (DuPont) [2,15]. 200 μL of DI water and 200 μL of isopropyl alcohol (Fisher Scientific) were added as carrier solvents. The catalyst inks were sonicated (Sonics Vibra-Cell) for 10 min 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 or Toray TGP-H-060) to create a gas diffusion electrode (GDE). The final catalyst loading was 1 mg cm^{-2} of Pt (50% mass Pt) for each electrode.

2.2. Fuel cell assembly and testing

To assemble the fuel cell, shown in Fig. 1, the cathode (Pt/C) and the anode (Pt/C) were placed on the opposite sides of a poly-methylmethacrylate (PMMA) window (0.15 cm thick unless otherwise specified), such that the catalyst-coated GDE sides face the 3 cm long and 0.33 cm wide window machined in PMMA [15]. The microfluidic chamber volume was 0.15 ml (0.2 or 0.1 ml when using a 0.2 or 0.1 cm thickness separator, respectively). The window has one inlet and one outlet from the side for the electrolyte flow, aqueous solutions of potassium hydroxide (KOH, Sigma–Aldrich, 85%, balance of H_2O). Two 1 mm thick copper-infused graphite windows were used as current collectors. Polycarbonate gas flow chambers (5 cm (L) × 1 cm (W) × 0.5 cm (H)) were used to introduce both hydrogen and oxygen gases (laboratory grade, S.J. Smith), at 10 SSCM each. The multilayer assemblies were held together with binder clips. Fuel cell testing was conducted using a potentiostat (Autolab PGSTA-30, EcoChemie) at room temperature. For all studies, electrolyte flow rate was maintained at 0.6 ml min^{-1} either

using a syringe pump (2000 PHD, Harvard Apparatus) or a recirculating piston pump (MCP-CPF with MFI 009 Pump Head, Harvard Apparatus). Fuel cell polarization curves were obtained by measuring steady-state currents at different cell potentials using Nova software (EcoChemie). The exposed geometric surface area of the electrode (1 cm²) was used to calculate the current and power densities. A reference electrode (Ag/AgCl in saturated NaCl, BASi) was placed at the outlet of the electrolyte stream to allow for the independent analysis of polarization losses on the cathode and the anode [14]. The reference electrode was fitted with a polyethylene frit (Princeton Applied Research) in place of the original Vycor® frit to prevent corrosion and contamination in alkaline media [9]. After each experiment, the fuel cell was disassembled and the electrodes were rinsed with deionized water, then dried for at least 30 min under a laboratory fume hood.

3. Results and discussion

3.1. Effect of electrode backing layers

The backing layer can play a major role in determining gas diffusion electrode properties. Beyond the basic properties of porosity and thickness, the deposition of the catalyst layer can vary greatly based on the structure of the backing layer. Surprisingly, this variance can occur for backing layers with the same specifications. Originally, the electrodes synthesized with the Sigracet 35 BC backing layers performed well, with overpotentials below 0.1 V for current densities below 50 mA cm^{-2} as shown in Fig. S1. However, electrodes created out of subsequent orders of Sigracet 35 BC yielded very high overpotentials and maximum current density below 150 mA cm^{-2} (Fig. S1). This poor performance is consistent with mass transport limitations at the anode, due to the steep upward trend deviating from linearity.

Many (>10) electrodes were painted to investigate whether this low performance was caused by poor painting technique. Although steps such as painting over 5 h, heating the electrodes to facilitate solvent evaporation, blowing nitrogen over the surface, and using smaller brushes were tried, none of these steps solved the problem or improved the electrode performance. Ultimately, the high performance from the previous batch was restored by switching to a different backing layer, Toray TGP-H-060 (Fig. S1). This backing layer contains 10 wt% PTFE, versus 5 wt% for Sigracet, and lacks the microporous layer found in the Sigracet. Fig. S1 shows the similar overpotentials for Toray and the original Sigracet electrodes. Although IR-corrections are possible based on our previous work [9], the overpotentials are shown as measured because the emphasis is on the difference between the newer Sigracet backing layer performance and the Toray performance. Subsequent anode overpotentials are not IR-corrected due to the identical electrolyte thickness and composition used in each set of experiments, indicating that the IR losses are identical.

The cause of this improved Toray performance was investigated through hydrophobicity testing. By placing a droplet of deionized water on the backing layer, the contact angle between the water and the backing layer was obtained. Fig. 2 shows that both the Sigracet and Toray backing layers are hydrophobic, with contact angles above 90 °C. The difference between the layers stems from their behavior in the presence of the 50:50 IPA:H_2O catalyst ink mixture. The Sigracet backing layer rapidly absorbs the catalyst ink mixture, which leads to flooding during cell operation and thus the mass transport limitations observed in Fig. S1. The Toray backing layer does not absorb the catalyst ink to the same degree, so the backing still allows gas transport during cell operation. This difference in behavior is the cause of the superior Toray performance.
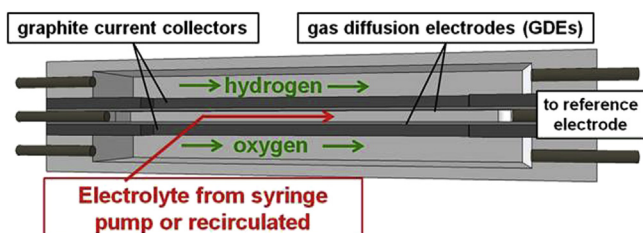

Fig. 1. Diagram of a microfluidic fuel cell with a flowing alkaline electrolyte.