

Letters

Microfluidic Hydrogen Fuel Cell with a Liquid Electrolyte

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We report the design and characterization of a microfluidic hydrogen fuel cell with a flowing sulfuric acid solution instead of a Nafion membrane as the electrolyte. We studied the effect of cell resistance, hydrogen and oxygen flow rates, and electrolyte flow rate on fuel cell performance to obtain a maximum power density of 191 mW/cm². This flowing electrolyte design avoids water management issues, including cathode flooding and anode dry out. Placing a reference electrode in the outlet stream allows for independent analysis of the polarization losses on the anode and the cathode, thereby creating an elegant catalyst characterization and optimization tool.

Introduction

The development of miniaturized, high-energy-density fuel cells for portable applications is an active area of research.¹ Of the various types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) that operate with hydrogen as the fuel have been studied for many years and have been developed the furthest.^{2–5} In PEMFCs, the protons generated at the anode as a result of the electro-oxidation of hydrogen are transported through a solid, proton-conducting membrane to the cathode where they form water through the oxygen reduction reaction

(ORR) at the cathode.⁶ When operated at high temperature (e.g., above ~80 °C), these porous polymer membranes dehydrate, leading to a significant drop in fuel cell performance. Various efforts to overcome this issue have focused on improving the hydration levels and the conductivity of polymer electrolyte membranes, for example, through the modification of the most common solid polymer electrolyte (Nafion) by using inorganic composites or through the synthesis of novel polymer membrane materials for high-temperature operation.^{7–9}

As an alternative to the optimization of membrane materials, phosphoric acid fuel cells (PAFCs) and alkaline fuel cells (AFCs) have been developed in which the anode and cathode are separated by phosphoric acid and potassium hydroxide electrolytes, respectively.^{6,10} The phosphoric acid electrolyte in a PAFC is embedded in a silicon carbide or polymer matrix, has low volatility at typical operation temperatures (150–200 °C), and provides

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chemical and electrochemical stability.^{6,11} In AFCs, which are more efficient than acidic fuel cells as a result of faster ORR rates in alkaline media, recirculating potassium hydroxide (KOH) is used as the electrolyte to aid in the efficient removal of water formed at the anode.^{6,12}

More recently, we^{13,14} as well as others^{15,16} have reported novel flowing electrolyte fuel cells that utilize the phenomenon of multistream laminar flow in microfluidic channels to keep the anode and cathode “compartments” separated. In these laminar flow fuel cells (LFFCs), an aqueous fuel stream (e.g., formic acid and methanol) and an aqueous electrolyte stream (e.g., 0.5 M sulfuric acid or 1 M potassium hydroxide) enter the channel in parallel without turbulent mixing, and their liquid–liquid interface acts as a virtual membrane to keep the contents of each stream separate.^{13–17} Oxygen can be provided to the cathode by saturating the electrolyte stream with air or oxygen.^{13,14,16,17} Abruna et al. have reported an LFFC operated with a H₂-saturated anode stream and an O₂-saturated cathode stream providing a maximum power density of up to ~ 1 mW/cm².¹⁷ Low solubility and low diffusivities of both gases in aqueous media cause the formation of depletion boundary layers on both electrodes, leading to fuel cell performance being limited by mass transport. To overcome these mass transport losses, we recently integrated an air-breathing gas diffusion electrode (GDE) as the cathode in an LFFC, leading to an improvement of the maximum power density to 26 mW/cm².¹⁸ Nuzzo et al. have reported a simpler microfluidic hydrogen fuel cell producing a maximum power density of up to 0.8 mW/cm².^{19,20} The passive delivery of H₂ and O₂ to the electrodes in this cell does lower the cell’s performance, but it also eliminates the need for pumps and other ancillary components that are required for the operation of a fuel cell with active fuel and/or oxidant supplies such as flowing liquid or gaseous streams.

Here, we report a novel microfluidic electrolyte fuel cell in which a flowing stream of sulfuric acid serves as the highly conductive liquid electrolyte between two gas-fed (H₂ and O₂) gas diffusion electrodes to overcome water management issues that are typically encountered in PEMFCs (e.g., anode dry out, cathode flooding, and membrane dehydration). The aqueous flowing electrolyte inherently avoids the occurrence of dehydration and minimizes cathode flooding, as water generated in the present design is effectively removed with the flowing electrolyte. We study the role of different design parameters—electrolyte concentration (ionic resistance) and hydrogen, oxygen, and electrolyte flow rates—on the room-temperature performance of the liquid electrolyte hydrogen fuel cell. This microfluidic fuel cell that is equipped with a reference electrode thus provides fuel cell researchers with a tool for the rapid, independent analysis of cathodes and anodes without other system characteristics such as water management becoming an issue.

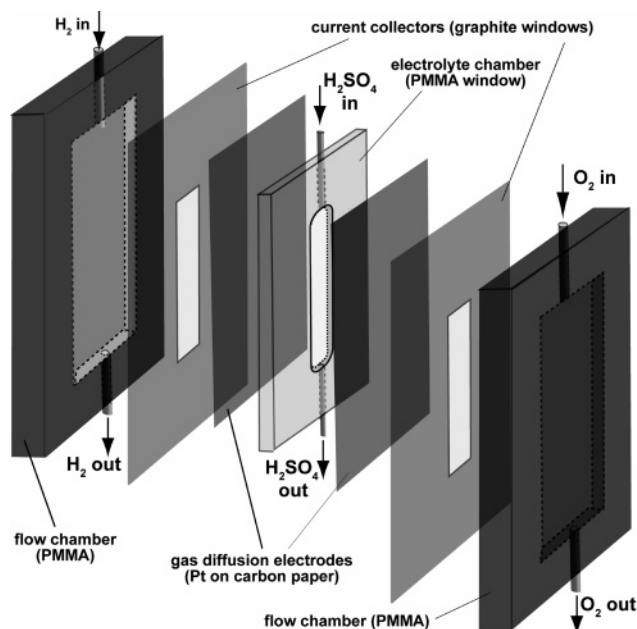


Figure 1. Schematic of a hydrogen fuel cell with an aqueous flowing electrolyte between two gas diffusion electrodes.

Experimental Section

Electrode Preparation. Catalyst inks are prepared by sonicating mixtures of 3 mg of platinum black (Alfa Aesar), 200 μ L of deionized water, 0.1 mg of 5 wt % Nafion solution in lower aliphatic alcohols (Aldrich), and 200 μ L of isopropyl alcohol for 1 h. We varied the platinum/Nafion ratio (Supporting Information) and obtained the best fuel cell performance with a ratio of 30:1. The anodes and the cathodes are prepared by painting this catalyst ink on a 0.99 cm² (3.3 cm long and 0.3 cm wide) rectangular area of Toray carbon paper (EFCG “S”-type electrode, E-TEK), followed by drying under a 250 W lamp (GE) to result in a catalyst loading of 3 mg/cm² and a Nafion loading of 0.1 mg/cm².

Fuel Cell Assembly and Testing. Two of these gas diffusion electrodes are placed on opposing sides of a 2-mm-thick PMMA sheet with a 3.3-cm-long and 0.3-cm-wide window machined in it to allow for the flow of the sulfuric acid electrolyte (Figure 1). The catalyst-covered sides of the gas diffusion electrodes face the electrolyte. Two 1-mm-thick graphite windows act as current collectors. The hydrogen and the oxygen gases each flow through a 5 \times 1 \times 0.5 cm³ chamber machined into a PMMA sheet (Figure 1). This layered assembly is held together using binder clips (Highmark), and no leaks were observed between the different layers. Polarization curves are obtained by holding the cell at constant potential using a potentiostat (Autolab PGSTAT-30) and measuring the steady-state current. The anode and the cathode potentials are recorded independently using an external Ag/AgCl reference electrode (BAS) placed in the electrolyte stream just after it exits the outlet. Current and power densities are calculated using the exposed geometric surface area of the electrodes (3.3 cm \times 0.3 cm = 0.99 cm²). All experiments reported here are performed at room temperature without recirculation of the electrolyte. The setup can easily be adjusted to allow for characterization at different temperatures. The electrolyte and gaseous streams could be guided through fine-gauge stainless steel tubing that is placed in a temperature-controlled bath. Alternatively, the various fuel cell components can be heated to the desired temperature by integrating heating elements and thermocouples.

Results and Discussion

Cell Design. In the microfluidic hydrogen fuel cell studied here, the Nafion membrane that is normally hot pressed between gas diffusion electrodes in a membrane electrode assembly of a PEMFC, a direct methanol fuel cell (DMFC), or a direct formic

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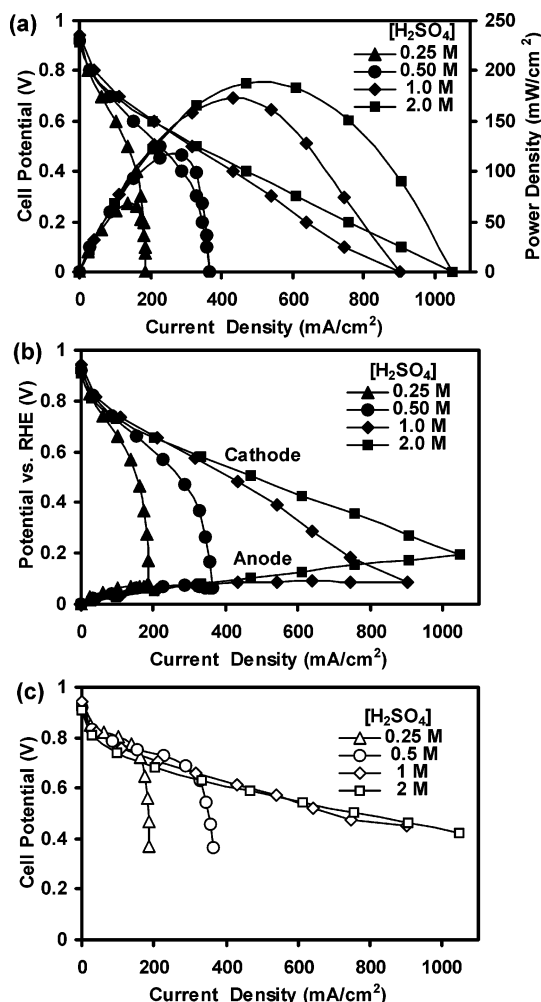


Figure 2. (a) Polarization and power density curves for a H_2/O_2 fuel cell with a flowing electrolyte stream of different $[\text{H}_2\text{SO}_4]$. Hydrogen and oxygen flow rates: 50 sccm each. Electrolyte flow rate: 0.3 mL/min. (b) Corresponding anode and cathode polarization curves. (c) Corresponding IR-corrected cell polarization curves.

acid fuel cell (DFAFC) is replaced with a flowing electrolyte comprising aqueous sulfuric acid (Figure 1). We expect that this simplified configuration will reduce or even avoid common water management issues such as cathode flooding, anode dry out, and membrane dehydration at high operation temperatures.

Effect of Electrolyte Concentration. First, we investigated the effect of different sulfuric acid (H_2SO_4) concentrations (i.e., 0.25, 0.5, 1, and 2.0 M H_2SO_4 electrolyte streams at a flow rate of 0.3 mL/min) on the performance of the fuel cells. Hydrogen and oxygen gases are supplied at a flow rate of 50 sccm each. Figure 2a shows that the peak power density increases from 69 to 187 mW/cm^2 upon increasing the H_2SO_4 concentration from 0.25 to 2.0 M. This increase in performance can be explained by the decrease of the internal cell resistance with increasing electrolyte concentration.²¹ Polarization curves of the individual electrodes obtained using an external Ag/AgCl reference electrode show that the anode suffers less polarization losses than the cathode (Figure 2b). Li et al. have reported similar anode and cathode losses for hydrogen PEMFCs using a dynamic hydrogen reference electrode.²² Figure 2b also shows that the mass transport-limited performance at high current density for the cells studied with 0.25 and 0.5 M H_2SO_4 electrolyte streams, as already evident

in Figure 2a, originates from the cathode side. At these high current densities, the rate of proton replenishment of the depletion boundary layer on the cathode is sufficient only if the fuel cell is operated with 1 or 2 M H_2SO_4 electrolyte streams (steeper proton concentration across the boundary layer). IR-corrected polarization curves (Figure 2c) obtained using resistance values for sulfuric acid solutions from the literature²¹ indicate that the cell polarizations acquired with different electrolyte concentrations are identical in the low current, ohmic regime, where the cells do not experience mass transport losses.^{6,10} The ohmic losses observed when operating with 0.25 or 0.5 M H_2SO_4 as the electrolyte can be attributed to the lower ionic conductivity of the solutions. We performed all further experiments with 1 M H_2SO_4 electrolyte because a higher H_2SO_4 concentration can lead to an increase in sulfate/bisulfate adsorption on the catalyst surface, thereby blocking catalytic sites.^{23,24}

Effect of Hydrogen and Oxygen Flow Rates. We also studied the effect of different hydrogen and oxygen flow rates (1.2–50 sccm) on fuel cell performance. The maximum power density increases initially with an increase in the hydrogen (oxygen) flow rate while using an oxygen (hydrogen) flow rate of 50 sccm, until it levels off at flow rates >5 sccm. (See Supporting Information for the graphs.) The corresponding cathode and anode polarization curves indicate that the mass transport losses on the anode (cathode) side have disappeared at a hydrogen (oxygen) flow rate of ≥ 10 sccm. The mass transport limitations at low flow rates can be attributed to low diffusion constants and the depletion of hydrogen (oxygen) within the water layer on the anode (cathode) catalyst surface.^{25,26} The change in flow rate affects the extent of wetting of the GDE matrix and catalyst layer as explained further in the Supporting Information.

Effect of Electrolyte Flow Rate. We also studied the effect of different electrolyte flow rates (0.0, 0.1, 0.3, and 1.0 mL/min) on fuel cell performance to highlight the ability to minimize or eliminate water management issues in this fuel cell configuration. Hydrogen and oxygen flow rates were kept at 50 sccm each to ensure a more than sufficient supply of fuel and oxidant. The polarization curves show inferior fuel cell performance in the absence of flow (0 mL/min), apparently as a result of mass transport issues at high current densities (Figure 3a). In contrast, when the electrolyte is flowing (0.1 mL/min or faster) the maximum power and current densities improve, and the mass transport losses gradually disappear. The individual cathode and anode polarization curves show that all mass transport losses occur on the cathode side (Figure 3b). Several factors contribute in different degrees to this dependency of the performance on the electrolyte flow rate. Most notably, water is formed at the cathode/electrolyte interface as a result of the ORR and, unlike in PEMFCs, this water will enter the flowing electrolyte stream rather than flood the cathode on the gas-phase side. The consumption of protons and the formation of water at the cathode will contribute to the formation of a proton-depletion boundary layer. In the presence of a flowing electrolyte stream, the thickness of this proton-depletion boundary layer is rapidly reduced, thus increasing the rate of oxygen reduction at sites closer to the gaseous, oxygen-containing phase. Second, the water content within the GDE may change with a change in the electrolyte flow rate. Whereas the change in the pressure balance between the liquid electrolyte and the gaseous streams will be very small,

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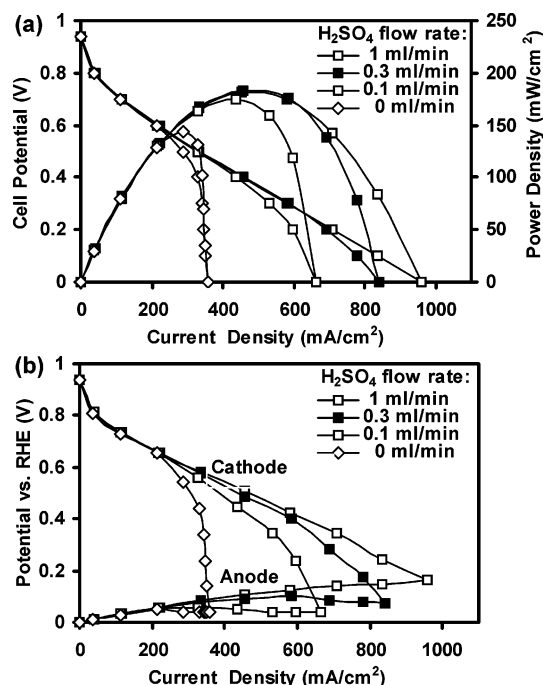


Figure 3. (a) Polarization and power density curves obtained using microfluidic H_2/O_2 fuel cells with different flow rates of the 1 M H_2SO_4 electrolyte (0, 0.1, 0.3, and 1 mL/min). The hydrogen and oxygen flow rates are 50 sccm each. (b) Corresponding anode and cathode polarization curves.

a lower flow rate of the gas phase will reduce the rate of water evaporation. All of the above factors give rise to a proton gradient within the catalyst layer, rendering certain catalytic sites more reactive than others. As shown previously, an increase in the thickness of the layer of water covering the catalytic sites will limit the transport of oxygen to those catalytic sites, and thus reduce fuel cell performance.^{25,26}

Conclusions

A hydrogen fuel cell in which the Nafion membrane commonly found in a PEMFC is replaced with an aqueous sulfuric acid stream was described. The use of a 1 M sulfuric acid solution at a flow rate of ≥ 0.3 mL/min as the electrolyte minimizes a number of issues normally encountered in PEMFCs, including fuel crossover, cathode flooding, anode dry out, and electrolyte dehydration at high operation temperatures. For example, hydrogen that enters the liquid electrolyte without reacting at the anode or water formed at the cathode is flushed away immediately by the flowing electrolyte. A concentration of 1 or 2 M sulfuric acid electrolyte also reduces ohmic losses due to cell resistance, and they could be further reduced by decreasing the electrode-to-electrode distance.

The cell can be operated such that mass transport-related performance limitations are eliminated, leading to a maximum power density of 191 mW/cm^2 at room temperature. Additionally, the electrolyte can be changed to improve cell performance. We observed an open circuit voltage (OCV) between 0.91 and 0.94 V, whereas PEMFCs reported in literature typically have an OCV of 1.00 V.²⁷ We attribute this drop in OCV to sulfate/bisulfate absorption from the flowing electrolyte, which is not present in PEMFCs. When we performed identical experiments using either KOH or HClO_4 as the electrolyte, we observed an OCV of 1.00 V, which corresponds to the OCV observed in PEMFCs. Further optimization of the catalyst and electrode formulation, including lowering of the catalyst loading to the commercial standard of ~ 0.1 mg/cm^2 , reduction of the electrode-to-electrode distance, and operation at higher temperature, has the potential to further enhance cell performance. From an application point of view, this cell requires electrolyte circulation similar to that of AFCs, such as those used in various space exploration missions. Also, CO_2 and/or carbonate poisoning of the electrolyte, a major problem encountered with AFCs, is not an issue with the present design.

This hydrogen fuel cell also has promise as a testing and optimization tool for novel catalysts and/or novel electrode assemblies because the anode and cathode performance can be analyzed independently by placing a standard reference electrode in the outlet stream of the flowing electrolyte. The data obtained are also not convoluted by the effects of water management issues because, for example, cathode flooding does not occur. Moreover, individual electrodes can be exchanged quickly. The cell also may find use in durability studies in which the circulating electrolyte is analyzed for the presence of species that have leached from a membrane electrode assembly while being tested over prolonged periods of time.

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Supporting Information Available: Effects of hydrogen and oxygen flow rates and the catalyst composition at the cathode. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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