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Nanoporous separator and low fuel concentration to minimize crossover in direct methanol laminar flow fuel cells

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ABSTRACT

Laminar flow fuel cells (LFFCs) overcome some key issues – most notably fuel crossover and water management – that typically hamper conventional polymer electrolyte-based fuel cells. Here we report two methods to further minimize fuel crossover in LFFCs: (i) reducing the cross-sectional area between the fuel and electrolyte streams, and (ii) reducing the driving force of fuel crossover, i.e. the fuel concentration gradient. First, we integrated a nanoporous tracketch separator at the interface of the fuel and electrolyte streams in a single-channel LFFC to dramatically reduce the cross-sectional area across which methanol can diffuse. Maximum power densities of 48 and 70 mW cm^{-2} were obtained without and with a separator, respectively, when using 1 M methanol. This simple design improvement reduces losses at the cathode leading to better performance and enables thinner cells, which is attractive in portable applications. Second, we demonstrated a multichannel cell that utilizes low methanol concentrations (<300 mM) to reduce the driving force for methanol diffusion to the cathode. Using 125 mM methanol as the fuel, a maximum power density of 90 mW cm^{-2} was obtained. This multichannel cell further simplifies the LFFC design (one stream only) and its operation, thereby extending its potential for commercial application.

1. Introduction

As next-generation portable electronics continue to require ever-increasing energy densities, microfuel cells have attracted significant interest as an alternative to conventional batteries [1–4]. Unlike batteries which carry a limited supply of fuel internally, microfuel cells consume fuel which is continuously replenished. Microfuel cells can be operated with a variety of fuels, including: hydrogen [5–8], methanol [8–11], and formic acid [12,13]. Compared to hydrogen and other gaseous fuels, liquid fuels are easier to store and transport, and have much higher energy densities per weight and volume. In particular, direct methanol fuel cells (DMFCs) have attracted much interest in portable applications due to the high energy density of methanol.

Although DMFCs offer a promising method of energy conversion, development of DMFCs has been hampered by issues related to the polymer electrolyte membrane (PEM) that separates the anodic and cathodic compartments. Water and/or thermal management is one such concern because Nafion, the most commonly used ionomeric material, must remain fully hydrated to facilitate proton transport, which limits stack and system operation to less than 100 °C. More significantly, the permeation of methanol through the Nafion membrane, i.e. methanol crossover, results in mixed potentials at the cathode, and consequently a dramatic decrease in cell performance [14–18].

A desire to help eliminate these membrane constraints led to the development of laminar flow-based fuel cells (LFFCs) [19–32]. By utilizing laminar flow on the microscale, the fuel and/or electrolyte (or oxidant) streams may be compartmentalized in a single microchannel or a series of parallel microchannels without the need for a physical barrier such as a Nafion membrane. Microfluidic streams flow directly over the catalytic region of an electrode without an intervening thick gas diffusion layer, thus achieving the minimum possible mass transport distance. The membraneless LFFC design utilizes a continuously flowing electrolyte to (i) minimize dry-out and flooding issues at the electrodes, (ii) facilitate by-product removal (i.e. carbon dioxide, carbonates), and (iii) enable fuel and media flexibility. Much work has been done in this field by our group [19–25] and others [26–32]. A

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recent review provides a thorough summary of the field of LFFCs [33].

In LFFC architectures presented to date, fuel crossover depends strongly on (i) cross-sectional area between the anode and cathode as well as (ii) the driving force, i.e. the concentration gradient. Here, we will present two approaches for reducing fuel crossover in LFFCs. At high concentrations of methanol (1–5 M), crossover can be mitigated by pressing the fuel concentration boundary close to the anode catalytic wall via high (differential) flow rates or by using wide channels. However, high flow rates reduce fuel utilization and wide channels increase electrode-to-electrode distances [34]. Our first, more effective approach to reduce fuel crossover involves placing a nanoporous separator at the fuel–electrolyte interface of an LFFC. This separator greatly minimizes the total cross-sectional area at the fuel–electrolyte interface, and hence, the area through which unreacted methanol molecules can crossover to the parallel-flowing electrolyte stream, and ultimately the cathode. This design improvement maintains small electrode-to-electrode distances for reduced volume and higher power density. Our second approach to reduce fuel crossover is to operate at low fuel concentrations, thereby decreasing the driving force for methanol crossover. In a methanol LFFC, crossover is limited to the slow process of diffusion, a concentration gradient-controlled phenomenon. By operating at low methanol concentrations (less than 100 mM), mixed potential effects are not observed when platinum is used as the cathode catalyst [24]. Below we will explore these two approaches using single and multichannel LFFCs.

2. Experimental

2.1. Single-channel methanol LFFC

2.1.1. Fabrication and assembly

The 6-μm thick polycarbonate separator (0.05-μm pore size, 6×10^8 pores cm^{-2}, Sterlitech Corporation) was placed between two identical 150-μm thick Kapton sheets, which were machined to have 4.8 cm (L) × 0.33 cm (W) flow channels. The small characteristic height (defined by the Kapton thickness) of the channels lead to low Reynolds numbers ($Re < 5$), enabling the fuel and electrolyte streams to flow laminarly in parallel on either side of the separator. The anode was centered on a polymer-impregnated graphite plate (McMaster), which functions as a current collector. The cathodic gas diffusion electrode (GDE) was placed in a 220-μm deep trench machined into a similar graphite plate. Within this trench, a serpentine flow channel was machined with a 1:1 channel to landing ratio, and channel dimensions of 1 mm (H) × 1 mm (W). This serpentine channel thus resides exactly beneath the cathodic GDE when it is placed in the trench. Two copper backing plates were placed on either side of the fuel cell to render a robust multilayer assembly as shown in Fig. 1a and b. A cartridge heater can be inserted into the copper plate on the anode side for studies at elevated temperatures. The entire apparatus was held together by 14 evenly spaced bolts, greatly reducing contact resistance between layers. This approach yields a leak-free cell; gaskets were not required.

2.1.2. Electrode preparation

An anode catalyst ink comprised of 10 mg cm^{-2} Pt–Ru 50:50 wt% alloy (Alfa Aesar) with 125 μL H_2O, 34.5 μL Nafion solution, and 125 μL isopropyl alcohol, and a cathode catalyst ink comprised of 2 mg cm^{-2} Pt–C 50:50 atom wt% alloy (Alfa Aesar) with 31.25 μL H_2O, 1.15 μL Nafion, and 31.25 μL isopropyl alcohol were used for all experiments reported here. The catalyst inks were sonicated (Branson 3510) for 1 h to obtain a uniform mixture, before being brushed onto Sigracet 35BC carbon paper. Similar to prior work [35,36], both electrodes were then hot-pressed (Carver Laboratory Press) at 1200 psi for 5 min at 130 °C to improve catalyst adhesion and electrode durability. For some experiments, an additional layer of Nafion 212 (Fuel Cell Scientific, Stoneham, MA), cleaned in a solution of 10 wt% nitric acid at 90 °C for 2 h, was bonded to the cathodic GDE, during the hot-pressing procedure.

2.1.3. Testing

Unless otherwise noted, the single-channel methanol LFFC was operated at 80 °C, with an O_2 supply (laboratory grade, S.J. Smith) of 50 sccm to the serpentine flow field, a fuel and electrolyte flow rate of 0.3 mL min^{-1}, a fuel stream of 1 M methanol with 1 M

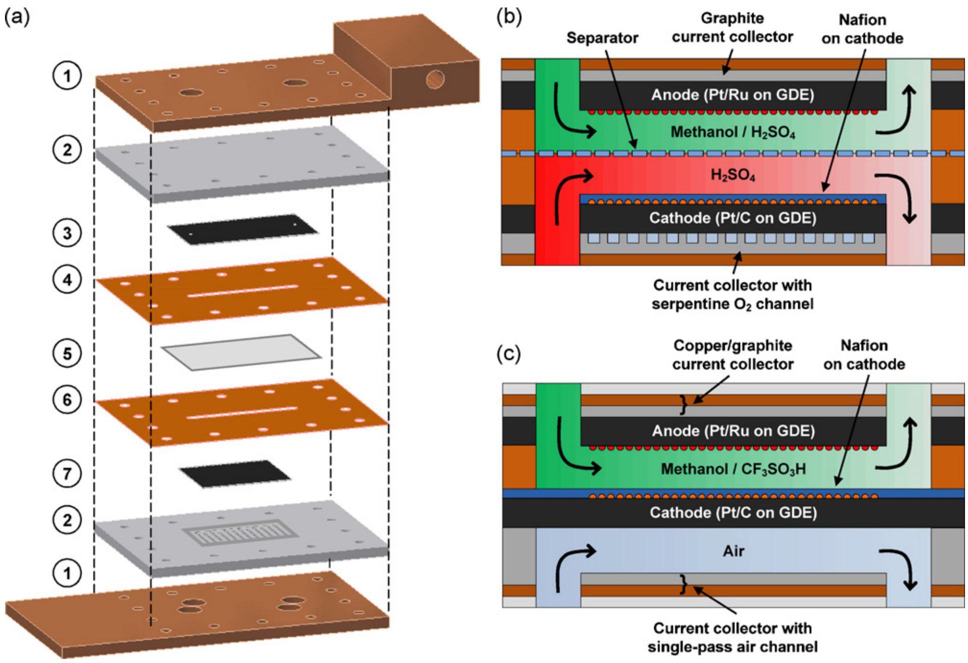

Fig. 1. (a) Exploded diagram of single-channel methanol LFFC (to scale), the numbered components correspond to: (1) copper backing plate with temperature control, (2) graphite current collector, (3) anode, (4) fuel channel, (5) separator, (6) electrolyte channel, and (7) cathode; (b) side-view schematic of single-channel methanol LFFC (exactly like (a)); (c) side-view schematic of multichannel methanol LFFC.