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Study of crossover and depletion effects in laminar flow-based fuel cells using electrochemical impedance spectroscopy

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ABSTRACT

The impedance characteristics of the laminar flow-based fuel cells (LFFCs), which are also called microfluidic fuel cells (MFFCs), are measured to study the crossover and depletion phenomena. To study the effect of the crossover and depletion separately, the impedances are measured at different flow rates simulating different crossover conditions; while the effect of depletion is controlled by keeping the current density constant through changing the fuel concentration at different flow rates. Then the depletion effect is studied by measuring the impedance characteristics of the cell at various fuel concentrations. It is shown that the crossover affects the moderate frequency ranges in the measured Nyquist plot; whereas depletion impacts the low frequency domain. Finally, the impedance measurements at various potentials suggest that increasing the current density increases the effect of crossover while decreases the effect of depletion. This could be the result of carbon dioxide production in the anode.

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Introduction

Portable devices currently rely on low energy density batteries with high weight which restricts their design possibilities [1]. Fuel cells offer an attractive alternative with their high energy densities, and greater variability in storage, handling and implementation within the device. The power density of the fuel cells can be further improved by miniaturization of the cell, which increases the surface-to-volume ratio, as the electrochemical reactions in fuel cells are surface based [2]. Miniaturized proton exchange membrane (PEM) fuel cells can meet this need, but are often limited by the same membrane associated issues that plague their larger counterparts [3]. The phenomenon of laminar flow, however, makes liquid fuels and oxidants attractive due to their ability to flow side by side without mixing at the low Reynolds numbers which are common in microfluidic systems [4]. The interface between liquids replaces the membrane in PEM fuel cells while simultaneously removing the need for water management. This type of cell is usually referred to as a laminar flow-based fuel cell (LFFC) or microfluidic fuel cell (MFFC).

The laminar flow regime of microfluidic channels removes the need for a proton exchange membrane, yet it has its own inherent complications. For instance, while laminar flow restricts advective mixing of the fuel and oxidant streams

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considerably, crossover still occurs due to diffusion and the formation of the mixing layer [5]. Upon reaching the cathode, the fuel causes mixed potential and lowers the open circuit potential and overall cell performance [4]. There are many factors which control the amount of crossover such as channel geometry and flow rate, however, by minimizing crossover the performance of the cell may be affected in adverse ways. One of the most popular methods for suppressing crossover, which does not require alteration of the geometry of the cell, is operation with a high flow rate. This is an attractive method because it not only reduces crossover, but also suppresses the concentration boundary layer that occurs at the electrode [3]. As the fuel is consumed in the concentration boundary layer, it is probable not to have enough fuel near the electrode to complete the reaction. This is referred to as the depletion effect. These two factors combined result in much higher performance. However this performance gain is coupled with very poor fuel utilization (usually <10%) [5].

An air-breathing cathode [6] can be used to replace the liquid oxidant stream by using an unreactive electrolyte stream and ambient air, providing oxygen to the cathode. Compared to a typical LFFC, this type of microfluidic fuel cell significantly reduces the probability of oxidant crossover to the anode [7]. As this is a relatively new branch of fuel cells, most LFFCs constructed to date are proof-of-concept cells designed to test the wide variety of fuels, oxidants, architectures, and operating conditions that can be used in a single channel [2,3,8]. In order to pursue full commercialization of LFFCs, it is necessary to break the inverse relationship between performance (achieved by high flow rates) and fuel utilization (achieved by low flow rates). To find the balance, a thorough modeling of the cell is required.

Among various modeling methods presented to study the electrochemical systems, electrochemical impedance spectroscopy (EIS) has been employed widely in fuel cell literature [9]. In this method, a small harmonic perturbation is applied to the system and the response is measured and investigated [10]. The impedance, then, is determined and generally plotted in a Nyquist (imaginary part vs. real part of impedance) or Bode (phase or magnitude) plots. Next, an equivalent circuit which has the same impedance characteristics as the measured impedances is determined to quantify and compare various impedance specifications.

Despite the widespread use of EIS in modeling and diagnosis of proton exchange membrane fuel cells [11,12] and other electrochemistry systems [13,14], there are a limited number of studies that use impedance spectroscopy to model laminar flow-based [15–18] or other microfluidic fuel cells [19–21]. Brushett et al. [15] studied effects of five different fuels on the performance of laminar flow-based fuel cells (LFFCs). They employed electrochemical impedance spectroscopy as a diagnostic tool to characterize a direct ethanol LFFC under both acidic and alkaline conditions. They measured the impedances of the fuel cell by applying a 10 mV perturbation in the frequency range of 10 kHz–30 mHz with 9 points/decade. They reported that the Nyquist plots show the same characterizations. However, the plot for the acidic medium is scaled up considerably. The Nyquist plots also show that the high frequency resistance (i.e., the intersection of the graph with the axis of the real part of impedance in the high frequency range) is approximately the same for the acidic and alkaline media.

Timperman et al. [16] investigated the effects of adding Pt and Ru_xSe_y onto oxide-carbon composites on the oxygen reduction reaction in a laminar flow-based fuel cells consuming methanol as fuel. They measured the impedance in the frequency range of 100 kHz to 0.1 Hz with the perturbation amplitude of 5 mV rms. They concluded that adding the Ru_xSe_y additive causes an ohmic loss affecting the polarization curve. Lee and Kjeang [17] modified the structure of vanadium fueled microfluidic fuel cells by employing a thin-film current collector. They have reported that the contact resistance has reduced by 32% using the current collector. They measured the impedance of the cell with/without the current collector by applying 100 mV rms perturbation in the frequency range of 100 kHz to 10 Hz. They reported that the high frequency resistance in their Nyquist plots shows a 32% reduction using the current collector. This reduction was in agreement with the 34% reduction in the slope of their measured polarization curve. Shaegh et al. [18] added a fuel reservoir above the anode electrode of an LFFC and claimed it could reduce the ohmic loss and the thickness of the depletion layer. They measured the impedance of their new cell including a small channel depth and reported that the high frequency resistance has been decreased.

As it was mentioned, the literature on the impedance characterizations of the laminar flow-based fuel cells is limited. In this paper, the Nyquist plots of an LFFC in various cell potentials, flow rates and fuel concentrations are presented. The effects of depletion and crossover on the arcs of the Nyquist plots in different ranges of frequency are investigated. Following the same procedure, the impedance of the cell in various voltages are measured and recorded. It is shown that the crossover affects the moderate frequency ranges in the measured Nyquist plot; whereas the depletion impacts the low frequency domain. Finally, the impedance measurements at various potentials suggest that increasing the current density increases the crossover while decreases the depletion.

Experimental setup

The schematic of the cross-section of the air-breathing laminar flow-based fuel cell (LFFC) used in this paper is shown in Fig. 1. A 3 mm × 27 mm channel was machined through a 2 mm thick polycarbonate plate to form the main

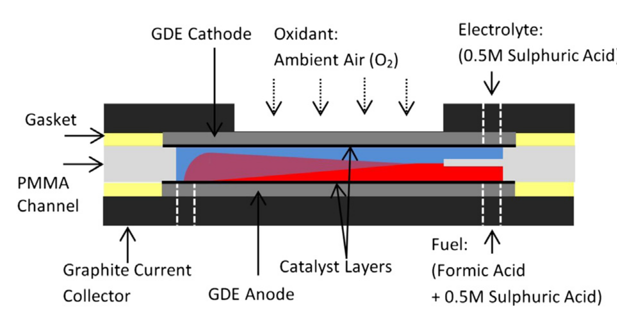

Fig. 1 – The schematic of the cross-section of the air-breathing laminar flow-based fuel cell.

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