The influence of size scale on the performance of fuel cells

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Abstract

Two fundamental scaling effects in a proton exchange membrane (PEM) fuel cell system are being discussed—scaling of flow channel size and catalyst particle size. Various micro/nanofabrication processes [lithography, physical vapor deposition, and focused ion beam (FIB) etch/deposition] were employed to produce a microscale experimental platform. In addition, multiphysics fuel cell models were utilized to verify the experimental results.

The modeling result suggests that fuel cell power density increases with decreasing channel size due to the reduced diffusion blockage of ribs and increased convection in microchannels. However, experimental observation revealed an optimum channel size with maximum power density. The discrepancy is explained by cathode flooding that the single-phase model is unable to account for.

A novel micro-electrochemical impedance spectroscopy technique, combining atomic force microscope with an electrochemical interface, confirmed a linear dependency of Faradic impedance on the triple-phase boundary length (TPB) in microscale catalyst particles. Interestingly, the particle perimeter dependency of Faradic impedance changes to particle area dependency as the particle size increases. This is explained by the generation of cracks in larger catalyst particles, which, in turn, serve as triple phase boundaries. The model prediction based on finite element method confirms the experimental observations.

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1. Introduction

Fuel cell systems are drawing increasing attention as a possible solution for improved power sources in stationary and portable power systems. Crucial for the successful design of fuel cells is an understanding of how the design and manufacturing process parameters influence performance. Design variables include electrolyte thickness, electrode and flow channel geometry, and catalyst particle size and shape, which, in turn, control the length of the triple-phase boundaries. Key parameters such as microstructure are equally important for the electrical behavior and the efficiency of fuel cells.

Flow channel geometry is of critical importance for the performance of fuel cells containing proton exchange membranes (PEM) but is of less concern for solid oxide fuel cells (SOFC). However, recent research showed that “planar” SOFC requires well-designed flow channel geometry, too [1,2]. In the future, metal oxide membranes are expected to shrink to tens of nanometers or less, hence, flow channel design is likely to become more important for SOFC systems as well. Ultra thin electrolytes require the presence of narrow support structures that impede gas flow. This will require the careful design of gas delivery channels to maximize fuel cell power density. The present study examines the influence of flow channel diameter and triple-phase boundary length (TPB) on fuel cell performance. In PEMs, the length of the TPB is expected to act as bottleneck for hydrogen entry into the electrolyte. Similarly, in SOFCs, cathode particles with fast oxygen surface reactions will incorporate most of the oxygen close to the triple-phase boundary [3].

Our current investigation is based on experiments and calculations with proton exchange membranes only. Defi-
nite conclusions for SOFC systems need to be drawn from separate experiments with solid oxide membranes.

2. Size scaling of flow channels

The adaptation of micromachining and microfabrication techniques has successfully enabled the prototyping of fuel cells with fine features and accuracy [4–6]. However, previous research has not properly addressed the transport phenomena in fuel cell systems—especially in micro flow channels [7–18]. To study the microscale flow phenomena, it is necessary to have a suitable platform for the rapid and cost-effective prototyping of micro flow channel fuel cells. We have found that microchannel structures based on photopolymers can be successfully integrated into PEM-type fuel cells [19,20].

2.1. Flow channel experiments

In the present investigation, parallel flow channels with varying dimensions were manufactured. We chose the parallel flow pattern because such structures are most suitable for exploring the convection phenomena. The channels and ribs had square cross-sections, simplifying associated geometric dimensions. This resulted in a single characteristic feature size for each flow channel. It was straightforward to observe the scaling behavior of flow channels by simply varying this characteristic parameter. Other dimensions, such as channel length and gas diffusion layer thickness, were held constant.

Total gas flow rate was identical for all tests to ensure the same stoichiometric number. It should be noted that this results in faster gas flow velocity in smaller channels. In addition, the pressure drop may increase in smaller channels. The consequence of these issues will be discussed later in this paper.

For comparison with experiments, 3-D multiphysics models were generated with commercial code (CFDRC from CFD Research). The models included 3-D multi-component diffusion and convection. Flow in porous media with electrochemical reaction was treated [21]. Nevertheless, certain assumptions existed in the model; most notably, the formation of liquid water on the cathode was ignored. This issue will be discussed later in this paper.

Five samples were prepared for experiments with feature sizes varying as 0, 5, 20, 100, and 500 μm. The 0-μm sample had no channels but only a flat area; thus, the gases were forced to flow only through the diffusion layer. The 5-, 20-, and 100-μm samples were fabricated with SU-8 photore sist (Microchem) using photolithography techniques [22]. Fig. 1(a) shows the brief process diagram. Because the channel structure is based on a polymer, metal current collection was sputter deposited as a final step. Fig. 1(b) shows a scanning electron microscope image of a 100-μm microchannel structure. The 500-μm sample was prepared by conventional machining of metal blocks.

All samples had an active area of 14 mm long and 14 mm wide (2 cm²). As discussed earlier, both channels and ribs had square cross-sections with the same dimensions. At the beginning and end of channels, slots of 14×1 mm were machined as gas inlet and outlet. Thus, gases enter and exit perpendicular to the channels. Excluding the inlet and outlet, the flow channel was 12 mm long.

The testing method of the flow channel was similar to that of conventional fuel cell systems. Conventional membrane electrode assemblies (MEAs) were obtained from a commercial vendor (BCS Technology, Byran, TX). The MEA active area was 14×14 mm, employing carbon cloth electrodes with Pt/C catalyst (1 mg/cm² loading) and Nafion® 115. In the tests, the MEA was placed between two SU-8 flow channels and sealed with thin silicon rubber gaskets. Two metal blocks mechanically clamped the assembly. A single MEA was used for all five samples, minimizing the discrepancy in activation and ohmic losses between the testing of samples.

Pure hydrogen and air, both 1 atm, were used in all tests. The flow rates were 30 and 80 scm for hydrogen and air, respectively. Both gases were heated and fully saturated at 50 °C before entering the fuel cell. The I-V curves were obtained using Solartron 1287 potentiostat.

2.2. Results and discussion

The flow channel scaling effect is shown in Fig. 1(c) for both the model and experimental results. Peak power density is plotted vs. feature size. The model predicts that performance increases as channel size decreases. As discussed earlier, gas velocity increases in smaller channels. Accordingly, smaller channels can remove water more efficiently by enhanced convection. Furthermore, the size of the rib is reduced to be even smaller than the thickness of gas diffusion. Therefore, reactant concentration is more uniformly distributed across the whole diffusion layer. This eliminates the so-called “dead zones” under the ribs. Similar results have been reported in other flow patterns [12].

Of course, as the channel size decreases, increased pressure drop becomes a concern. However, in a miniature fuel cell, the active area is relatively small and the absolute length scale is also short. Accordingly, the penalty from pressure drop may be less significant than the benefits of enhanced flow through the microchannels. The pressure drop data from the model confirm this speculation in Fig. 1(c). Here, the pressure drop has been converted to power density using the following equation for comparison convenience.

\[ W_{\text{Pressure}} \left( \text{W/cm}^2 \right) = \frac{P \left( \text{Pa} \right) \times A_{\text{Inlet}} \left( \text{m}^2 \right) \times V_{\text{inlet}} \left( \text{m/s} \right)}{A_{\text{Cell}} \left( \text{cm}^2 \right)} \]
Here, $W_{\text{Pressure}}$, $P$, $A_{\text{Inlet}}$, $V$, and $A_{\text{Cell}}$ stand for power loss associated with pressure drop per cell unit area, pressure drop, flow inlet area, flow inlet velocity, and fuel cell area, respectively. This power loss is equivalent to the power consumption of a pump to accommodate the specified pressure drop and flow rate, assuming 100% efficiency.

From Fig. 1(c), the loss due to pressure drop is significantly smaller than the increase in the peak power density as the channel size decreases. Thus, the employment of microchannels may increase the power density of the fuel cell despite the pressure drop, especially for single-phase flow.

Fig. 1(c) also shows the experimental results. Interestingly, the cell performance peaks at a certain feature size and decreases with the continued scale-down of feature size. This may be explained by water condensation in the cathode. In the test samples, the volume of the flow channel is directly proportional to feature size. This means that the same amount of water occupies more area in smaller channels. Thus, flooding area in the flow channels may increase inversely proportional to feature size. This issue is not captured properly by the model due to the assumption of single-phase flow. Detailed investigation using electrochemical impedance spectroscopy strongly suggests that smaller channels are more susceptible to flooding. A thorough discussion of this topic will be published in the near future.

One of the unique transport phenomena in micro flow channels is the kinetic behavior of gas flow. Considering that the mean free path of an air molecule is of the order of $0.1\ \mu m$, the transition from continuum to kinetic transport is expected to commence when the gas channel diameter is reduced below $10\ \mu m$. However, due to the water blockage in the microchannels, the transition may happen at a larger feature size. Any model based on continuum treatment does not properly consider the kinetic effect in microchannels. The proper treatment and analysis of this issue is left for future work.
In addition, dimensional discrepancy may exist between the model and the experiment. Due to the deformation of gas diffusion layer, or even the roughness of its surface, the actual geometry of channels in the experiment may not exactly match that of the model.

3. Size scaling of triple-phase boundary

Using a focused ion beam system (FIB), we have prototyped Nafion-based PEMFCs with micron- and submicron-sized geometrically simple Pt-catalyst microstructures to measure their electrochemical characteristics. By varying the size and shape of these Pt-catalyst features, we have been able to extract exact scaling relationships between the geometry of the Pt-catalyst structures and their electrochemical properties. (Refer to similar studies on solid oxide fuel cell cathodes [23–25]). These Pt-catalyst features are directly patterned on the surface of the Nafion electrolyte, thus, we are directly probing the Pt-Nafion interface that is so important to a PEMFC. Unlike investigations conducted in aqueous electrolyte environments, these results are inherently applicable to real-world PEMFC devices.

3.1. Triple-phase boundary experiments

Fig. 2(a) depicts the experiment configuration. Commercially available “half-cell” fuel cell MEAs were obtained from BCS Technologies. These half-cell MEAs employed a Nafion 115 electrolyte membrane on one side, of which was hot pressed a 0.5 cm² carbon cloth catalyst-electrode structure. This large-area electrode served as the reversible reference and counter electrode. The other side of the MEA was left purposely bare. The Pt-catalyst electrode structures under investigation were then patterned on this bare electrolyte surface. The half-cell MEAs were either mounted onto a reusable copper flux-flow structure electrode block with vacuum groove sealing or were permanently laminated to a copper-plated printed circuit board flux-flow structure electrode. Hydrogen gas was introduced through the flow structure to the sealed anode compartment, where it was delivered to the large-area counter/reference electrode. The Pt structures on the bare electrolyte top surface were exposed to ambient air. A Gamry PC4/750 potentiostat-impedance system was used for all electrochemical measurements. Tests were conducted at room temperature; H₂ flow rate at the anode was regulated to 5 sccm.

The electrochemical properties of these Pt structures were probed using either gold-coated tungsten needles in a micromanipulator under an optical microscope or an AFM with a conductive doped-diamond coated tip, where electrochemical measurements could be obtained directly through the conductive AFM tip. Further elaboration on the use of the AFM as a localized electrochemical probe is planned for a future publication and will not be discussed here.

The platinum catalyst structures were directly written onto the topside electrolyte surface using an FEI Strata Dual-Beam 235 FIB. The rapid-prototyping nature of the FIB allowed us to create a wide-ranging set of simple platinum catalyst features for investigation. Most of the platinum features investigated were simple circular electrodes (see Fig. 2(b)), ranging in size from several hundred microns down to several hundred nanometers; however, other platinum catalyst features, such as rectangles and grids, were also explored. All platinum catalyst features had a nominal deposited thickness of 2 nm.

3.2. Results and discussion

The microscale platinum circles pictured in Fig. 2(b) are fully functioning fuel cells. In fact, they may be some of the world’s smallest PEMFCs ever measured. Fig. 3(a) shows the absolute I-V curves for three different circular fuel cells with radii varying from 10- to 40-μm. The absolute performance of these tiny fuel cells is insignificant; note the small values for current. Not surprisingly, the larger the fuel cell, the greater absolute current that it delivers. Fig. 3(b) reports the results from the same three circular Pt structures, but now normalized by area; on an area-normalized basis, these results argue that smaller fuel cells are better. Intriguingly, the I-V curves of the three fuel cells are roughly comparable if they are scaled relative to their circumferences rather than their areas, as shown in Fig. 3(c).
To understand this scaling phenomenon, it is necessary to consider the fundamental electrochemical characteristics of the Pt-catalyst structures. A systematic impedance study allows us to separate the contributions of electrolyte resistance \( R_e \) and faradic impedance \( R_f \) of the oxygen reduction reaction (ORR). The results of this study are given in Fig. 4(a) and (b). As Fig. 4(a) reveals, \( R_e \) for the Pt-electrode structures is proportional to \( r/C_0^2 \) for large-area electrodes and proportional to \( r/C_0^1 \) for small-area electrodes.

For small electrodes (when the electrode size, \( r \), is much smaller than the electrolyte thickness, \( t \)), the measured point contact resistance can be shown to be inversely proportional to the electrode radius [26]:

\[
R_e = \frac{\rho}{4r}, \quad r \ll t
\]  

(1)

Whereas for \( r \gg t \), the resistance is inversely proportional to the electrode area:

\[
R_e = \frac{\rho t}{r^2}, \quad r \gg t
\]  

(2)

Thus, Fig. 4(a) relates a purely geometrical effect, owing to the transition from an area-related electrolyte resistance.
for $r \gg t$ to a point-contact-dominated spreading resistance for $r \ll t$. This expected result is also recovered in a simple finite element simulation, as shown by the dotted line in Fig. 4(a). A parametric best fit of the finite element simulation to the experimental data is obtained for simulation values of Nafion thickness $t=90 \ \mu m$ and Nafion resistivity $\rho=3000 \ \Omega \ cm$. (Nominal reference values for dry Nafion 115 are $t=125 \ \mu m$ and $\rho=10–100 \ \Omega \ cm$ [27–29].) Because the electrolyte in our experiments is subjected to a desiccating high vacuum environment prior to electrochemical measurement, it is unsurprising that our experimentally fit resistivity values are high.

Perhaps more surprising are the results in Fig. 4(b), which show that $R_f$ is also roughly proportional to $r^{-2}$ for large electrodes and proportional to $r^{-1}$ for small electrodes. Note that the faradic impedance is several orders of magnitude larger than the electrolyte impedance. This indicates that $R_f$ for the ORR dominates the electrochemical behavior of these circular micro fuel cells. (The losses from $R_e$ are negligible in comparison.)

For electrodes smaller than about 40 $\mu m$, we see a direct relation between Pt-catalyst structure circumference and $R_f$. Considering the 2-$\mu m$ thickness of the catalyst structures, the bulk of the electrode area cannot participate in the ORR process. Instead, only the perimeter participates as an active triple-phase boundary (TPB) for the faradic reaction. The roughly $r^{-2}$ dependence for the larger Pt electrodes is believed to arise from a cracking process due to the dimensional instability of the Nafion electrolyte. Postmortem electron microscope analysis of Pt-catalyst structures confirms that cracking typically occurs for electrodes greater than about 40 $\mu m$. The cracking is believed to be due to the expansion of the Nafion electrolyte upon removal from the vacuum environment and exposure to ambient humidity. This area-distributed cracking introduces additional TPB sites in the larger electrode structures, which should scale roughly proportional to the electrode area. For Pt electrodes smaller than 30 $\mu m$, no cracking is witnessed. For these small, unbledmed electrodes, then, it is possible to extract a faradic resistance per unit TPB length ($R_{TPB}$). $R_{TPB}$ is calculated as:

$$R_{TPB} = \frac{R_f}{2\pi r}$$

From the data in Fig. 4(b), $R_{TPB}$ can be estimated at roughly $R_{TPB}=6 \times 10^7 \ \Omega \ \mu m$.

As mentioned previously, the faradic impedance dominates the electrochemical behavior of these micron-sized catalyst structures. Thus, catalyst structures with an increased TPB length per unit area should show proportionally improved catalytic performance. In Fig. 4(c), a uniform 40×40 $\mu m$ square electrode is compared with a sectioned 40×40 $\mu m$ square electrode. The two electrodes have the same total Pt area, but the sectioned electrode has five times greater TPB length. (Each interior section contributes two lengths of TPB.) As the impedance spectra for the two structures clearly show, the faradic resistance of the sectioned electrode is 1/5 that of the uniform electrode.

4. Conclusions

(1) Microchannels were successfully integrated in miniature fuel cells. Model results predicted that the adaptation of microchannels leads to improved performance. Experiments confirmed the model prediction. At the same time, flooding can become a serious issue in microchannels. More detailed investigation on this issue and model improvements for flooding are left for future work.

(2) Having determined a quantitative value for the resistance per triple-phase boundary length in a PEMFC, we infer the requirements for TPB densities for a high-performance PEMFC. For most fuel cell requirements, a cathodic ORR resistance of around 0.15 $\Omega \ cm^2$ is acceptable [30]. This implies a TPB density on the order of $10^6 \ cm/cm^2$. Assuming plane packed spherical platinum particles, each of which contributes an average TPB on the order of its projected circumferential length, this implies that a catalyst particle size smaller than 30 nm is necessary to achieve the required ORR resistance.

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References
