Effects of reactant crossover and electrode dimensions on the performance of a microfluidic based laminar flow fuel cell

Isaac B. Sprague a, Doyoung Byun b, Prashanta Dutta a,b,∗

a School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164-2920, USA
b Department of Aerospace Information Engineering, Konkuk University, Seoul 143-701, Republic of Korea

Abstract

A mathematical model is developed to simulate the performance of a laminar flow fuel cell with reactant crossover using the Poisson–Nernst–Plank (PNP) equations. The model includes a more general treatment of reactant (fuel or oxidant) crossover than the common method where it is assumed that the crossover flux is fully utilized as crossover current. This new model allows for the analysis of very narrow channels and estimation of parasitic crossover current at both the anode and the cathode. It also allows for the consideration of a laminar flow fuel cell with a significant amount of reactant crossover where the crossover species are not fully consumed by the crossover current. Moreover, the combination of the PNP equations and the general reactant crossover treatment reveal the two-dimensional developing region for electrode mixed potentials which is a novel result. The parameters considered in this study are electrode length and separation (channel height). Numerical results show that the reactant crossover, transport limitations, and Ohmic losses are the primary performance limitation factors. The current distributions along the anode and cathode are presented as well as the reactant concentrations at the anode as evidence of these performance limitations. It is also shown that the fluid velocity field, as it changes with channel height, plays a small role in the development of the depletion boundary layer.

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1. Introduction

In the past decade, the paradigm of using micro fuel cells for portable power applications has inspired novel innovations in fuel cell technology. One such example is the laminar flow fuel cell (LFFC), which utilizes colaminar flow to maintain the separation between the anode and cathode instead of a solid electrolyte such as the membrane used in polymer electrolyte membrane (PEM) fuel cells. The original concept of a LFFC was first presented as a vanadium redox cell in 2002 [1]. LFFCs were then investigated experimentally by addressing parameters such as flow rates or fuel concentrations [2–4]. Further adaptations of the original LFFC concept have also been proposed, usually focusing on the electrode structure such as an air-breathing cathode [5,6], electrodes comprised of graphite rods aligned in the streamwise direction [7], and reactants fed through porous electrodes [8], among others.

Mathematical models are also important in understanding and optimizing a new device concept such as LFFCs. Presently, in literature, there exist a number of models for laminar flow fuel cells. In simplified models, reactant consumption has been used to study fuel utilization for a variety of electrode configurations [9] and multiple reactant inlets along the electrodes [10]. Models that account for the interdependence of cell potential and current density have been used to investigate device level performance [11–13]. An advanced model that accounts for multistep reaction kinetics such as the oxygen reduction reaction has also been presented [14]. Recently, we presented a more general model for LFFC that uses the Poisson–Nernst–Plank (PNP) equations along with Navier–Stokes equations [15]. This model provides a more fundamental representation of ion transport within the electrolyte by considering the electromigration in the system. The electrochemistry of these models is fundamentally similar to the models for PEM fuel cells that are ubiquitous in electrochemistry [16,17]. However, it is common for PEM fuel cell models to also account for fuel crossover, which has been entirely neglected from the mathematical studies of LFFCs.

Fuel crossover is the phenomenon where the fuel supply at the anode bleeds over into the cathode catalyst layer which adversely affects the overall fuel cell performance. In a fuel cell without crossover, fuel oxidizes at the anode releasing electrons, however, are routed through an electric circuit to the

* Corresponding author at: Department of Mechanical and Materials Engineering, Washington State University, P.O. Box 642920, Pullman, WA 99164-2920, USA.
Tel.: +1 509 335 7989; fax: +1 509 335 4662.
E-mail address: dutta@mail.wsu.edu (P. Dutta).

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Nomenclature

**English characters**
- Concentration, mM
- **C**₅, Sterne capacitance, F
- **D** Diffusion coefficient, m² s⁻¹
- e⁻ Electron
- **F** Faraday’s constant, C mol⁻¹
- H Half channel height, m
- J Current density, A m⁻²
- K Rate constant
- L Channel length, m
- N Number of electrons involved in kinetic reaction
- P Pressure, Pa
- R Ideal gas constant, J K⁻¹ mol⁻¹
- S Stoichiometric coefficient
- T Absolute temperature, K
- V Fluid velocity vector, m s⁻¹
- X Position along channel, m
- Y Position across channel, m
- Z Ionic charge

**Greek characters**
- **β** Kinetics symmetry factor
- ΔΦ₅ Potential drop across Sterne layer, V
- **ε** Permittivity, F m⁻¹
- λ₅ Thickness of Sterne layer, s₅/C₅, m
- **μ** Viscosity, Pa s
- **ρ** Density, kg m⁻³
- **Φ** Electrolyte potential, V
- **Ψ** Electrode potential, V
- **ω** Ion mobility, m² mol⁻¹ s⁻¹

**Subscripts**
- A Anode
- An Anode
- **C** Cation
- Ca Cathode
- **Cell** Device level values
- E Electrolyte
- El Electrode
- **F** Fuel
- FO Fuel oxidation
- FR Fuel reduction
- O Oxidant
- OO Oxidant oxidation
- OR Oxidant reduction
- S Sterne layer
- **Start** Start of electrode
- **Stop** End of electrode

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cathode. The protons and electrons at the cathode are then consumed by the oxidant reduction reaction producing the waste by-product of the cell. The flow of electrons through the electric circuit is the useable work produced by the fuel cell. When fuel crossover occurs, there is fuel present in the cathode creating a cathode fuel oxidation reaction. This cathode fuel oxidation releases electrons and charged ions locally, which are then consumed by the oxidant reduction reaction. This reduces the amount of electrons that are required from the anode, effectively short circuiting the fuel cell. The parasitic current, often referred to as leaking current, at the cathode resulting from fuel crossover has experimentally been shown to reduce the overall cell current at a given cell potential in a PEM direct methanol fuel cell (DMFC) [18]. Fuel crossover also reduces the potential of a cathode half cell of a PEM DMFC because of the mixed potentials [19,20].

A number of studies have reported modeling of fuel crossover in PEM fuel cells [21–23], but no such work exists for the LFFC. In LFFC, the lack of a physical separation can permit oxidant as well as fuel to crossover and impact device performance adversely. It is also possible that the amount of crossover could be significant enough that it is no longer appropriate to assume that the crossed over reactants are fully consumed. Therefore, a simple, yet more general, method for representing reactant crossover is introduced that can account for both fuel and oxidant crossover. This model is then used to study the performance and reactant crossover in a LFFC operating with different electrode lengths and separations.

2. Model development

For this study, a simple straight microchannel was considered with two inlet channels and a single outlet as shown in Fig. 1. The computational domain starts at X = 0 where the two inlet channels meet at the start of the main channel. The outlet is at X = L where the flow is considered fully developed. The main channel is twice as tall as the inlet channel height, H, and the walls are located at Y = ±H. The electrodes are located along the channel walls with the anode at Y = −H and the cathode at Y = H. The start of the electrodes along the channel is X = XStart and the end is X = XStop. A simple redox reaction of fuel (F) and oxidant (O), with a cation (C) being produced by fuel oxidation and consumed by oxidant reduction was considered. The stoichiometric equations for the half reactions for fuel oxidation and oxidant reduction become:

Fuel oxidation: \( S_F F \rightarrow S_C C + n e^- \) \hspace{1cm} (1a)

Oxidant reduction: \( S_C C + n e^- + S_O O \rightarrow \) waste \hspace{1cm} (1b)

and the overall redox reaction is then:

Overall: \( S_F F + S_O O \rightarrow \) waste \hspace{1cm} (1c)

where \( n \) represents the number of electrons involved in the reaction. The value of \( n \) depends on which specific reactants are used in the overall reaction. A binary electrolyte was used consisting of the cation that participates in the reaction and is balanced by an anion \((A)\) each with a unit charge, \( z_C = -z_A = 1 \). By taking the cation as the working ion we are assuming an acidic electrolyte. It should be noted that an alkaline electrolyte could be considered quite easily by taking the anion as the working ion. This would assume a binary electrolyte where the anion participates in the reaction and is balanced by the cation and the remainder of the model development would remain unchanged. An alkaline electrolyte could possibly produce different results than an acidic electrolyte but this compa-
The system of equations produced by Eqs. (4)–(6) is nonlinear and highly coupled. A numerical scheme is necessary to solve them across a two-dimensional domain with the complex boundary conditions given by Table 1. An in-house numerical model is developed to simulate LFCC with reactant crossover. The detail of the numerical scheme is presented elsewhere [15].

3. Results and discussion

For this study, a straight channel LFCC, as shown in Fig. 1, is considered with the channel half height ranging from $H = 50\, \mu m$. The concentration distributions are governed by the steady state Nernst–Plank equation which reduces to:

$$\nabla \cdot \mathbf{J}_i = 0$$

(4)

The potential distribution in the electrolyte is governed by Poisson equation [24]:

$$-\nabla \cdot (\varepsilon_E \nabla \Phi) = F \sum z_i C_i$$

(5)

Here, the right hand side of the equation is charge density, which is the sum of the total charge for all of the species present. For neutral species such as the fuel and oxidant, the ionic charge is zero. So they do not contribute to the total charge density.

The flow field is governed by the steady state Navier–Stokes [24] and continuity equations:

$$\nabla \cdot (\rho \mathbf{V} \mathbf{V}) = \nabla \cdot (\mu \nabla \mathbf{V}) - \nabla P - F \sum z_i C_i (\nabla \Phi)$$

(6a)

$$\nabla \cdot (\rho \mathbf{V} \mathbf{V}) = 0$$

(6b)

2.1. Boundary conditions

Table 1 lists the boundary conditions used for Eqs. (4)–(6) in the computational domain which has five basic boundaries: the fuel inlet, oxidant inlet, outlet, walls, and electrodes. For the electrolyte potential at the electrodes, an adaptation of the Stern model for the inner double layer is used (Bonnefont et al. [25]):

$$\Phi = \Psi_E + \frac{\varepsilon_S}{C_s} \frac{\partial \Phi}{\partial V}$$

(7a)

The second term on the right hand side of this boundary condition is equivalent to the potential drop across the Stern layer, $\Delta \Phi_s = \Phi - \Psi_E$, which is assumed to be linear and continuous with the potential in the electrolyte. The inlet fluid velocity vector, $\mathbf{V}_{in}$, is calculated from an analytical solution of Eq. (6) for forced convection in rectangular ducts [26]:

$$\mathbf{V}_{in} = \mathbf{V}_{Max} \left[ 1 - \left( \frac{2|Y - H/2|}{H} \right)^2 \right] \cdot i + 0 \cdot j$$

(7b)

where $\mathbf{V}_{Max}$ is the specified input.

2.2. Numerical formulation

The system of equations produced by Eqs. (4)–(6) is nonlinear and highly coupled. A numerical scheme is necessary to solve them across a two-dimensional domain with the complex boundary conditions given by Table 1. An in-house numerical model is developed to simulate LFCC with reactant crossover. The detail of the numerical scheme is presented elsewhere [15].

### Table 1: Boundary conditions used to solve the system of governing equations.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Fuel inlet</th>
<th>Oxidant inlet</th>
<th>Channel outlet</th>
<th>Channel wall</th>
<th>Electrodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i = A$</td>
<td>$C_1 = C_2$</td>
<td>$C_1 = C_2$</td>
<td>$\frac{\partial C_1}{\partial x} = 0$</td>
<td>$N_1 = 0$</td>
<td>$N_A = 0$</td>
</tr>
<tr>
<td>$i = C$</td>
<td>$C_1 = C_2$</td>
<td>$C_1 = C_2$</td>
<td>$\frac{\partial C_1}{\partial x} = 0$</td>
<td>$N_C = 0$</td>
<td>$N_C = \frac{C_1}{j_{FO}}(j_{FO} - j_{OA})$</td>
</tr>
<tr>
<td>$i = O$</td>
<td>$C_1 = C_2$</td>
<td>$C_1 = C_2$</td>
<td>$\frac{\partial C_1}{\partial x} = 0$</td>
<td>$N_O = 0$</td>
<td>$N_O = \frac{C_1}{j_{OO}}$</td>
</tr>
<tr>
<td>$i = 0$</td>
<td>$C_1 = 0$</td>
<td>$C_1 = 0$</td>
<td>$\frac{\partial C_1}{\partial x} = 0$</td>
<td>$N_0 = 0$</td>
<td>$N_0 = \frac{C_1}{j_{OR}}$</td>
</tr>
<tr>
<td>$5$</td>
<td>$\frac{\partial C_1}{\partial x} = 0$</td>
<td>$\frac{\partial C_1}{\partial x} = 0$</td>
<td>$\frac{\partial C_1}{\partial x} = 0$</td>
<td>$\frac{\partial C_1}{\partial x} = 0$</td>
<td></td>
</tr>
<tr>
<td>$6$</td>
<td>$\mathbf{V} = \mathbf{V}_{in}$</td>
<td>$\mathbf{V} = \mathbf{V}_{in}$</td>
<td>$P = 0$</td>
<td>$</td>
<td>\mathbf{V}</td>
</tr>
</tbody>
</table>

The difference between fuel oxidation (Eq. (2a)) and fuel reduction (Eq. (2b)) is the crossover current and the difference between oxidation and reduction kinetics can be applied to both electrodes. In this work, the oxidation and reduction kinetics are represented as:

Fuel oxidation : $j_{FO} = F n \left( k_{FO} C_F e^{-\frac{(1 - \beta)\Delta \Phi_F F}{RT}} \right)$ (2a)

Fuel reduction : $j_{FR} = F n \left( k_{FR} C_F e^{-\frac{\beta \Delta \Phi_F F}{RT}} \right)$ (2b)

Oxidant oxidation : $j_{OO} = F n \left( k_{OO} e^{-\frac{(1 - \beta)\Delta \Phi_F F}{RT}} \right)$ (2c)

Oxidant reduction : $j_{OR} = F n \left( k_{OR} C_O e^{-\frac{\beta \Delta \Phi_F F}{RT}} \right)$ (2d)

where an oxidation current is positive and a reduction current is negative by convention. The concentration terms, $C_F$, $C_O$, and $C_C$, are the reactants taken at the electrode of interest. The drop across the Stern layer $\Delta \Phi_S$ is the driving mechanism for kinetics. The rate constants, $k_{FO}$, $k_{FR}$, $k_{OO}$, and $k_{OR}$, can be unique to the anode or cathode depending on the reaction conditions at a particular electrode such as catalyst composition or temperature. In this work, the rate constants for the anode and cathode are considered equivalent. The net current at a specific electrode is the combination of these various currents:

Electrode current : $j_E = (j_{FO} - j_{FR}) + (j_{OO} - j_{OR})$ (2e)

The fuel crossover present in a cell is accounted by using a universal computational electrode model such as this. For example, at the cathode the difference between fuel oxidation (Eq. (2a)) and fuel reduction (Eq. (2b)) is the crossover current and the difference between oxidant oxidation (Eq. (2c)) and oxidant reduction (Eq. (2d)) is the power producing current. So at the cathode where there will be an ample supply of oxidant and potentially a minimal amount of fuel, the power producing current will be greater than the crossover current and the net electrode current will be negative.

The flux density of the reactant species and the electrolyte components is given by:

$$n_i = \nabla C_i - D_i \nabla C_i - z_i F C_i \nabla \Phi$$

(3)

where $i$ indicates the specific species and $i = C, A, F, O$. The flux density is comprised of three components: advection, diffusion, and electromigration. The first term on the right hand side of Eq. (3) is advection, and is important to consider for LFCCs which have a flowing liquid electrolyte. The second term is diffusion and the third term is electromigration, which is critical to the function of fuel cells because it is the primary motive force for the charged ions to migrate from one electrode to the other. It is obvious from Eq. (3) that the flux density of a charged ion is dependent on the potential gradient in the electrolyte.
to $H = 2.5 \, \text{mm}$, while the length of the channel kept constant at $L = 5 \, \text{mm}$. The start of the electrode is at $X_{\text{Start}} = 50 \, \mu\text{m}$ and the end of the electrode ranges from $X_{\text{Stop}} = 100 \, \mu\text{m}$ to $X_{\text{Stop}} = 5 \, \text{mm}$. The entire operating range of the LFCC is considered from short circuit to open circuit. The input to the model are the electrode potentials, $\Psi_{\text{An}}, \Psi_{\text{Ce}}$, and the model output is the overall current cell density $J_{\text{Cell}}$. The anode electrode potential $\Psi_{\text{An}}$ is specified as zero, while the cathode electrode potential $\Psi_{\text{Ce}}$ is increased incrementally from zero until the total cathode current density, $J_{\text{Cell,Ce}}$, equals zero, which corresponds to the open circuit load. The average electrode current density is calculated by:

$$J_{\text{Cell,El}} = \frac{1}{X_{\text{End}} - X_{\text{Start}}} \int_{X_{\text{Start}}}^{X_{\text{End}}} J_{\text{El}}(X) \, dX \quad (8)$$

and from this the overall cell current density is found as:

$$J_{\text{Cell}} = J_{\text{Cell,An}} = -J_{\text{Cell,Ca}} \quad (9)$$

Table 2 provides the values of all of the remaining parameters used to obtain numerical results.

### 3.1. Cell performance

The VI plots for various channel heights and electrode lengths are presented in Fig. 2 and reveal the complicated nature of LFCCs. Fig. 2a shows VI plots for $X_{\text{Stop}} = 100 \, \mu\text{m}$ and channel heights ranging from $100 \, \mu\text{m}$ to $5 \, \text{mm}$. It is apparent that as the channel height increases there is a slight decrease in fuel cell performance. The exception is the $H = 50 \, \mu\text{m}$ case where the channel is so narrow that the reactants have had a chance to crossover and mixed potentials have developed. The implication of reactant crossover will be discussed later. A case of no reactant crossover is also presented by only considering fuel oxidation at the anode and oxidant reduction at the cathode. This case of $H = 50 \, \mu\text{m}$ without reactant crossover yields the best performance, though these results cannot be realized in practice. This shows the necessity of adding reactant crossover, at least in a narrow channel. The case of $H = 2500 \, \mu\text{m}$ yields the worst performance because the cell's internal resistance for cation conduction across the electrolyte is a function of channel height and will increase as the channel height increases. Therefore, as the height increases the Ohmic potential drop across the cell will also increase yielding a lower current density for the same cell potential. The impact of channel height becomes more severe with longer electrode lengths as evidenced by the increased difference in maximum cell current density between cells with $H = 500 \, \mu\text{m}$ and $H = 2500 \, \mu\text{m}$ for the longer electrode lengths of $X_{\text{Stop}} = 500 \, \mu\text{m}$ (Fig. 2b), $X_{\text{Stop}} = 1000 \, \mu\text{m}$ (Fig. 2c), and $X_{\text{Stop}} = 5000 \, \mu\text{m}$ (Fig. 2d). At the longer electrode lengths, the cell with channel height of $50 \, \mu\text{m}$ (without reactant crossover) no longer has the superior performance. This is due to transport limitations which will be discussed later. It should also be noted that the cell with $H = 250 \, \mu\text{m}$ and $X_{\text{Stop}} = 5000 \, \mu\text{m}$ suffers from slight reactant crossover.

Fig. 2 shows that increasing the electrode length also decreases the cell current density for equivalent cell potentials. This is because the local current densities decrease along the electrode. So when they are averaged along the channel length, a lower overall current density is obtained. It is important to note that the total current produced by the cell is greater, although the current densities are lower. Fig. 3 shows the local anode current density distribution along the channel length for $X_{\text{Stop}} = 5000 \, \mu\text{m}$. This includes total current density as well as individual components such as the fuel oxidation, fuel reduction, and the parasitic oxidant crossover current density. The total local current density is given by Eq. (2e), which consists of power producing current and reactant crossover current. Fig. 3a presents the current distribution for a $100 \, \mu\text{m}$ tall channel with $\Psi_{\text{Cell}} = 20 \, \text{mV}$. This loading is very close to the cell’s open circuit load because of the significant performance drop from the reactant crossover. Fig. 3b–d shows the local current density breakdowns for a cell with $H = 250 \, \mu\text{m}$ (Fig. 3b), $H = 500 \, \mu\text{m}$ (Fig. 3c), and $H = 2500 \, \mu\text{m}$ (Fig. 3d) operating with a cell load of $\Psi_{\text{Cell}} = 400 \, \text{mV}$. This loading is near the peak power density for the given fuel cells. For all of the cells, there is no current within the first $50 \, \mu\text{m}$ where there is no electrode present on the channel wall. Then at the start of the electrode, $X = X_{\text{Start}}$, there is a rapid increase in fuel oxidation. Further along the electrode the fuel oxidation decreases leading to a lower local current density along the electrode. The fuel reduction current is constant along the cell. As channel height increases the magnitude of the fuel reduction current increases. The increase in fuel reduction current with increasing channel height causes an overall lower net electrode current density. There is no fuel reduction in Fig. 3a because the cell loading is too low to motivate a fuel reduction current. The reason for the increased fuel reduction current with increasing height needs further investigation; but it is clear that it leads to the lower overall fuel cell performance with the taller heights shown in Fig. 2. The oxidant crossover current density is zero for the entire electrode in Fig. 3c and d. However, for Fig. 3a and b the crossover current is not zero and plays a role in the local current density.

The breakdown of local current density for the cathode is shown in Fig. 4. The net current for the cathode is a reduction current which is negative by convention. This yields a negative net current density for the cathode. Fig. 4a shows the cathode distribution for a fuel cell with channel height $H = 50 \, \mu\text{m}$ and $\Psi_{\text{Cell}} = 20 \, \text{mV}$. The other figures show fuel cells with a cell loading of $\Psi_{\text{Cell}} = 400 \, \text{mV}$ and channel heights of $H = 250 \, \mu\text{m}$ (Fig. 4b), $H = 500 \, \mu\text{m}$ (Fig. 4c), and $H = 2500 \, \mu\text{m}$ (Fig. 4d). The local oxidant reduction current density has a different distribution than the fuel oxidation distribution along the anode. There is an initial spike at the start of the electrode and then a very rapid decrease before it stabilizes to a slower decrease. The oxidant oxidation current is zero even at the higher fuel cell load in Fig. 4b–d unlike the fuel reduction current along

### Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
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<td>$D_o$</td>
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<td>$\chi_s$</td>
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<td>$\omega_{\text{la}}$</td>
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<tr>
<td>$\omega_{\text{le}}$</td>
<td>$1 \times 10^{-12}$ m² mol⁻¹ s⁻¹</td>
</tr>
</tbody>
</table>
3.2. Transport limitations

LFFCs rely on the flowing stream in the channel to supply the reactants to the electrodes. There are, however, performance limitations associated with the reactant transport. The decrease in local current density along the electrodes shown in Figs. 3 and 4 is a result of the reactants being depleted as they flow along the electrodes. This is known as the depletion boundary layer and it occurs near the electrodes. As reactants are consumed at the electrodes, the reactant supply immediately adjacent to the electrode becomes depleted and additional reactants must diffuse in from the bulk flow. As the reactant stream continues along the electrode, this depleted zone grows as reactants are consumed at a quicker rate than they are replaced by diffusion. The concentration distribution of the reactants along the anode for the fuel cells presented in Fig. 3 is shown in Fig. 5a. It is apparent that the available fuel at the anode decreases along the channel.

Another source of reduced reactant supply to the electrodes is the diffusional mixing that occurs from one stream into the other. For example, as fuel diffuses into the oxidant stream the total amount of fuel in the fuel stream is also reduced. Eventually, in a long enough channel for a given channel height the fuel will be completely mixed between the two streams and the concentration of fuel in both streams will be equal to half of the starting concentration in the fuel stream. The amount of mixing can be characterized by the transverse diffusional broadening which is the distance that the species from one stream has diffused into the other at a given position along the channel [27]. When the transverse diffusional broadening is thicker than the half channel height, the amount of fuel available at the anode will be reduced. Fig. 5b shows the concentration distribution of fuel and oxidant along the anode for channels without electrode kinetics. By neglecting kinetics, the concentration distributions are only a function of cross-channel diffusion. For a channel with $H=50 \mu m$, the amount of fuel available to the anode is significantly reduced and for a channel with $H=250 \mu m$ the amount of fuel available to the anode is slightly reduced at positions further downstream. For taller channels ($H=500 \mu m$ and $H=2500 \mu m$), the concentration of fuel along the anode wall is not depleted due to cross-channel diffusion.

The depletion boundary layer thickness and transverse diffusional broadening increase as the stream flows downstream. This can be seen in the fuel concentration distribution across the channel at different positions along the channel, which is shown in Fig. 6 for a cell operating at short circuit and an electrode length of $X_{stop} = 5000 \mu m$. For a narrow channel of $H=50 \mu m$ (Fig. 6a), both the transverse broadening and the depletion boundary layer thickness are greater than the half channel height at the chan-
Fig. 3. Local current density distribution along the anode for various channel heights. The total current density is composed of fuel oxidation, fuel reduction, and total oxidant crossover current. The fuel cells presented are operating at a cell loading of $\Psi_{cell} = 20$ mV for (a) $H=50$ μm and $\Psi_{cell} = 400$ mV for (b) $H=250$ μm, (c) $H=500$ μm, and (d) $H=2500$ μm.

nel outlet leading to a uniform but depleted concentration of fuel. For $H=250$ μm (Fig. 6b), the transverse broadening is thicker than the half channel height at the channel outlet and, therefore, fuel crossover occurs. Also, the depletion boundary layer and transverse broadening overlap in the fuel stream leading to poorer fuel replenishment to the anode. The taller channels (Fig. 6c and d) top and bottom walls are separate enough for fuel crossover to occur and maintain the inlet concentration of fuel in the bulk fuel stream; but the effect of the depletion boundary layer is apparent near the anode electrode.

Figs. 5 and 6 suggest that the cells with $H=50$ μm and $H=250$ μm suffer from transport limitations. The case of $H=50$ μm and no reactant crossover clearly shows these transport limitations by isolating them from reactant crossover limitations. As the electrode length increases, a more significant portion of the electrode is suffering from a lack of reactants causing the overall performance to decrease. This is evident by the decrease in overall performance of this cell relative to the performance of a cell without transport limitations such as $H=500$ μm or $H=2500$ μm for increasing electrode length in Fig. 2.

3.3. Velocity field

Closer inspection of Figs. 5a and 6c and d reveal that the concentration of fuel along the anode for $H=2500$ μm is less than that for $H=500$ μm. However, the taller channel height has a lower cell current density as shown in Fig. 2d, which would suggest that the reactants should be consumed at a lower rate. The reason for the more severe depletion boundary layer is that the reactant replenishment due to advection is less because the fluid velocity field is affected by channel height. The inlet velocity was specified by the maximum velocity in the inlet channels, $V_{max}$; therefore, a taller channel height will yield a lower fluid velocity near the channel wall and the depletion boundary layer. Lower reactant replenishment will lead to lower reactant concentration available to the electrodes and an increase in transport limitations. This would suggest that at least a portion of the decrease in performance for increasing channel height is due to a velocity field linked transport limitation. To evaluate the significance of the fluid velocity contribution to the channel height performance trend, cells with a constant velocity field of $V = (2/3)V_{max} \cdot i + 0 \cdot j$ are presented in Fig. 7. The concentration distribution along the anode for fuel and oxidant is shown in Fig. 7a. The concentration of fuel along the anode for a cell with $H=2500$ μm is no longer less than that for $H=500$ μm. This confirms that a cell with a constant velocity field does not have transport limitations related to velocity distribution. Fig. 7b shows a VI plot of the same fuel cells. Since the same performance trends are present (i.e. lower overall performance for $H=2500$ μm than for $H=500$ μm) in both cases, the velocity field only plays a very minor role on performance.
Fig. 4. Local current density distribution along the cathode for various channel heights. The total current density is composed of oxidant oxidation, oxidant reduction, and total fuel crossover current. The fuel cells presented are operating at a cell loading of $\Psi_{\text{cell}} = 20 \text{ mV}$ for (a) $H = 50 \mu\text{m}$ and $\Psi_{\text{cell}} = 400 \text{ mV}$ for (b) $H = 250 \mu\text{m}$, (c) $H = 500 \mu\text{m}$, and (d) $H = 2500 \mu\text{m}$.

Fig. 5. Reactant concentration distribution along the anode for various channel heights and cell operating conditions for $X_{\text{stop}} = 5000 \mu\text{m}$. The reactants shown are fuel ( ) and oxidant ( ) for $H = 50 \mu\text{m}$, fuel ( ) and oxidant ( ) for $H = 250 \mu\text{m}$, fuel ( ) and oxidant ( ) for $H = 500 \mu\text{m}$, and fuel ( ) and oxidant ( ) for $H = 2500 \mu\text{m}$. (a) A laminar flow fuel cell identical to the fuel cells presented throughout this work and operating at a cell load of $\Psi_{\text{cell}} = 400 \text{ mV}$ and (b) a straight microchannel without electrodes.
Fig. 6. Concentration distribution of fuel across the channel for different positions along the channel and different channel heights. The electrode length in all sub-figures corresponds to $X_{\text{stop}} = 5000\,\mu\text{m}$ and the cells are operating at a short circuit load ($\Phi_{\text{cell}} = 0\,\text{mV}$). At the channel inlet the fuel concentration is set to $C_F = C_E$ for $-H < Y < 0$ (fuel inlet) and $C_F = 0$ for $0 < Y < H$ (oxidant inlet). The different channel heights shown are: (a) $H = 50\,\mu\text{m}$, (b) $H = 250\,\mu\text{m}$, (c) $H = 500\,\mu\text{m}$, and (d) $H = 2500\,\mu\text{m}$.

Fig. 7. A laminar flow fuel cell with a constant velocity field of $\mathbf{V} = 2/3V_{\text{m}}$ operating at a cell load of $\Phi_{\text{cell}} = 400\,\text{mV}$. (a) Reactant concentration distributions along the anode for various channel heights for $X_{\text{stop}} = 5000\,\mu\text{m}$. The reactants shown are fuel (---) and oxidant (---) for $H = 50\,\mu\text{m}$, fuel (---) and oxidant (---) for $H = 250\,\mu\text{m}$, fuel (---) and oxidant (---) for $H = 500\,\mu\text{m}$, and fuel (---) and oxidant (---) for $H = 2500\,\mu\text{m}$. (b) A Vi plot for the laminar flow fuel cell with constant velocity field presented in (a).
Fig. 8. Two cases of high reactant crossover in a laminar flow fuel cell with a channel height of $H = 50 \mu m$, and $X_{Stop} = 5000 \mu m$. Case 1 has a reactant diffusion coefficient of $D_f = D_o = 9.9109 m^2 s^{-1}$ and case 2 has a reactant diffusion coefficient of $D_f = D_o = 2.4777 m^2 s^{-1}$. Contour plots of the potential distribution throughout the electrolyte are shown for (a) case 1 and (b) case 2. The distribution of potential drop across the Stern layer, the motive force for electrode kinetics, is shown for both the anode and cathode for case 1 and case 2 in (c) and (d), respectively. Finally, the electrolyte potential across the channel is shown at the start of the electrode, $X = X_{Start}$, and the end of the electrode, $X = X_{Stop}$, for (e) case 1 and (f) case 2.

3.4. Reactant crossover

Reactant crossover can be seen in several of the LFFC configurations, which drastically affect performance by creating mixed potentials at the electrodes. In Fig. 2, the channel with $H = 50 \mu m$ suffers from increasing reactant crossover starting at the shortest electrode and up to the longest. Whereas, the channel with $H = 250 \mu m$ only suffers slight crossover with the longest electrode. The mixed potentials caused by reactant crossover reduce the cell potential for equivalent current densities compared to the case without reactant crossover. A reduced open circuit potential (OCP) is most obvious in Fig. 2b–d for $H = 50 \mu m$, but is also present in Fig. 2a for $H = 50 \mu m$ and Fig. 2d for $H = 250 \mu m$. The reduction in OCP is a well-known symptom of fuel crossover [18–20]. The cause
of the reactant crossover is a relatively large transverse diffusional broadening evident in Fig. 6a and b. The presence of reactant at the wrong electrode (i.e. fuel at the cathode shown in Fig. 6) leads to the parasitic crossover current that causes the mixed potentials. This can be seen as the oxidant crossover current in Fig. 3a and b as well as fuel crossover current in Fig. 4a and b.

The mathematical treatment for reactant crossover presented in this work predicts some novel behaviors that are not shown before. These behaviors are most obvious in a narrow channel \((H = 50 \mu m)\) operating with an electrode length of \(X_{Stop} = 5000 \mu m\). This is because of the significant amount of reactant crossover that occurs as seen in Figs. 5 and 6a. In fact, Fig. 5b shows that the concentration of the fuel and oxidant are equivalent \((H = 50 \mu m)\) for the downstream portion of the anode. Also, Eq. (2a) shows that for a negative drop across the Stern layer, like the one that occurs at the anode for a cell loading from short circuit, the fuel oxidation current is retarded while Eq. (2d) shows that oxidant reduction would be accelerated. Therefore, for equivalent concentrations of fuel and oxidant at the anode, the oxidant reduction current will be greater than the fuel oxidation as shown in Fig. 3a. In Figs. 3a and 4a, the crossover currents become larger than the power producing currents for the downstream portions of the electrodes. This yields a net negative local current density at the anode and positive local current density at the cathode indicating that the current of cations across the electrolyte is now backwards for the downstream portion of the LFFC. Another interesting phenomenon seen in Fig. 5a is that the concentration of the crossed over oxidant is depleted as the flow continues along the anode. This would suggest that with high levels of reactant crossover, the crossover currents are subjected to the same transport limitations presented earlier. This cannot be captured by the ubiquitous assumption that the crossover species is entirely consumed by the parasitic crossover current.

Reactant crossover of the magnitude present in this LFFC will create strong mixed potentials that have implications on the potential distribution within the electrolyte. Fig. 8 presents a closer look at the effect of crossover for two fuel cells constructed with such a channel \((H = 50 \mu m, L = 5 \text{ mm}, X_{Start} = 50 \mu m, X_{Stop} = 5 \text{ mm})\): one with \(D_H = D_O = 9.9109 \text{ m}^2 \text{ s}^{-1}\) operating at a cell load of \(\Psi_{Cell} = 20 \text{ mV}\) (case 1) and a second fuel cell with \(D_H = D_O = 1/4 (9.9109) \text{ m}^2 \text{ s}^{-1}\) operating at a cell load of \(\Psi_{Cell} = 150 \text{ mV}\) (case 2). Fig. 8a and b shows contour plots of the potential in the electrolyte for case 1 and 2, respectively. For both cases, the electrolyte potential distribution is unaffected by mixed potentials at the start of the electrode. Then, as reactants crossover and mixed potentials begin to develop, the potential distribution changes significantly, especially in the bulk electrolyte. The potential distribution across the channel in Fig. 8a eventually stabilizes around \(X = 200 \mu m\) which coincides with the position along the channel where the two reactant streams are fully mixed, shown in Fig. 5a and b. The region of changing potential distribution is the developing region for mixed potentials. The potential distribution across the channel in Fig. 8b stabilizes near the channel outlet which is expected because the diffusion coefficient for the reactants was reduced by a factor of four. The change in potential occurs as the fuel cell is compensating for the necessary change in overpotential to accommodate the mixed potentials. This change in potential must occur in the electrolyte and not in the electrode because the electrodes are typically a high conducting metal and it is accurate to assume that the potential gradient within the electrode is negligible relative to the potential gradient within the electrolyte. Fig. 8c and d shows the potential drops across the Stern layer (which is analogous to overpotential but the more accurate motive force for electrode kinetics as shown in Eq. (2) along the electrodes for case 1 and 2, respectively. It is clear that initially the fuel cell requires one set of potential drops for current equilibrium. However, with the introduction of reactant crossover, the potential drops across the Stern layer must adjust to maintain conservation of current. Also, very near the start of the electrode, \(X = X_{Start}\), the drops across the Stern layer change radically. This is a result of the developing region of the diffuse double layer. Fig. 8c and d also shows that the drop across the Stern layer is negative for the anode and positive for the cathode, which is expected. However, the drop across the Stern layer at the anode in Fig. 8c is affected by oxidant crossover so substantially that it becomes positive downstream. Fig. 8e presents the potential distribution across the channel in the bulk electrolyte for case 1 at the start of the electrode, \(X = X_{Start} = 50 \mu m\), and at the end of the electrode, \(X = X_{Stop} = L = 5000 \mu m\). The gradient across the channel switches signs from the start of electrode to the end of electrode. This occurs because the current flows in the opposite direction at the electrode end due to the high levels of reactant crossover. Fig. 8f shows the same phenomenon for case 2 in which a greater effect of reactant crossover on potential distribution across the cell is observed. This is because case 2 is operating at a higher cell load than case 1 and requires a larger adjustment of overpotentials to maintain conservation of current. It would be expected that any amount of reactant crossover would result in a change in the electrolyte potential distribution as shown in Fig. 8e and f, just not to the same degree. Still, this phenomenon would hold for any case of reactant crossover.

4. Conclusions

A mathematical model for LFFC is developed by considering reactant crossover, and the performance of LFFC was evaluated numerically with various electrode configurations. It was shown that the narrower channels suffer from reactant crossover that reduces performance. For the narrowest channel with the longest electrode \((H = 50 \mu m \text{ and } X_{Stop} = 5000 \mu m)\), the potential distribution across the channel was significantly impacted by the reactant crossover. To maintain the conservation of current, the potential drop across the Stern layer must be different for different levels of reactant crossover. This impact on the electrolyte potential cannot be represented by the simple charge conservation models typically presented for fuel cells. Instead, the PNP equations, which account for the strong interaction between the electrolyte potential and the concentration of the charged ions within the electrolyte, are needed to capture this change in potential distribution. It was also shown that the reactant crossover is so significant in this fuel cell that crossed over species are not fully consumed. This fact questions the validity of common assumptions used in the modeling of reactant crossover in fuel cells. Furthermore, the magnitude of the local parasitic current from reactant crossover became greater than the power producing local current density reversing the direction of current.

In this study, the spacing and length of the electrodes were varied from a narrow channel with \(H = 50 \mu m\) to a very tall channel of \(H = 2500 \mu m\) and electrode lengths from an impractically short length to an impractically tall channel ending at \(X_{Stop} = 100 \mu m\) to an electrode as long as the channel ending at \(X_{Stop} = 5000 \mu m\). For these configurations, a trend of decreasing cell current density with increasing electrode length as well as decreasing cell current density with increasing channel height was obtained. Also, fuel cells with shorter channel heights were shown to suffer from transport performance limitations at the longer electrode lengths even when reactant crossover is neglected.

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References