Multiphase Non-Isothermal Modeling of a Flowing Electrolyte - Direct Methanol Fuel Cell

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Direct Methanol Fuel Cell (DMFC)

- DMFC is an electrochemical device that produces electricity from methanol and an oxidant such as air.
- Low temperature fuel cell (50-120 °C)
- Advantages:
  - Low cost liquid fuel
  - High energy density of methanol
- Disadvantages:
  - The slow reaction kinetics of the methanol oxidation
  - Methanol crossover through the membrane
  - Water management

\[ \text{Overall} \quad CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O \]
Flowing Electrolyte-Direct Methanol Fuel Cell (FE-DMFC)

Amount of methanol is transported from the anode to the cathode and causing performance degradation.

To decrease this problem,

- Kordesch proposed a novel solution which is the flowing electrolyte concept to prevent crossover whereby the anode and cathode are separated by a flowing liquid electrolyte, such as diluted sulfuric acid.
Literature Survey

Various FE-DMFC models in the literature:

• Kjeang et al. (2005, 2006) studied the methanol crossover reduction in the flowing electrolyte channel with different operating parameters.
• Colpan et al. (2011, 2012) develop 1D-2D model to predict how the performance of the cell changes under different fluid velocity at the anode, cathode, and flowing electrolyte channel inlets.
• Ouellette et al. (2014) extended Colpan’s a one-dimensional FE-DMFC model to predict how the performance of the changes the inlet concentration of the FE, as well as the flow rate and thickness of the flowing electrolyte channel (FEC).
• Sabet-Sharghi et al. (2013) studied experimentally the FE-DMFC to compare its performance to regular DMFC
• Ouellette et al. (2015) developed a single domain, multiphase FE-DMFC model to find maximum power density and minimal methanol and water crossover, a parametric study were conducted using a previously described one-dimensional, multiphase model of (FE-DMFC).
Objectives

• To develop a multi-phase non-isothermal 2D model of a FE-DMFC that couples the following governing equations:
  • Charge transport
  • Continuity
  • Momentum
  • Species transport for methanol, water, and oxygen
  • Energy

Although there are several two phase non-isothermal DMFC models in the literature. There is not any models about non-isothermal FE-DMFC.

For this reason, firstly 2D non-isothermal, two phase FE-DMFC model develop using with COMSOL Multiphysics 5. And also, these parametric analysis were done.

• Anode and cathode inlet temperature of the FE-DMFC has been studied
Modeling Assumptions

The main assumptions of the models are as follows:

- Methanol is fully consumed at the interface of the cathode catalyst layer and cathode backing layer
- The fuel cell operates under steady state conditions.
- The inlet FEC velocity profile is uniform
- The BLs and CLs have the same porous properties.
- All fluids are ideal and exist in equilibrium.
COMSOL Modeling

In order to solve the governing equations, the built-in modules have been used in COMSOL.

- **The Transport of Diluted Species** interface is used to compute the concentration field of a dilute solute in a solvent species in the fuel cell.
- **The Secondary Current Distribution** interface is used to define the transport of charged ions and current conduction in each layer.
- **The Free and Porous Media Flow** interface is used to compute the fluid’s velocity and pressure.
- **Heat Transfer in Fluids interface** is used to compute temperature distribution.

- All these modules and user defined functions were used to develop the model.
Governed Equations

· Mass
\[ \nabla \cdot (\rho \mathbf{u}) = \left( \sum M^k S_{gen}^k \right) - \left( \sum M^k \left( \nabla \cdot N_e^k \right) \right) = S_{gen} + S_{trans} \]

· Momentum
\[ \frac{\rho}{\varepsilon_p} \left( (\mathbf{u} \cdot \nabla) \frac{\mathbf{u}}{\varepsilon_p} \right) = \nabla \left[ -P I + \frac{\mu}{\varepsilon_p} (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2\mu}{\varepsilon_p} (\nabla \cdot \mathbf{u}) I \right] - \left( \mu K^{-1} + \beta_F |\mathbf{u}| \right) \frac{S_{gen}}{\varepsilon_p^2} \mathbf{u} + F \]

· Species
\[ \nabla \left[ -D_{ig} \nabla C_i^k + u_i^k C_i^k \right] = S_{gen}^k \]

· Energy
\[ \nabla \left( -k_{eff} (\nabla T) + \gamma_T c_p_{eff} \rho \mathbf{u} T \right) = S_T \]

· Charge
\[ 0 = \nabla \left( \sigma_s \nabla \phi_s \right) + S_{c,s} \]
\[ 0 = \nabla \left( \sigma_l \nabla \phi_l \right) + S_{c,l} \]
Species transport

\[ \nabla \left[ -D_{ig}^k \nabla C_i^k + u_{ig}^k C_i^k \right] = S_{gen}^k \]

\[ \nabla \cdot \left[ -D_{ig}^{H_2O} \nabla C_{H_2O} + u_{ig}^{H_2O} C_{H_2O} \right] = S_{gen}^{H_2O} - \nabla \cdot \left[ -D_{ig}^T (\nabla T) + \varepsilon e n_d^{H_2O} \frac{i}{F} \right] = S_{gen,eff}^{H_2O} \]

Methanol transport

\[
D_{MeOH}^{ig} = D_{MeOH}^1 + \frac{D_{MeOH}^k}{k_{MeOH}} + D_{e}^{MeOH}
\]

\[ u_{ig}^{MeOH} = \gamma_{MeOH} u \left( s + \frac{1}{k_{MeOH}} \right) + j_i \left( \frac{1}{\rho_{l}} - \frac{1}{k_{MeOH}} \right) + \left( e \frac{\gamma_{MeOH}^k i}{C_{MeOH}^k} \right) - \left( D_{MeOH}^{eff} \frac{\partial (1/k_{MeOH})}{\partial T} \right) \nabla T \]

Water transport

\[ u_{ig}^{H_2O} = \gamma_{H_2O} u \]

\[ D_{ig}^{H_2O} = \begin{cases} 
D_{g}^{H_2O} + D_{l}^{H_2O} & \text{if } C_{H_2O} \leq C_{g, sat} \\
D_{cap}^{H_2O} + D_{l, eff}^{H_2O} & \text{if } C_{g, sat} < C_{H_2O} \leq C_{l}^{H_2O} \\
D_{g}^{H_2O} + D_{l, eff}^{H_2O} & \text{if } C_{H_2O} = C_{l}^{H_2O} 
\end{cases} \]

\[ S = \frac{\lambda_{w,c} - \lambda_{w,l}}{\lambda_{w,c} - \lambda_{w,l}} = \frac{C_{H_2O}^{l} - C_{g, sat}^{l}}{C_{l}^{H_2O} - C_{g, sat}^{l}} \]

\[ D_{cap}^{H_2O} = \frac{\sigma (\cos \theta) \sqrt{2K} \lambda_{w,c} \frac{\partial J}{\partial S}}{C_{l}^{H_2O} - C_{g, sat}^{l}} \frac{C_{H_2O}^{l} - C_{g, sat}^{l}}{\rho_{l} - \rho_{g}} \]

\[ D_{l, eff}^{H_2O} = \begin{cases} 
\rho_{l} \frac{D_{l, eff}^{H_2O}}{M_{e}} \frac{\partial \lambda_{w,c}}{\partial s} & \text{if } C_{H_2O} \leq C_{g, sat}^{l} \\
M_{e} \frac{C_{l}^{H_2O} - C_{g, sat}^{l}}{\partial s} & \text{if } C_{H_2O} \geq C_{g, sat}^{l} 
\end{cases} \]

General form

For water
### Source/Sink Terms

<table>
<thead>
<tr>
<th>Source/Sink Terms</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{\text{gen}}^{\text{MeOH}}$</td>
<td>$0$ - $\frac{j}{6F}$</td>
</tr>
<tr>
<td>$S_{\text{gen}}^{\text{O}_2}$</td>
<td>$0$ $0$ $0$ $0$ $0$ $0$ $\frac{-j}{4F} - 2\frac{j_{\text{water}}}{6F}$ $0$</td>
</tr>
<tr>
<td>$S_{\text{gen}}^{\text{H}_2\text{O}}$</td>
<td>$0$ $-\frac{j}{6F} - \nabla\left(\varepsilon_{\text{w},\text{ACX}} n_d^{\text{H}_2\text{O}} \frac{i}{F}\right)$ $-\nabla\left(n_d^{\text{H}<em>2\text{O}} \frac{i}{F}\right)$ $-\nabla\left(\eta_d^{\text{H}<em>2\text{O}} \frac{i}{F}\right)$ $\frac{j}{2F} + 2\frac{j</em>{\text{water}}}{6F} - \nabla\left(\varepsilon</em>{\text{w},\text{CLC}} n_d^{\text{H}_2\text{O}} \frac{i}{F}\right)$ $0$</td>
</tr>
<tr>
<td>$S_{\text{gen}}^{\text{CO}_2}$</td>
<td>$0$ $\frac{j}{6F}$ $0$ $0$ $0$ $0$ $\frac{j_{\text{exothermic}}}{6F}$ $0$</td>
</tr>
<tr>
<td>$S_{\text{gen}}^{T}$</td>
<td>$\frac{(i_e)^2}{\sigma_e} + \left(\frac{(i_e)^2}{\sigma_e} + j_i \left[T \Delta S_{\text{gen}}\right] \frac{6F}{6F}\right)$ $\frac{(i_e)^2}{\sigma_e}$ $\frac{(i_e)^2}{\sigma_e}$ $\frac{(i_e)^2}{\sigma_e}$ $\frac{(i_e)^2}{\sigma_e}$ $\left(\frac{(i_e)^2}{\sigma_e}\right)$</td>
</tr>
</tbody>
</table>

### CLs

\[
\nabla \left[ D_{\text{H}_2\text{O}}^{\text{H}_2\text{O}} M^{\text{H}_2\text{O}} (\nabla C_{\text{H}_2\text{O}}) + D_{\text{MeOH}}^{\text{MeOH}} M^{\text{MeOH}} (\nabla C_{\text{MeOH}}^{\text{MeOH}}) - M^{\text{MeOH}} \nabla \left( \varepsilon_{\text{MeOH}}^{\text{MeOH}} \frac{i}{F} \right) C_{\text{MeOH}}^{\text{MeOH}} - M^{\text{H}_2\text{O}} \nabla \left( \varepsilon_{\text{w}}^{\text{H}_2\text{O}} C_{\text{MeOH}}^{\text{H}_2\text{O}} \frac{i}{F} \right) C_{\text{MeOH}}^{\text{H}_2\text{O}} + M^{\text{H}_2\text{O}} D_{\text{w}}^{\text{H}_2\text{O}} \frac{d C_{\text{MeOH}}^{\text{H}_2\text{O}}}{dt} \frac{d \lambda_{\text{w}}}{dt} \nabla T \right]
\]
Meshing in Comsol

As shown in Figure:

- Mapped mesh is used.
- At the ACL and CCL, the mesh size is further decreased (i.e. the number of nodes are increased). This decrease is necessary in order to ensure the convergence of the solution.
- The number of elements are 220000.
## Baseline Condition and Geometric Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Length</td>
<td>50×10⁻³</td>
<td>m</td>
</tr>
<tr>
<td>Active Area</td>
<td>2.5×10⁻³</td>
<td>m²</td>
</tr>
<tr>
<td><strong>Thickness</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ABL and CBL</td>
<td>0.24×10⁻³</td>
<td>m</td>
</tr>
<tr>
<td>AFC and CAC</td>
<td>1.5×10⁻³</td>
<td>m</td>
</tr>
<tr>
<td>AM and CM</td>
<td>0.183×10⁻³</td>
<td>m</td>
</tr>
<tr>
<td>FEC</td>
<td>0.610×10⁻³</td>
<td>m</td>
</tr>
<tr>
<td>ACL and CCL</td>
<td>28×10⁻⁶</td>
<td>m</td>
</tr>
<tr>
<td>Cell Temperature</td>
<td>80</td>
<td>°C</td>
</tr>
<tr>
<td><strong>Anode</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inlet methanol concentration</td>
<td>4</td>
<td>mol L⁻¹</td>
</tr>
<tr>
<td>Methanol flow rate</td>
<td>5</td>
<td>mL min⁻¹</td>
</tr>
<tr>
<td><strong>FEC</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid concentration</td>
<td>0.65</td>
<td>mol L⁻¹</td>
</tr>
<tr>
<td>Sulfuric acid inlet flow rate</td>
<td>10</td>
<td>mL min⁻¹</td>
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<tr>
<td>Outlet pressure</td>
<td>1</td>
<td>atm</td>
</tr>
<tr>
<td><strong>Cathode</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outlet pressure</td>
<td>1</td>
<td>atm</td>
</tr>
<tr>
<td>Inlet air flow rate</td>
<td>500</td>
<td>mL min⁻¹</td>
</tr>
</tbody>
</table>
Results

(a) Methanol  (b) Oxygen  (c) Saturation  (d) Temperature

Fig. 3 Distribution of methanol concentration (a), oxygen concentration (b), saturation (c) and temperature (d) at a cell voltage of 0.4 V (I = 1360.4 A m$^{-2}$) at 80°C cell temperature.
• The oxygen concentration primarily decreases along the thickness-wise direction.
• Although the oxygen concentration also decreases in the length-wise direction, its decrease is very small in comparison to the thickness-wise decrease due to the much higher velocity in the length-wise direction, allowing for a low residence time within the CAC.
• The decrease in oxygen concentration within the CBL and CCL is primarily attributed to the higher mass transport resistance within these porous layers, in comparison to the CAC.

Figure 4. Concentration of oxygen at the bottom, mid, and top of the cell with different cell voltages.
As the cell voltage decreases, the liquid saturation within the ACL decreases due to the consumption of methanol and water, and the production of carbon dioxide.

At the lowest cell voltage, 0.3 V, the liquid saturation decreases to a value of 0.89 (a 1% decrease).

The cathode also showed the same type of trend. However, in this case, the liquid saturation profile increased from a value of 0.1 to 0.11 at a cell voltage of 0.3 V.

This increase in liquid saturation is due to the combination of water crossover from the FEC to the cathode and due to the generation of water from the ORR and MOR from any crossed over methanol.
• The CCL is the warmest layer due to the heat generated by Ohmic heating as well as the electrochemical reactions.
• The highest temperature difference achieved within this fuel cell was ~3.5°C at a cell voltage of 0.3 V.
• The next warmest location was within the ACL, for the same reasoning; where the highest temperature difference was ~2.8°C at a cell voltage of 0.3 V.
• The FEC does cool the fuel cell, especially near the anode and cathode outlets,
it was found that there was a small thermal entrance length (~0.8 cm) for the coldest temperature due to the fact that for a given flow rate or stoichiometry, the velocity of methanol is rather low in comparison to air.

• Near the anode entrance however, anode temperature caused the CCL to cool by ~3°C at a cell voltage of 0.9 V and ~0.5°C at cell voltage of 0.3 V, as shown in Fig. 9.
• This difference in temperature caused gaseous water to migrate to this colder zone, where it condensed. This process is known as the heat pipe effect.
it was found that unlike the anode, the air thermal entrance length was much larger than that of the anode’s.

In the tested cases, the 40°C and 60°C inlet temperature cases did not reach the cell temperature by the cathode exit, due to the high cathode velocity.

At the lowest inlet CAC temperature, this caused the mid-plane temperature to be ~10°C lower than that of the set point temperature. This caused a flooding condition within the CAC, driven by the heat pipe effect.

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**Figure 10.** Temperature distribution of at the mid of the CAC along the length (y) direction at 0.3 V with different air temperatures.

**Figure 11.** Temperature difference of the bottom of the cell at 0.3 V with different inlet CAC temperatures.
Conclusions

• The temperatures at the anode and cathode inlet were changed to investigate the effect of the temperature distribution on the entire cell and to observe the heat pipe effect.

• For anode side, it was found that there was a small thermal entrance length (~0.8 cm) for the coldest temperature due to the fact that for a given flow rate or stoichiometry, the velocity of methanol is rather low in comparison to air.

• For cathode side, it was found that unlike the anode, the airs thermal entrance length was much larger than that of the anode’s. In the tested cases, the 40°C and 60°C inlet temperature cases did not reach the cell temperature by the cathode exit, due to the high cathode velocity.

• When comparing the fuel cell’s temperature distribution, when the cathode’s inlet temperature is varied, it was found that this parameter influenced the overall temperature more significantly than that of the anode inlet temperature. This is primarily attributed to the air’s low thermal conductivity and high velocity.
Acknowledgments

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