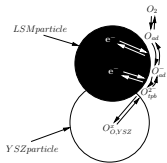


# MATHEMATICAL MICRO-MODEL OF A SOLID OXIDE FUEL CELL COMPOSITE CATHODE

## Background

- The cathode processes of a hydrogen-fueled SOFC contributes to a majority of the electrochemical losses
- These losses may be attributed to the following processes:
  - The slow kinetics of the oxygen reduction reaction ( $O_2 + 4e^- \leftrightarrow 2O^{2-}$ )
  - Limitation of oxygen supply to the reaction sites
- These two phenomena are influenced by the operating conditions (T, pO<sub>2</sub>), the electrocatalyst-electrolyte materials and the electrode microstructural parameters (particle size, porosity, composition, thickness)
- One possible mechanism for the oxygen reduction reaction in the LSM/YSZ system is shown in Figure 1.



- Diffusion of oxygen molecules to the TPB location
- Dissociative adsorption of oxygen species onto the catalyst surface
- Transfer of electronic charge to oxygen species
- Surface diffusion of charged oxygen species
- Diffusion of oxygen ion through electrolyte material

FIGURE 1: ORR processes

- Composite cathodes enhance the electrochemical performance by increasing the reaction sites
- To maximize the performance of a composite cathode, a number of parameters need to be optimized

## Objectives

- The objectives of this project are the following:
  - To develop a predictive mathematical model of a solid oxide fuel cell composite cathode
  - To perform a parametric study of a 1-D composite cathode
  - To simulate a 2-D planar SOFC composite cathode
- Although there are many mathematical models available in the literature, few of them complete the necessary cycle between experimental observation and model prediction

## Composite Cathode

- A composite cathode incorporates a mixture of electro-catalyst particles (LSM) and electrolyte particles (YSZ) and thereby increases the triple phase boundary (TPB)

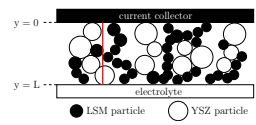


FIGURE 2: Simulation domain of 1-D composite cathode

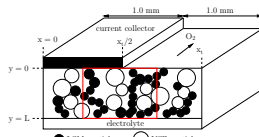


FIGURE 3: Simulation domain of 2-D composite cathode

## Model Development

### Charge Transport

$$\lambda_{TPBL} \times [i_{anodic} - i_{cathodic}] = -\nabla \cdot (\sigma_{el}^{eff} \nabla \phi_{el}) = \nabla \cdot (\sigma_{io}^{eff} \nabla \phi_{io}) \quad (1)$$

### Species Transport (Stefan Maxwell)

$$-\frac{\lambda_{TPBL}}{4F} \times [i_{anodic} - i_{cathodic}] = \sum_{j=1, j \neq i}^n \frac{X_j N_i - X_i N_j}{c D_{i,j}} \quad (2)$$

Others  $i_0 = i_0^{ref} \left( \frac{O_2}{O_2^{ref}} \right)^\gamma$ ,  $\sigma_j^{eff} = \frac{\sigma_j}{(1-\epsilon)\phi_j P_j}$ ,  $D_{O_2-N_2}^{eff} = \left( \frac{\tau}{\epsilon D_{O_2-N_2}} \right)^{-1}$  (3)

### Boundary conditions (see Figure 2&3 for geometry)

- $y=0$  (1-D)  $\phi_{el} = 0$ ,  $\mathbf{n} \cdot \mathbf{J}_{io} = 0$ ,  $w_{O_2} = 0.21$
- $y=0$  (2-D)  $0 < x < \frac{x_t}{2}$ :  $\phi_{el} = 0$ ,  $\mathbf{n} \cdot \mathbf{J}_{io} = 0$ ,  $\mathbf{n} \cdot \mathbf{N} = 0$   
 $\frac{x_t}{2} < x < x_t$ :  $\mathbf{n} \cdot \mathbf{J}_{el} = 0$ ,  $\mathbf{n} \cdot \mathbf{J}_{io} = 0$ ,  $w_{O_2} = 0.21$   
 $\mathbf{n} \cdot \mathbf{J}_{el} = 0$ ,  $\phi_{io} = \eta$ ,  $\mathbf{n} \cdot \mathbf{N} = 0$
- $y=L$

### Input Parameters

- Electrochemical: Exchange current density ( $i_0$ ), charge transfer coefficients ( $\alpha$ ), reaction orders ( $\gamma$ )
- Microstructural: LSM and YSZ particle size ( $r_{el}$ ,  $r_{io}$ ), cathode thickness ( $L$ ), porosity ( $\epsilon$ ), composition, TPBL ( $\lambda_{TPBL}$ )

## Experimental

### Determination of exchange current density, charge transfer coefficients, reaction orders

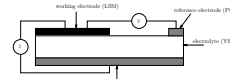


FIGURE 4: 3-electrode setup

$$\eta_{cathode} = V_m - I_m R_s$$

$R_s$  = serial resistance (impedance spectroscopy)

### Estimation of microstructural parameters

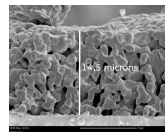


FIGURE 5: SEM of cathode

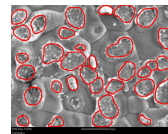


FIGURE 6: Fingerprint of etched electrolyte surface for TPBL determination

### 3-electrode results and estimated parameters

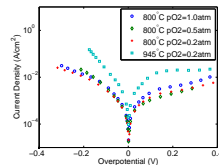


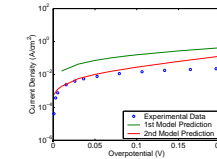
FIGURE 7: I-V characteristics

Parameter	Value
TPB line length	$1.7 \mu\text{m}/\mu\text{m}^2$
$i_0$ (cathodic)	$5.03 \times 10^{-5} \text{ A/m}$
$i_0$ (anodic)	$5.36 \times 10^{-5} \text{ A/m}$
$\gamma$ (reaction order)	0.4
$\alpha_c$ (cathodic)	0.5
$\alpha_a$ (anodic)	1.5
$E_a$ (activation energy)	140 kJ/mol

All parameters evaluated at 945°C, 0.2atm

## Simulation Results and Discussion

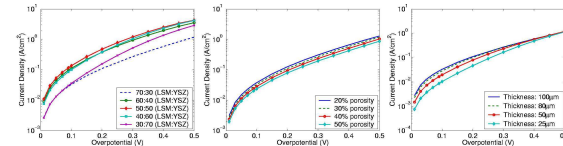
### Model Validation (using 1-D model)



Model Parameters: 60 vol% LSM, 40 vol% YSZ, 10% porosity, 15 $\mu\text{m}$  thickness, 1 $\mu\text{m}$  LSM and YSZ particle radius  
3-electrode cell parameters: 60 vol% LSM, 40 vol% YSZ, 1 $\mu\text{m}$  LSM particle radius  
Note: 2nd model prediction obtained by decreasing the calculated  $\lambda_{TPBL}$  by an order of magnitude

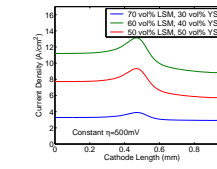
### Parametric Study (using 1-D model)

- Base case: 70 vol% LSM, 30 vol% YSZ, 30% porosity, 100 $\mu\text{m}$  thickness, 1 $\mu\text{m}$  particle radius



- Composition: 50 vol% LSM, 50 vol% YSZ was found to be the best composition. This is attributed to higher TPB line length and better YSZ conductivity
- Porosity: The trend was that the lower the porosity, the better the performance. This is caused by many factors: less pore space results in more particle contacts and higher TPB line length, as well as higher effective conductivities. This also indicates that the rate of the electrochemical reaction plays a more important role than species diffusion.
- Thickness: Simulations show that thicker cathodes perform better than thinner cathodes up to an overpotential of about 0.5V. Further investigation is required to understand this behaviour.

### 2-D Planar Cathode Results



- Non-uniform current density distribution
- More current is produced under the current collector than under the channel. This trend does not change for overpotentials up to 0.5V
- The highest performance is predicted for a 60 vol% LSM, 40 vol% YSZ composite cathode, which differs from the prediction of the 1-D model
- Further investigation is required to explain this phenomenon

## Conclusions and Future Work

- Mathematical modelling is a useful tool for optimizing composite cathode design
- Simulation results indicate that cathode electrochemical performance is significantly influenced by composition and porosity
- Accurate microstructural parameters are required for a reliable predictive model
- Future work will further develop the R&D cycle via experimental measurements and model validation. The current model will be extended to include the energy balance equation.

## Acknowledgements

- Financial support from CAMM and NSERC
- SOFC research team at FCRC and the Student Fuel Cell Network