

Numerical Simulation of Electrolyte-Supported Planar Button Solid Oxide Fuel Cells

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Abstract: 8 mol% Yttria (Y_2O_3) stabilized Zirconia (ZrO_2) [YSZ] and 10 mol% SC_2O_3 -1 mol% CeO_2 - ZrO_2 [SCSZ] are good candidates as electrolyte material in solid oxide fuel cells (SOFC). A layered electrolyte design was proposed and the effect it has on the electrochemical performance of a single cell was investigated. The simulations predicted that hybrid (YSZ/SCSZ/YSZ) layered electrolytes had a power density increase of up to 52.33% over conventional pure YSZ electrolytes. The multiphysics model utilized Secondary Current Distribution, Transport of Concentrated Species, and Free and Porous Media Flow nodes in the COMSOL Multiphysics Batteries and Fuel Cells module. The model was validated against published experimental results.

Keywords: SOFC, electrolyte, YSZ, SCSZ, modeling, simulation

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical conversion devices that utilize ceramics as their electrolyte material for oxygen conduction. Compared to other types of fuel cells, they operate at relatively high temperatures, typically 400°C to 1000°C, and have an electrical efficiency over 50% and combined heat and power efficiency over 80% [1]. SOFCs also have great fuel flexibility, and are ideal for stationary and auxiliary power generation. However, the power density produced by electrolyte-supported SOFCs at a lower temperature range is not that high, due to high ohmic resistance losses in the electrolyte affecting the SOFC performance.

A fuel cell consists of three main parts: two porous electrodes and an electrolyte that separates them. For a H_2 - O_2 SOFC, H_2 (fuel) at the anode sites is oxidized to provide free electrons and generate the H^+ protons. Air (oxidant) enters the cell at the cathode where oxygen is undergoes reduction process to form

negative O^{2-} ions. The O^{2-} ions pass through the electrolyte and react with H^+ protons at the anode to form water. The electrolyte material is a good ionic conductor but it exhibits almost no electronic conductivity, and hence allows O^{2-} ions to pass through but no electrons are allowed to pass. The electrolyte should also be very dense, so that no fuel or air can pass through.

The electrolyte in a SOFC should be as thin as possible to reduce ohmic losses and, thus maximize performance. The cell, however, must be mechanically strong enough to not crack or fail under electrochemical and mechanical load and, yet operate at high temperatures. While single cells can be anode, cathode or electrolyte supported, with much work done in the past on anode-supported cells, the research presented in this paper focuses on the electrolyte-supported cell design.

One way to improve cell performance is to use better electrolyte materials, and therefore the goal of this research is to run multiphysics simulations to predict the performance of SOFCs with Yttria and Scandia-Ceria stabilized Zirconia layered electrolyte configurations, which can provide higher ionic conductivities and high power densities during operation. The idea of the presented research is to develop a layered electrolyte design, where 8 mol% Yttria (Y_2O_3) stabilized Zirconia (ZrO_2) [YSZ] and 10 mol% SC_2O_3 -1 mol% CeO_2 - ZrO_2 [SCSZ] electrolyte layers will be combined into one layered electrolyte enhancing both ionic conductivity and mechanical stability. A discussion of the electrolyte design considerations will follow as well as a description of the multiphysics model. The results and validation of the model will also be discussed..

2. Electrolyte Design

YSZ is the most explored and used electrolyte material for high temperature SOFCs and it is a material of choice for numerous SOFC applications. While YSZ has good ionic

conductivity at 1000°C, at lower operational temperatures the ionic conductivity decreases and ohmic losses increase [2]. SCSZ is a better choice for the electrolyte material, as it exhibits much higher ionic conductivity at lower operational temperatures [3], but it exhibits cubic to rhombohedral phase transition which affects both the electrolyte and overall cell performance [4, 5]. In addition SCSZ is more sensitive to the poisoning by impurities present in the fuel [6], which is why any exposure to the anode side could affect its long term operation. This leads to structural instability as well as higher sensitivity to impurities of the SCSZ electrolyte, which degrades the SOFC performance.



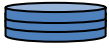


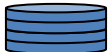



YSZ	YSZ- xSCSZ- YSZ	SCSZ	Layers
			3-Layered
			4-Layered
			6-Layered

Figure 1 - Electrolyte Designs; x=1, 2, and 3

Therefore, to utilize the favorable properties of YSZ and SCSZ, a layered electrolyte design has been adopted. The idea of the layered electrolyte design is to place thin YSZ electrolyte layers on the outer surfaces of thin SCSZ electrolyte layers and varying the assembly configuration. Each single layer of YSZ and SCSZ material is a circular disk with a radius of 10mm and a thickness of 30µm. A total of nine electrolyte designs were considered in this research (**Figure 1**). These were 3-, 4- and 6-layered designs using only YSZ or only SCSZ layers stacked one upon the other as well as laminate designs consisting of 1YSZ/2SCSZ/1YSZ, 1YSZ/2SCSZ/1YSZ and 1YSZ/4SCSZ/1YSZ layers or YSZ/xSCSZ/YSZ, where x=1, 2 and 3 (**Figure 1**). For the laminate YSZ/xSCSZ/YSZ designs the volume fraction of each of the layers is different which would affect the ionic conductivities of the assembled electrolytes. Besides, as the coefficient of thermal expansion, Young's modulus and Poisson ratios of YSZ and SCSZ slightly differ

[7, 8], the appearance of thermal residual stresses in different layers is expected which might increase robustness and mechanical strength of the layered electrolytes, which will be a subject of further research. The nine electrolyte designs were produced and tested for ionic conductivity (**Table 4**).

3. Modeling Methodology

The geometry of the single electrolyte-supported cell being modeled is presented in **Figure 2**, where the inlet and outlet flow directions of the fuel and oxidant are also shown. $(La_{0.6}Sr_{0.4})_{0.99}Co_{0.2}Fe_{0.8}O_3$ perovskite with electronic conductivity of 2300 S/m [13-17] was used as cathode material and Ni-YSZ cermet with electronic conductivity set to 650,000 S/m [9-12] was used as anode material. The porosity value for the electrodes was set to 40% and the ionic conductivity for anode and cathode was set to 1 S/m and 5.15 S/m respectively. The dimensions of the parts of the modeled single cell are summarized in **Table 1**. The modeling was done in COMSOL Multiphysics 4.2a with the Batteries & Fuel Cells module. The physics used in the modeling included electrochemistry and fluid mechanics. The three nodes that were used in COMSOL were: Secondary Current Distribution, Transport of Concentrated Species, Free and Porous Media Flow. The geometry of the cell was developed in COMSOL and the meshing was done in COMSOL using free tetrahedral elements.

Assumptions made in the model:

- Steady state condition, neglecting any transient conditions at the start-up or end of cycle.
- Material properties remain constant.
- The model focuses on the individual fuel cell; interconnects and other aspects of the fuel cell system are not considered.
- All the fluids are assumed to follow the ideal gas law.
- Heat transfer effects like joule heating are not considered.
- The electrolyte is considered to be very dense and the porosity is considered zero or negligible.

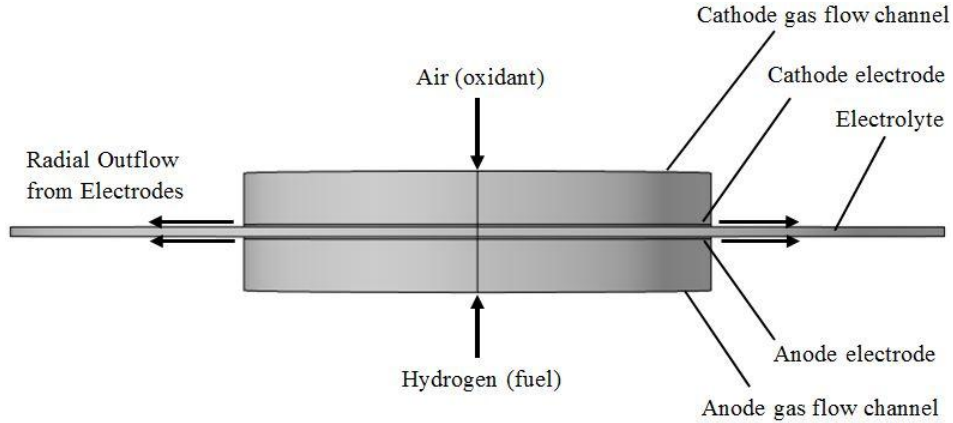


Figure 2 - SOFC Model

To solve for the current-voltage relationship in a SOFC, the voltage can be solved from current or vice versa. In this model, a parametric sweep of the polarization overpotential was done; hence calculating current from voltage. To account for the electrochemical reactions, the following equations will be employed. Starting with the charge balance,

$$\nabla \cdot \mathbf{j}_{et} = Q_{et} \quad \nabla \cdot \mathbf{j}_{ey} = Q_{ey} \quad [1]$$

$$\mathbf{j}_{et} = -\sigma_{et} \nabla \Phi_{et}, \quad \mathbf{j}_{ey} = -\sigma_{ey} \nabla \Phi_{ey} \quad [2]$$

The activation overpotential, η , represents the loss in voltage that the fuel cell needs to sacrifice to overcome the activation barrier. The activation overpotential is given by,

$$\eta = \Phi_{et} - \Phi_{ey} - E_{eq} \quad [3]$$

The non-linearized Butler Volmer equation can be used to calculate the local current density in the fuel cell,

$$\mathbf{j} = j_0 \left[\left(\frac{c}{c_0} \right)_R \exp \left\{ \frac{n\alpha F}{RT} \eta \right\} - \left(\frac{c}{c_0} \right)_P \exp \left\{ \frac{-n(1-\alpha)F}{RT} \eta \right\} \right] \quad [4]$$

The mass conservation of the individual charges is given by,

$$\rho \frac{\partial}{\partial t} (m_i) + \rho (\mathbf{u} \cdot \nabla) m_i = -\nabla \cdot \mathbf{f}_i + R_i \quad [5]$$

The Maxwell-Stefan law is used to solve for the diffusion flux term, \mathbf{j} ,

$$\mathbf{f}_i = -\rho m_i \sum_{k=1}^Q \tilde{D}_{ik} \mathbf{d}_k - D_i^T \frac{\nabla T}{T} \quad [6]$$

The fluid flow is considered to be incompressible. Flow through flow channels is

considered laminar and is solved using the Navier-Stokes equations. The flow through the porous electrodes is solved using the Brinkman equations of mass and momentum conservation.

$$\frac{\partial}{\partial t} (\varepsilon_{et} \rho) + \nabla \cdot (\rho \mathbf{u}) = Q_s \quad [7]$$

$$\frac{\rho}{\varepsilon_{et}} \left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \frac{\mathbf{u}}{\varepsilon_{et}} \right) = -\nabla p + \nabla \cdot \left[\frac{1}{\varepsilon_{et}} \left\{ \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \right\} \right] - \left(\frac{\mu}{k} + Q_s \right) \mathbf{u} + \mathbf{F} \quad [8]$$

Table 1 - Dimensions of SOFC Components

Anode & Cathode thickness	50 μm
Electrolyte layer thickness	30 μm
Anode & Cathode diameter	10 mm
Electrolyte diameter	20 mm
Gas flow channel height (Anode & Cathode)	1 mm
Gas flow channel diameter (Anode & Cathode)	10 mm

4. Results and Discussion

The model developed in this research was validated by the work of Sembler et al. [19]. The paper by Sembler et al. is actually a numerical simulation study and it was validated against the experimental results of anode-supported SOFC produced by Joongmyeon Bae et al. [18]. There are some key parameters that are difficult to measure by experimental techniques. These

parameters are charge transfer coefficient (α) at anode and cathode; and exchange current density at anode and cathode (j_0); appearing in the Butler-Volmer equation (Eqn. [4]). The charge transfer coefficient is assumed by most researchers to be equal to 0.5, and this value makes sense because 0.5 means the forward reaction rate is equal to the backward reaction rate. Therefore, the value of α was assumed to be 0.5. Now the exchange current density at anode and cathode were varied so as to fit the experimental data, by keeping all other conditions and parameters constant. This process was followed for 1123 K, 1023 K and 923 K. As can be seen in **Figure 3**, the simulations results match the results from the paper. This proves the validity of the modeling methodology used and now the model can be declared validated.

The modeling results are summarized in **Tables 2** and **3**. The SOFC with SCSZ electrolytes have the highest power density and the ones with YSZ electrolyte the least. This seems aligned with the measured ionic conductivity of the materials. The performance of the SOFC with hybrid layered electrolytes seems to be in between the performance of the SCSZ and YSZ electrolyte SOFCs. **Table 3** also shows the percentage increase from YSZ to YSZ-SCSZ-YSZ, and YSZ-SCSZ-YSZ to SCSZ. **Figures 4** to **6**, show the current density-voltage-power density of the 3-layered, 4-layered and 6-layered electrolyte SOFCs respectively. Ohmic losses increases with electrolyte thickness and hence power density decreases with an increase in the electrolyte layers.

Table 2 - Maximum Power Densities (W/m²)

	YSZ	Y-xS-Y	SCSZ
3-Layered	3243.41	3739.38	4798.72
4-Layered	2807.7	3479.07	4488.77
6-Layered	2093.38	3188.95	3658.03

Table 3 – Maximum Power Density Increase

	% increase (YSZ to Y-xS-Y)	% increase (Y-xS-Y to SCSZ)
3-Layered	15.29	28.33
4-Layered	23.91	29.02
6-Layered	52.33	14.71

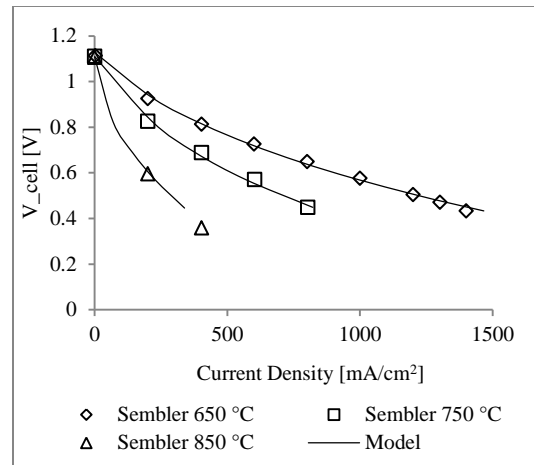


Figure 3 - Validation

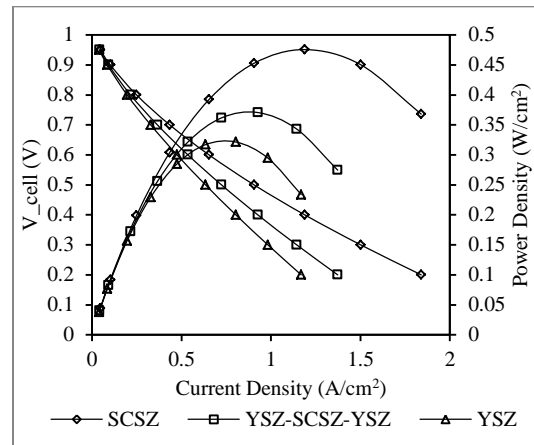


Figure 4 - 3-Layered SOFCs

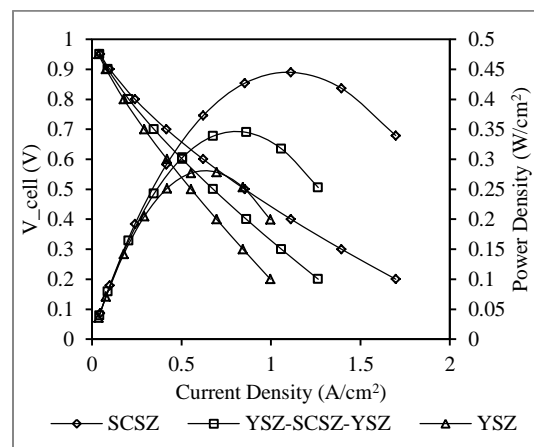


Figure 5 - 4-Layered SOFCs

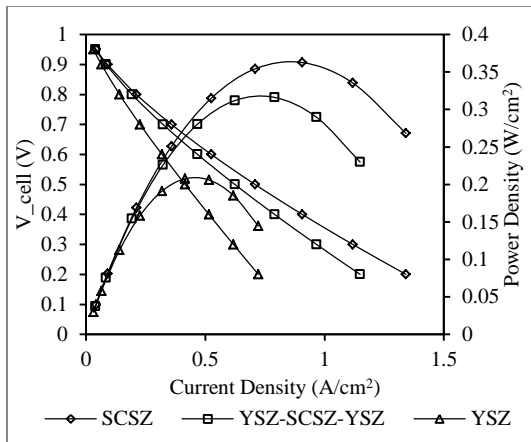


Figure 6 - 6-Layered SOFCs

5. Conclusion

A layered-design for ZrO_2 based electrolytes was proposed and implemented for electrolyte-supported planar button shaped SOFCs. The two electrolyte materials used were YSZ and SCSZ. The electrolytes were produced and tested. A model of the SOFC was developed in COMSOL and the measured ionic conductivity values were used in the model. The simulation results showed that the hybrid layered electrolytes YSZ-xSCSZ-YSZ electrolytes demonstrated optimal performance and stability compared to the pure YSZ or pure SCSZ electrolytes. The percentage variation in the maximum power density of the SOFC with different electrolytes can be seen in **Table 3**. The thicker the electrolyte, higher the ohmic losses and hence the performance will lower. The mechanical strength of all the electrolytes has not been estimated yet. The choice of the electrolyte will then depend on the specific application; it will be a balance between power density required and strength of electrolyte required. The model was validated against results from a different SOFC.

6. References

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7. Acknowledgements

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8. Appendix

Nomenclature:

\mathbf{j}	Current density vector [A/m ²]
\mathbf{j}_{et}	Current density vector, electrode [A/m ²]
\mathbf{j}_{ey}	Current density vector, electrolyte [A/m ²]
j_0	Exchange current density [A/m ²]
Q_{et}	Electrode current source/sink term [A/m ²]
Q_{ey}	Electrolyte current source/sink term [A/m ²]
Φ_{et}	Electrode potential [V]
Φ_{ey}	Electrolyte potential [V]
σ	Ionic conductivity of electrolyte [S/m]
$\sigma_{et,eff}$	Electrode effective conductivity [S/m]
$\sigma_{ey,eff}$	Electrolyte effective conductivity [S/m]
E_{eq}	Equilibrium voltage of fuel cell [V]
η	Overpotential or voltage loss in fuel cell [V]
c_R	Concentration of reactant [mol/m ³]
$c_{0,R}$	Concentration of reactant at standard conditions [mol/m ³]
c_P	Concentration of product [mol/m ³]
$c_{0,P}$	Concentration of product at standard conditions [mol/m ³]
n	Number of electrons transferred in the reaction
α	Charge transfer coefficient
F	Faraday's constant [$F \approx 96,400$ C/mol]
R	Ideal gas constant [$R = 8.314$ J/mol·K]
T	Temperature [K]
ρ	Density [kg/m ³]
m_i	Mass fraction of individual species
\mathbf{u}	Velocity [m/s]
\mathbf{f}	Mass diffusion flux term of individual species [kg/m ³ ·s]
R_i	Reaction rate of individual species [kg/m ³ ·s]
\check{D}_{ik}	Multicomponent Fick diffusivities [m ² /s]
\mathbf{d}_k	Diffusional driving force [1/m]

D_i^T Thermal diffusion coefficient [kg/m·s]

ε_{et} Porosity of electrode

Q_s Mass source/sink term [kg/m³·s]

p Pressure [N/m² or Pa]

μ Dynamic viscosity of fluid [kg/m·s]

I Identity tensor

F Body force term [kg/m²·s²]

k Permeability of media [m²]

Table 4 - Electrolyte Conductivities

3-layered		4-layered		6-layered		6-layered		6-layered	
YSZ-1SCSZ-YSZ		YSZ-2SCSZ-YSZ		YSZ		YSZ-4SCSZ-YSZ		SCSZ	
T °C	σ (S/m)	T °C	σ (S/m)	T °C	σ (S/m)	T °C	σ (S/m)	T °C	σ (S/m)
500.22	0.11	500.06	0.12	501.03	0.08	500.16	0.16	496.52	0.21
550.10	0.27	550.38	0.32	550.12	0.21	550.42	0.43	547.30	0.52
600.99	0.63	601.36	0.74	602.19	0.43	601.57	0.98	598.71	1.40
651.54	1.29	652.08	1.51	653.03	0.83	651.94	2.01	649.66	2.92
701.92	2.38	702.40	2.76	702.05	1.57	701.98	3.61	700.40	5.07
752.24	3.86	752.56	4.49	752.40	2.68	752.57	5.88	751.21	7.94
802.55	6.01	802.91	6.89	802.73	4.24	803.36	8.86	802.00	11.62