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A Distributed Electrochemistry Modeling Tool for Simulating SOFC Performance and Degradation

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III.G.5 A Distributed Electrochemistry Modeling Tool for Simulating SOFC Performance and Degradation

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Fiscal Year (FY) 2011 Objectives

- Develop a multi-dimensional cell-level distributed electrochemistry (DEC) modeling tool that can simulate solid oxide fuel cell (SOFC) performance by solving the coupled and spatially varying multi-physics that occur within the membrane electrode assembly (MEA).
- Extend the DEC modeling tools to include the capability to simulate graded electrode microstructures.
- Validate the model for an SOFC operating on various fuel gas compositions.
- Investigate the effect of electrode microstructure on the electrochemical performance.

FY 2011 Accomplishments

- Developed a continuum cell-level DEC model that describes the electrode microstructure and solves the distributed electrochemistry through the MEA in multiple dimensions.
- Validated the DEC modeling tool by simulating an experimental button cell for a range of operating conditions.
- Performed an optimization exercise based on anode microstructure to demonstrate the DEC model capabilities and its sensitivity to structural changes.

Introduction

The SOFC is an excellent candidate for stationary and distributed power generation due to the high power density and flexibility to run on coal gas and alternative fuel sources such as landfill gas and pipeline natural gas. To be viable for this application the cost per kW and cell longevity of SOFCs must be further improved. Experimental efforts are ongoing to improve the initial performance and durability of SOFCs through the use of novel materials and microstructural designs. Experimental design and testing of SOFCs is a complex, time consuming process. Computational modeling, which is able to simulate the multi-physics occurring within a SOFC, can be used to inform and guide experimental efforts and help to reduce the amount of experimental testing necessary for new designs and materials. The distributed electrochemistry model, which has been developed under this work, is capable of investigating the electrochemistry and local conditions with the SOFC MEA based on the local microstructure and multi-physics. The DEC model can calculate the global current-voltage (I-V) performance of the cell as determined by the spatially varying local conditions through the thickness of the electrodes and electrolyte. The simulation tool is able to investigate the electrochemical performance based on characteristics of the electrode microstructure, such as particle size, pore size, electrolyte and electrode phase volume fractions, and triple phase boundary (TPB) length. It can also investigate performance as affected by fuel and oxidant gas flow distributions and other environmental/experimental conditions such as temperature and fuel gas composition. The long-term objective for the DEC modeling tool is to investigate factors that cause electrode degradation and the decay of SOFC performance which decrease longevity.

Approach

The DEC model is a three-dimensional multi-physics model which solves for the reactive transport of gas species, ion transport, current density and electric potential. The model is based on a commercial computational fluid dynamics code (STAR-CD) and employs a user-defined module to solve the distributed electrochemistry and provide source terms for the gas species and electric potential. In the anode and cathode, the charge transfer is solved using a modified Butler-Volmer formulation which is based on the rate limiting step for the electrochemical reactions within each electrode [1]. The DEC model includes all three phases of the composite electrodes (gas, electrolyte phase, electrode phase), and the TPBs throughout the full thickness of the electrodes. This allows the model to solve for the electrochemistry throughout the electrodes without defining a set reactive zone; the coupled multi-physics solution, not a specific layer dimension, determines the extent of the reactions into the electrodes. The DEC model can also handle spatially varying microstructural properties and compositions within the electrodes. For example, the model allows for electrode layers with unique structural properties, such as porosity or particle size.

In the work presented here, the composite anode electrode phase material is nickel (Ni) and the electrolyte phase material is yttria-stabilized zirconia (YSZ). The electrolyte layer is comprised of fully dense YSZ. In the composite cathode, the electrode phase material is strontium-doped lanthanum manganese oxide (LSM) and the electrolyte phase is YSZ.

A schematic of the computational domain used for the simulation results presented in this report is given in Figure 1. The model geometry represents the test section of a button cell testing apparatus [3]. A two-dimensional axisymmetric model geometry was created to represent the test section (see dashed line in Figure 1). The model domain includes the fuel flow region from the fuel feed tube to the anode, and the air flow region above the cathode surface. Within the MEA, the anode is separated into two layers with separate property definitions to investigate the performance of a graded anode. The base layer is 17 microns thick, and the support layer makes up the remaining 1,100 µm of the anode thickness.

Results

Model Validation

Jiang and Virkar [3] performed tests to examine the relationship between SOFC performance and gas transport in porous anodes. To validate the DEC model, simulations were performed to replicate the H_2-He and H_2-N_2 cases over the full range of dilution ratios they tested. The structural parameters used in the DEC model for all validation cases are summarized in Table 1. For the calculations the DEC model settings were made such that the performance matched at one experimental fuel composition. All other simulations were made with no changes to the model except for the fuel compositions and operating voltages. Without including all the details of these validation cases, which are part of the subject of a journal article submitted for publication [4], the simulation results for the N_2-H_2 cases from that work are

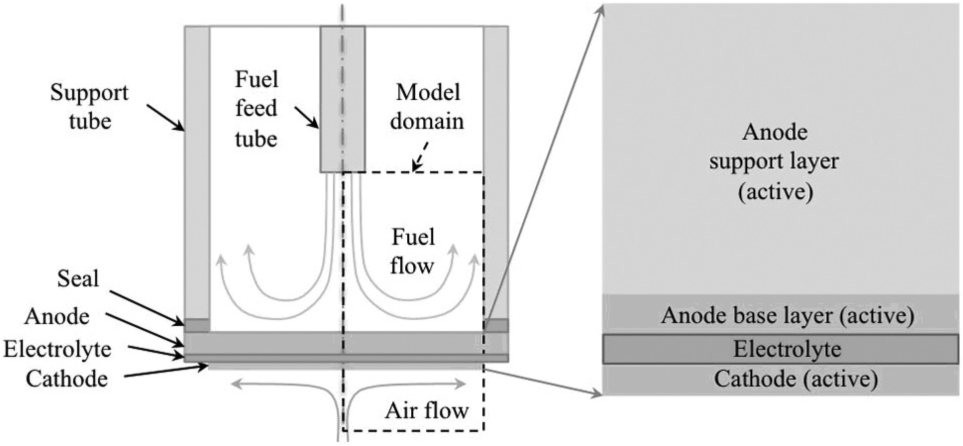

FIGURE 1. Schematic View of the Experimental Testing Section and Computational Domain Used for the DEC Model Simulation Results

TABLE 1. Structural Parameters Used for All Validation Cases

	Thickness, micron	Volume fraction			Particle radius, micron		Pore radius, micron	Tortuosity factor
		YSZ	Pores	Ni/LSM	YSZ	Ni/LSM		
Anode	1,100	0.274	0.35	0.376	0.5	0.5	0.5/0.8	2.5
Electrolyte	10	1.0	0.0	0.0	-	-	-	-
Cathode	30	0.315	0.35	0.335	0.5	0.5	0.5	2.5

plotted in Figure 2. In the figure, the symbols represent the experimental data and the modeled performance is shown by the solid and dashed curves. The performance predicted by the DEC model matched the data very well for operating voltages up to about 0.9 V for all N_2 dilutions. The maximum difference between predicted and experimental peak power was 12%, and the maximum difference between predicted and measured limiting current density was 11% including all N_2 dilution cases. Results of the validation test cases indicate that the DEC model accurately predicts the gas diffusion effects of the anode-supported SOFC. The accuracy of the DEC model predictions over the range of fuel compositions considered suggests the DEC modeling tool is suitable for calculating peak power and current density for operating voltages up to ~0.9 V for simple fueling cases.

Anode Optimization Exercise

The DEC model can be used to consider the structural and compositional design of the electrodes. To demonstrate this capability, an optimization study was performed in the anode. The optimization study used five separate steps to systematically increase the performance of the anode. For the optimization case the 50% N_2 validation case (operating at 0.8 V and 800°C) was used as the baseline of performance (Step 1) and anode modifications are made cumulatively to improve the performance. The first optimization step (Step 2) is to decrease the thickness of the anode by 50% from 1,100 μm to 550 μm. Figure 3 shows the resulting I-V performance of the "thin" 550 μm anode case (gray curves) compared to the "50% N_2" case (black curves) and the experimental data (symbols) for that case are included in the figure for reference. After Step 2, the current density increased at 0.8 V from 0.862 to 0.914 A/cm^2 and the gas diffusion limitations of the thicker anode have been substantially decreased as indicated by the limiting current density, which increased from about 2.4 to 3.5 A/cm^2. Of note also is the substantially increased peak power due to the thinner anode.

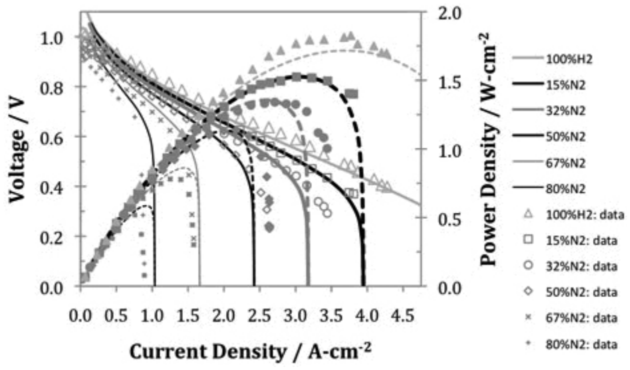

FIGURE 2. Comparison of the DEC model simulation results with experimental N_2-H_2 button cell data [3]. Symbols represent the experimental data, and the DEC modeled performance is shown by the solid and dashed curves.

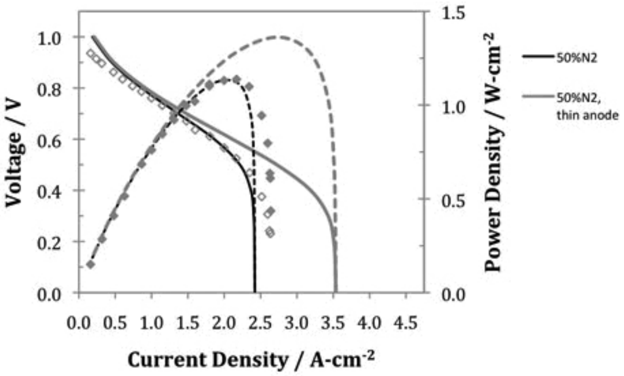

FIGURE 3. Modeled performance for "thin" (0.55 mm) anode (gray curves) compared to model validation case (black curves) and experimental data (symbols) for a button cell with 1.1 mm thick anode. All cases operating on 50% N_2 50% H_2 fuel at 800°C.

Step 3 of the optimization enhances the performance (of the 550 μm anode case) by increasing the average pore radius and porosity in the anode support layer to further decrease gas transport limitations within the anode. Assuming the optimal particle size and associated pore size in the base layer will be small to maximize the TPB length, the pore size is increased only in the support layer, from 0.8 μm to 2.0 μm. Also, the porosity in the support layer is increased from 0.35 to 0.45. These changes applied to the support layer increased the current density to 0.935 at 0.8 V.

In Step 4, the ionic conductivity in the anode base layer is increased by 90%. This is done by increasing the YSZ fraction (from 0.274 to 0.35). The porosity within the base layer was simultaneously decreased from 0.35 to 0.30 such that the Ni fraction could remain relatively high at 0.35 equal to the YSZ fraction. The additional result of these changes in the fractions of the three phases was an increase of 23% in TPB length. The increased ionic conductivity and TPB result in a considerable increase of the current density at 0.8 Volts to a value of 1.162 A/cm^2.

Step 5, the final optimization step for this exercise, is to decrease the average YSZ and Ni particle radii in the anode base layer from 0.5 to 0.3 μm, and increase the porosity from 0.30 back to 0.35 while maintaining equal fractions of the solid phases at 0.325. The physics affected by these changes are a three-fold increase in TPB, a slight decrease in the ionic conductivity compared to the previous case, and a return to the better gas transport associated with the more open porosity. The effect on the performance is substantial, with the current density now at 1.401 A/cm^2. This step and the steps preceding it are summarized in Table 2.

TABLE 2. Microstructural Parameter Changes Applied for Anode Optimization Cases

Step	Structural parameters changed	Physics effected compared to baseline	Current density, A/cm^2 at 0.8 V
1	Baseline (1,100 mm anode)	Baseline physics	0.862
2	+ Model anode thickness decreased to 550 mm	Increased gas transport	0.914
3	+ Increase porosity and pore size in anode support layer (from 0.35 to 0.45, and 0.8 mm to 2.0 mm)	Increased gas transport	0.935
4	+ Increase YSZ fraction in anode base layer (from 0.274 to 0.35, porosity decreased from 0.35 of 0.30)	90% increase in ionic conductivity, 23% increase in TPB, and decreased gas transport in base layer	1.162
5	+ Decrease particle radius of YSZ and Ni from 0.5 to 0.3 mm, increase porosity back to 0.35 (slight decrease in YSZ and Ni compared to Step 4)	70% increase in ionic conductivity, 300% increase in TPB, and return to gas transport in base layer as in case 3	1.401

The Faradaic current density distributions in the anode resulting from the local charge transfer for the above steps 1, 2, 4, and 5 are shown in Figure 4. Step 3 is not shown because its current density is very similar to both Steps 1 and 2. Note that in Figure 4 the Faradaic current density is larger for the higher case numbers coinciding with the higher global (I-V) current density numbers summarized in Table 2. The Faradaic current density distributions show the effects of microstructural changes made in the optimization exercise. The baseline (Step 1) is the lowest performing case and has the smallest current density. Step 2 overlays Step 1 except near the electrolyte layer where the current is higher. These two cases feature very similar structural properties in both the base and support layers and have very smoothly decreasing current density values that are diminishingly small, but non-zero for about 30 microns into the anode. Steps 4 and 5 have current density distributions shaped differently than the other cases. Step 4 has a maximum value slightly less than Step 2, but the volume of the current is larger for a greater distance into the anode with a slightly faster rate of decrease in the anode beyond the 17 micron thick base layer; while Step 5 has by far the largest maximum current density. The current density of Step 5 decreases smoothly through the base layer then decreases sharply within the courser, more porous support layer where the TPB density and ionic conductivity are smaller.

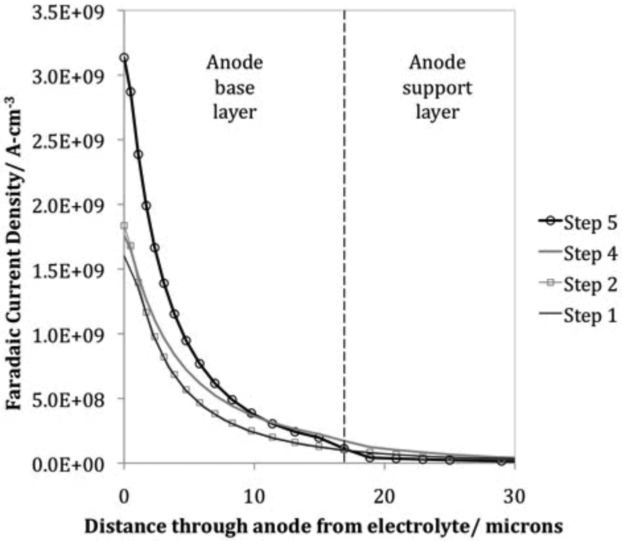

FIGURE 4. Faradaic Current Density Distributions in the Anode for the Optimization Steps 1, 2, 4, and 5

Conclusions and Future Directions

During FY 2011, the DEC modeling tool was developed to simulate realistic SOFC performance. The DEC model calculates the global performance of the SOFC based on the local conditions and multi-physics within the MEA. The model is able to accurately reproduce experimental data at various operating voltages and gas compositions. An effective properties approach is used to model the SOFC electrodes, which allows the porous microstructure to be included in the model via effective parameters based on the structural properties of the electrodes. The DEC model results presented here included:

- Validation of the DEC model against experimental button cell data. The validation cases demonstrate the suitably of the DEC modeling tool to represent the performance and gas transfer limitations of anode supported SOFCs by successfully matching experimental data for a fuel cell operating on various fuel gas compositions.
- An anode optimization exercise, which demonstrates the sensitivity of the DEC model to the electrode microstructure. Changes to microstructural properties that affect the gas transport, ion transport, TPB length, and the distributed charge transfer through layered or graded electrodes were shown to have the greatest effect on SOFC performance.

Further development of the DEC model is needed to investigate degradation mechanisms that result in damage to the electrodes and electrochemical performance decay. The validation and demonstration of the DEC model has laid the framework for considering the degradation and long-term performance of SOFCs. The DEC model can now be expanded to look at degradation and performance problems of interest to the Solid State Energy Conversion Alliance industrial team members. Such problems might include: examining the conditions within the anode in the event of fuel supply interruption and the evolution of events leading up to Ni oxidation, or sulfur from a diesel fuel reformer poisoning of the anode in an auxiliary power supply unit on board a tractor-trailer.

FY 2011 Publications/Presentations

1. K.P. Recknagle, E.M. Ryan, and M.A. Khaleel, "Numerical Modeling of the Distributed Electrochemistry and Performance of Solid Oxide Fuel Cells," ASME 2011 International Mechanical Engineering Congress & Exposition, Denver, Colorado, November 2011.

2. K.P. Recknagle, E.M. Ryan, and M.A. Khaleel, "Distributed Electrochemistry Modeling Tool for Investigating Solid Oxide Fuel Cell Performance," Power Sources, 2011.

3. E.M. Ryan, K.P. Recknagle, and M.A. Khaleel, "Modeling the Electrochemistry of an SOFC through the Electrodes and Electrolyte," ECS Trans., vol. 35, issue 1, 2011.

References

1. H. Zhu and R.J. Kee, "Modeling Distributed Charge-Transfer Processes in SOFC Membrane Electrode Assemblies," Journal of The Electrochemical Society, 2008. 155(7): p. B715-B729.

2. W.G. Bessler, S. Gewies, and M. Vogler, "A New Framework for Physically Based Modeling of Solid Oxide Fuel Cells," Electrochemica Acta, 2007. 53(1): p. 1782-1800.

3. Y. Jiang and A.V. Virkar, "Fuel Composition and Diluent Effect on Gas Transport and Performance of Anode-Supported SOFCs," Journal of The Electrochemical Society, 2003. 150(7): p. A942-A951.

4. K.P. Recknagle, E.M. Ryan, and M.A. Khaleel, "Distributed Electrochemistry Modeling Tool for Investigating Initial and Long-Term Solid Oxide Fuel Cell Performance," Power Sources, 2011.