Electrode Coarsening and Temperature Distribution Effects on Long-Term Electrochemical Degradation of SOFC Stacks

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Overview

Long term performance stability of solid oxide fuel cell (SOFC) stacks is a key requirement for their commercial success. At the cell level, one of the primary modes of degradation comes from grain coarsening and the resulting changes in microstructure properties. A cell-level multi-physics model to predict the changing properties and performance loss as a function of time and temperature caused by coarsening in the electrodes of an LSM-YSZ/YSZ/Ni-YSZ SOFC has been implemented in the SOFC-MP stack modeling tool. This enhanced modeling tool enables analyses of degradation due to coarsening at the stack scale.

Objectives

Bridge the scales between microstructure and stack by coupling the NETL electrode models in the PNNL stack models to advance the overall modeling capability for:

- Identifying cell properties and conditions that will provide optimal initial performance and minimal degradation using 2-D stack models.
- Performing 3-D analysis of long-term stack degradation and reliability.

Technical Approach

- Modify stack model polarization dependencies for compatibility with the cell-level model and match initial state-of-the-art stack performance.
- Incorporate electrode property models and time-evolution functions into the stack electrochemistry model and test.
- Develop and implement logic defining the evolution of multiple property model parameters into SOFC-MP stack modeling tool (2D and 3D versions).
- Exercise SOFC-MP in geometry comparison and structural reliability analysis.

Key Model Equations

Solid particle growth $$d_i^4 - d_{i,0}^4 = K_{D,i}\Delta t \qquad K_{D,i} = K_{D_0 i} * e^{\frac{-E_{A,i}}{\kappa_B T}}$$

Triple-phase boundary length (L_{TPB}) $$l_{TPB} = l_{TPB}^0 \frac{d_{Ni,0}^3}{d_{YSZ,0}} * \frac{d_{YSZ}}{d_{Ni}^3}$$

Pore size $$d_{p,i} = d_{p,i}^0 \left(\frac{d_{Ni}}{d_{Ni,0}} * \frac{V_{Ni}}{V_{solid}} + \frac{d_{YSZ}}{d_{YSZ,0}} * \frac{V_{YSZ}}{V_{solid}} \right)$$

Tortuosity and electronic conductivity $$\tau_i = \tau_i^0 \left(\frac{d_i}{d_{i,0}} \right)^{\frac{3}{2}} \qquad \sigma_i^{eff} = \sigma_i \frac{V_i}{\tau_i}$$

Concentration polarization with Knudsen diffusion

$$D_{eff,i} = \frac{\varphi}{\tau^n} \left(\frac{1 - \alpha_{i,m} y_i}{D_{i,m}} + \frac{1}{D_{k,i}} \right)^{-1} \qquad D_{k,i} = \frac{2}{3} \left(\frac{8RT}{\pi M_i} \right)^{1/2}$$

Activation polarization with explicit L_{TPB}

$$i_0 = A_{BV,TPB} * \left(\frac{l_{TPB,mean}}{l_{TPB,mean}^0} \right) e^{\frac{-E_{BV}}{RT}} \qquad l_{TPB,mean} = 2 / \left(\frac{1}{l_{TPB,a}} + \frac{1}{l_{TPB,c}} \right)$$

Effect of Stack Geometry on Degradation Rate

The stack modeling tool SOFC-MP-2D is used to compare the expected initial and long-term performance of two planar 23x23 cm 16-cell stacks in co-flow and counter-flow configurations and operating at 760°C within an insulated enclosure within a NGFC System with fuel and air recycle fractions of 64-69% U_F and 12% U_A per pass.

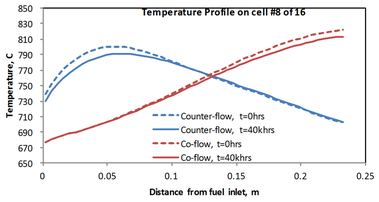

Figure 1: Temperature profile along the 8th cell of 16-cell co-flow and counter-flow stacks at t=0 and t=40k hours.

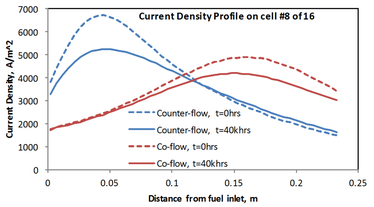

Figure 2: Current density profile along the 8th cell of 16-cell co-flow and counter-flow stacks at t=0 and t=40k hours.

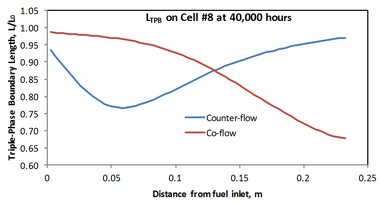

Figure 3: Triple-phase boundary length profile along the 8th cell of 16-cell co-flow and counter-flow stacks after 40,000 hours of operation.

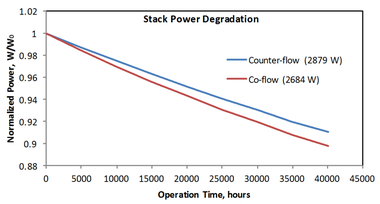

Figure 4: Counter-flow and co-flow stack power degradation over time due to electrode coarsening.

The average initial temperature of the two stacks was 760°C with the co-flow case having the larger temperature difference along the cell, as shown in Figure 1. The fuel flow direction is from left to right in Figures 1-4, while the air flow direction changes to simulate the co-flow or counter-flow configuration. Note that by 40,000 hours the maximum temperature is decreased by ~10°C in both cases.

As seen in Figure 2, current density distributions follow the local temperature, though both flow configurations experience reduction of current density toward the fuel exit due to fuel depletion. The initial stack current was 6.4% larger in the counter-flow case.

The decrease in current density at 40,000 hours (Figure 2) is a result of decreasing triple-phase boundary length (Figure 3) over time at temperature caused by electrode particle coarsening.

Figure 4 shows that despite identical size and shape and average cell temperature, the counter-flow stack had 6.4% higher initial power and less total degradation after 40,000 hours operation (9% versus 10%).

Degradation Model Implementation in SOFC-MP and Analyses Summary

- The lower order electrode grain coarsening degradation mechanism developed by NETL was implemented in the PNNL stack level thermo-electrochemistry simulation software SOFC-MP.
- 2-D simulations with counter-flow and co-flow stacks operated at the same average temperature indicated larger high temperature regions in counter flow case resulting in higher stack current.
- The final L_{TPB} distribution in the counter-flow stack had a minimum where fuel was still rich, but was sufficient to support electrochemical reactions.
- The counter-flow stack out-performed the co-flow stack initially and had a lower degradation rate over time.
- The change in a co-flow stack's operating temperature due to performance degradation from the electrode grain coarsening mechanism did not adversely affect the stack mechanical reliability.

SOFC-MP 3D Implementation for Reliability

After validating the stack performance degradation due to electrode grain coarsening with SOFC-MP 2D models, the degradation model was later implemented in the SOFC-MP 3D to predict the long-term performance loss and accompanying changes in the operating temperatures in current industrial stacks. The effect of such performance degradation on the mechanical reliability is also studied using a representative generic design.

Figure 5 shows the performance degradation in a generic co-flow design stack with ~400 cm^2 active cell area. The electrochemistry under degradation was simulated for a target cell voltage of 0.73V and adiabatic boundary conditions. The stack power degraded about 7% in 40,000 hours with reduction in the fuel and oxidant utilizations.

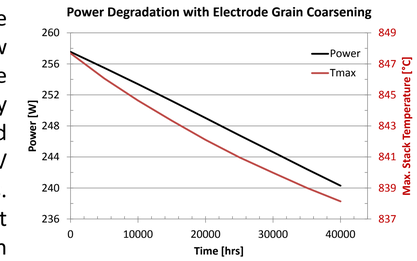

Figure 5: Simulated performance degradation in a generic design stack with PNNL SOFC-MP 3D software.

The peak operating temperatures and thermal gradients in the stack slightly reduced (Figure 6) over time along with the performance resulting in a relatively reduced component stresses and mildly improved stack mechanical reliability as summarized in Table 1. The results indicate electrode coarsening degradation mechanism alone may not adversely affect the stack structural reliability.

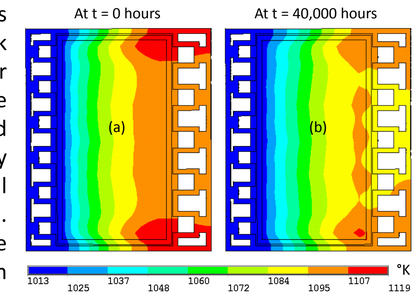

Figure 6: Thermal gradients in the stack under un-degraded (a) and degraded (b) operating states.

Table 1: CARES® Reliability Analysis Summary at Un-degraded and Degraded Operating States

Stack Component	Un-Degraded (t = 0 hrs)		Degraded (t = 40,000 hrs)	
	Max. Stress [Pa]	Prob. Of Failure, P_f (%)	Max. Stress [Pa]	Prob. Of Failure, P_f (%)
Air Seal	4.70E+06	0	4.82E+06	0
Fuel Seal	6.00E+06	0	6.05E+06	0
PEN Seal	3.92E+06	0	3.90E+06	0
Electrolyte	7.20E+07	3*	7.14E+07	2*
Anode	8.10E+06	0	8.10E+06	0
Cathode	9.71E+06	0	7.67E+06	0
Cathode Contact	1.95E+06	10	1.09E+06	2
Stack Overall P_f	12%		4%	

NOTES: *Localized risk of rupture at corners observed

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