Prediction of performance degradation due to grain coarsening in SOFC electrodes

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Multiphysics model supplemented with a semi-empirical coarsening sub-model

Background

- Multiphysics model of button cell calibrated to experimental polarization and impedance data for a range of temperatures
- Empirical equations added to certain parameters (i.e. double layer capacitance C_{DL} and exchange current density i_0)
- Microstructural properties obtained from reconstruction of PFIB data of cell similar to the one tested experimentally
- Property and grain coarsening models developed with guidance from experimental data also from the literature [1][2]
- Combined multi-physics and grain coarsening models

Multiphysics Model [3]

Charge conservation

$$a_s^{eff} C_{DL} \frac{\partial(\varphi_e - \varphi_i)}{\partial t} + \nabla \cdot \left(-\sigma_e^{eff} \nabla \varphi_e\right) = i_F$$

$$a_s^{eff} C_{DL} \frac{\partial(\varphi_i - \varphi_e)}{\partial t} + \nabla \cdot \left(-\sigma_i^{eff} \nabla \varphi_i\right) = -i_F$$

Dense Electrolyte: $\nabla \cdot (-\sigma_i \nabla \varphi_i) = 0$

Species Transport

$$V_p \frac{\partial \phi}{\partial t} = \nabla \cdot \left(D_\phi^{eff} \nabla \phi\right) - S_\phi$$

Property models

Diffusion: $D_\phi^{eff} = \frac{V_p}{\tau^2}\left(\frac{1-\alpha_{i,m}y_i}{D_{i,m}} + \frac{1}{D_{K,i}}\right)^{-1}$

Conductivity: $\sigma_i^{eff} = \frac{V_i}{\tau_i}\sigma_{i,0}$

Butler-Volmer Type Equation

Local Overpotential: $\eta = \varphi_e - \varphi_i - \eta_{eq}$

Anode:

$$i_{Fa} = i_{0a}^{eff}\{exp\left[\frac{\alpha n F \eta}{RT}\right] - exp\left[-\frac{(1-\alpha)nF\eta}{RT}\right]$$

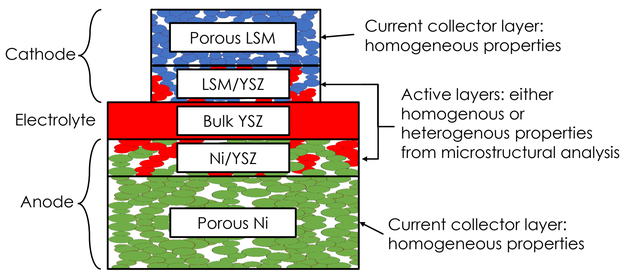
$$i_{0a}^{eff} = i_{0a} l_{TPB,a} \left(P_{H_2}\right)^a \left(P_{H_2O}\right)^b$$

Cathode:

$$i_{Fc} = i_{0c}^{eff}\{exp\left[\frac{\alpha n F \eta}{RT}\right] - exp\left[-\frac{(1-\alpha)nF\eta}{RT}\right]$$

$$i_{0c}^{eff} = i_{0c} l_{TPB,c} \left(P_{O_2}\right)^m$$

- Transport equations discretized via finite volume method (see details in [3])



Grain Coarsening Model

Begin with Ostwald ripening applying parameters from Kennouche [1]

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

Assuming YSZ particles smaller than Ni (or LSM) particles:

$$l_{TPB} = l_{TPB}^0 \frac{d_{Ni,0}^3}{d_{YSZ,0}} * \frac{d_{YSZ}}{d_{Ni}^3}$$

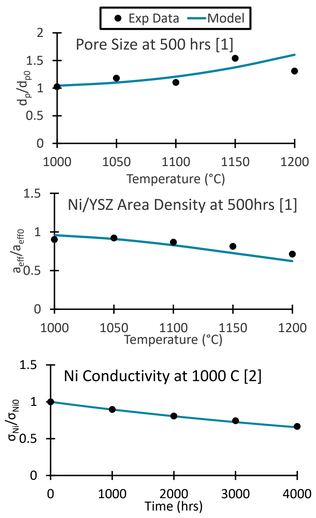
Additional data from Kennouche [1] used to derive/validate models for interfacial area density and pore size

$$a_{eff} = a_{eff,0}\left(\frac{d_{Ni,0}}{d_{Ni}} * \frac{V_{Ni}}{V_{Solid}} + \frac{d_{YSZ,0}}{d_{YSZ}} * \frac{V_{YSZ}}{V_{Solid}}\right)$$

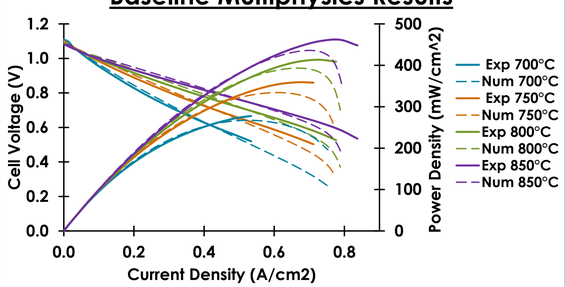
$$d_p = d_{p,0}\left(\frac{d_{Ni}}{d_{Ni,0}} * \frac{V_{Ni}}{V_{Solid}} + \frac{d_{YSZ}}{d_{YSZ,0}} * \frac{V_{YSZ}}{V_{Solid}}\right)$$

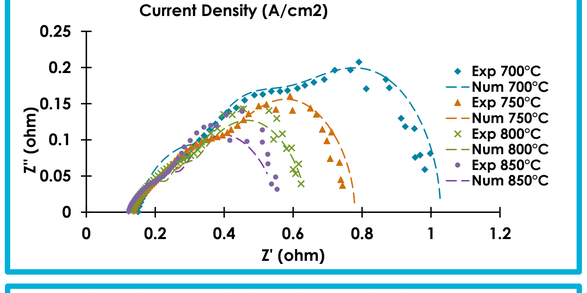
Second set of data from Simwonis [2] was analyzed to derive/validate tortuosity model

$$\tau_i = \tau_{i0}\left(\frac{d_i}{d_{i,0}}\right)^{3/2}; \quad \sigma_i^{eff} = \sigma_i \frac{V_i}{\tau_i}$$



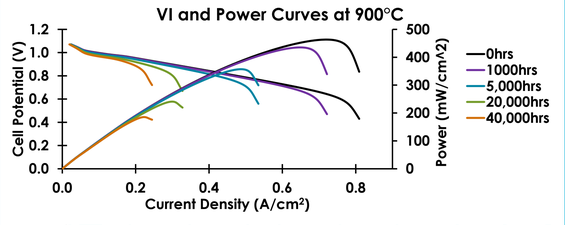
Baseline Multiphysics Results

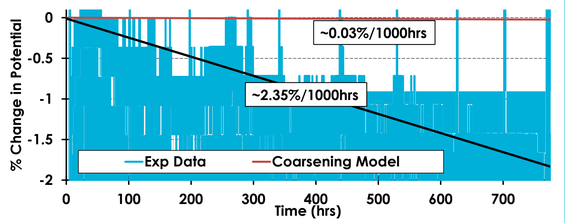




Predicted Degradation due to Grain Coarsening

Degradation Rate at 0.25 A/cm2	
Temp (°C)	%/1000 hrs
750	0.03%
800	0.07%
850	0.16%
900	0.39%
950	0.91%

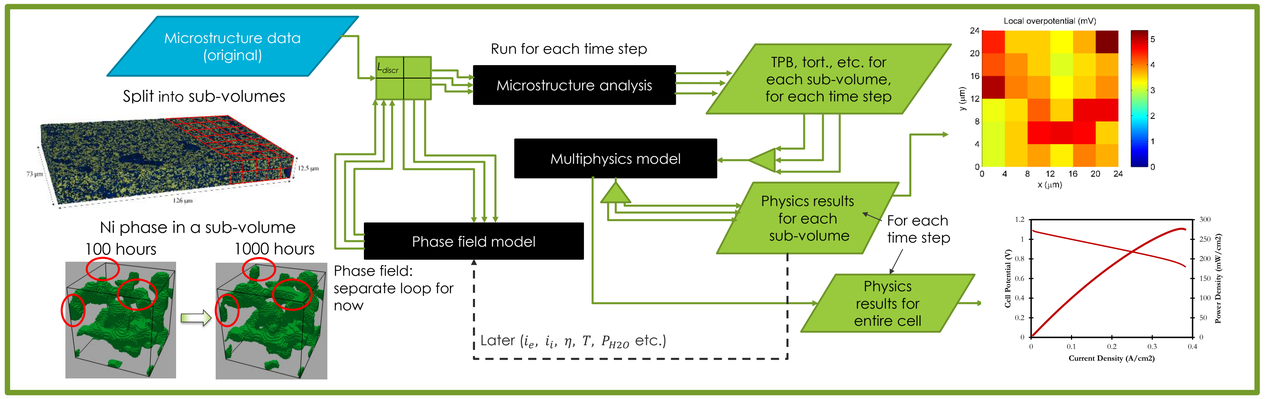




Conclusions from Multiphysics Model

- Degradation due to coarsening is strongly dependent on operating temperature
- Operating at high temperatures (>850°C) produces degradation rates which are not sustainable over the desired lifetime of the cell for this particular set of microstructural properties
- At 750°C, the model predicts that very little degradation is due to coarsening compared to total degradation rate

Integration with phase field model and microstructure analysis tool



Background

The goal of the integrated model is to accurately predict SOFC degradation due to coarsening by combining the capabilities of:

1. Microstructure analysis tool
2. Phase field model
3. Cell level multi-physics model

The model analyzes real or synthetic microstructur data by applying multiphysics model to micro-cell (24x24 μm in this study) with real or synthetic data applied in cell active layers

Phase Field Model

Three phases:

YSZ ($C_{YSZ} = 1$, $\eta_j^{YSZ} = 1$), Ni/LSM ($C_{Ni/LSM} = 1$, $\eta_j^{Ni/LSM} = 1$) and pore ($C_{YSZ} = C_{Ni/LSM} = 0$, $\eta_j^{Ni/LSM} = \eta_j^{YSZ} = 0$)

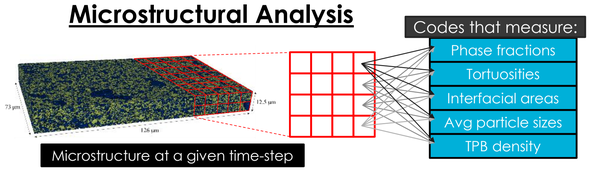
Free energy: $F = \int\left\{f_{bulk}(C_i, \eta_j^i) + \sum_{i,k}\frac{\kappa_\eta^{ik}}{2}(\nabla\eta_k^i)^2 + \sum_{j\geq i}\frac{\kappa_C^{ij}}{2}(\nabla C_i \cdot \nabla C_j)\right\}d^3r$

f_{bulk} keeps (C_i, η_j^i) around (0,0) or (1,1)

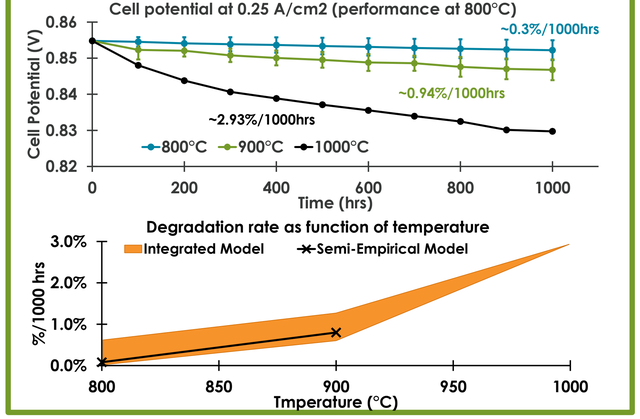
Cahn-Hilliard equation, conservative: $\frac{\partial C_i}{\partial t} = \nabla \cdot \left[M_c \nabla\left(\frac{\delta F}{\delta C_i}\right)\right]$

Allen-Cahn equation, non-conservative: $\frac{\partial \eta_j^i}{\partial t} = -M_\eta\left(\frac{\delta F}{\delta \eta_j^i}\right)$

Microstructural Analysis

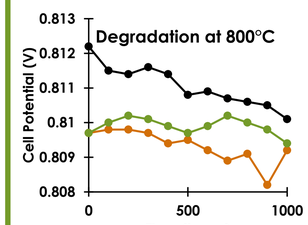


Results from Real Microstructure Data



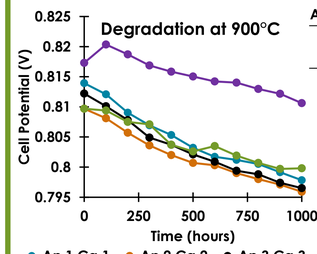
Results from Synthetic Microstructure Data

- 5 different synthetic microstructures with varying electrode phase particle size were coarsened at 800°C and 900°C
- Multiphysics model is applied to phase field results of each anode and cathode microstructure and predictions of performance degradation rates are produced for every combination



Degradation of each electrode combination at 800°C (%/1000hrs)				
	Cathode #			
Anode#	2	3	4
2	0.06%	0.15%	0.13%
3	0.17%	0.26%	0.24%
4	~0.0%	0.12%	0.04%

Initial Average Properties of synthetic microstructures					
Cathode #	1	2	3	4	5
d_{LSM} (μm)	0.49	0.6	0.61	0.65	0.69
l_{TPB} ($1/\mu m^2$)	2.77	2.15	2.34	2.41	1.95
Anode #	1	2	3	4	5
d_{Ni}(μm)	0.51	0.61	0.61	0.67	0.74
l_{TPB} ($1/\mu m^2$)	1.52	1.49	1.52	1.4	1.42



Degradation of each electrode combination at 900°C (%/1000hrs)					
	Cathode #				
Anode#	1	2	3	4	5
1	1.93%	1.81%	1.80%	1.72%	1.54%
2	1.79%	1.70%	1.68%	1.63%	1.42%
3	2.03%	1.93%	1.93%	1.84%	1.66%
4	1.39%	1.29%	1.28%	1.22%	1.02%
5	1.27%	1.11%	1.10%	1.02%	0.82%

Conclusions from Integrated Model

- The integrated multi-physics and phase field model is demonstrated and compared to a similar analysis performed by semi-empirical model
- Results show that the degradation rates decrease significantly with increasing initial particle size while initial performance is relatively unaffected (specifically at 900°C)
- The proposed model is capable of predicting performance degradation due to coarsening of any given combination of synthetic/experimentally obtained microstructures relatively quickly and cheaply (compared to experiments)
- Future work will include phase field model which considers effects of local variations in gas concentrations, current densities and temperature obtained by multiphysics model

References:

[1] Kennouche, David, et al. Journal of Power Sources 307 (2016): 604-612.

[2] D. Simwonis, et al, Solid State Ionics, 132, 241 (2000)

[3] T. Yang, et al, "Prediction of SOFC Performance with or without Experiments: A Study on Minimum Requirements for Experimental Data", Int. J. Electrochem. Sci., (2017).

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