Phase field modeling of microstructure and conductivity evolution in SOFC electrodes

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Introduction

Purpose of this research:

- Simulate microstructure evolution and coarsening in SOFC electrodes;
- Predict property evolution associated with electrode coarsening.

Phase field model of SOFC electrodes:

- Capable of simulating long term microstructure evolution [1].
- Properties of electrode can be extracted directly from simulated microstructures.
- Need wide range of tunability with respect to various interfacial energies in the electrodes.

Phase field modeling

- Phase-field parameters:
  - Phase fraction C_i (conserved)
  - Order parameter η_j^i (non-conserved)
- Free energy

$$F = \int \left\{ f_{bulk}(C_i, \eta_j^i) + \sum_{i,k} \frac{\kappa_\eta^{ik}}{2} (\nabla \eta_k^i)^2 + \sum_i \frac{\kappa_c^{ii}}{2} (\nabla C_i)^2 + \sum_{j>i} \frac{\kappa_c^{ij}}{2} (\nabla C_i \cdot \nabla C_j) \right\} \mathrm{d}^3 r$$

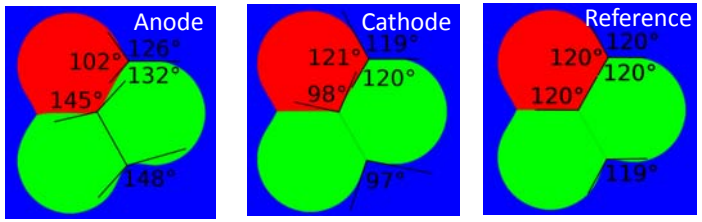
- Bulk free energy density f_{bulk} keeps (C_i, η_j^i) around (0,0) or (1,1).
- Crossing terms of parameter gradients improves the tunability of interfacial energies.
- Evolution of C_i (representing electrolyte and electrode phases): Cahn-Hilliard equation.

$$\frac{\partial C_i}{\partial t} = \nabla \cdot \left[M_c \nabla \left(\frac{\delta F}{\delta C_i} \right) \right]$$

- Evolution of η_j^i (representing different polycrystalline grains): Allen-Cahn equation

$$\frac{\partial \eta_j^i}{\partial t} = -M_\eta \left(\frac{\delta f}{\delta \eta_j^i} \right)$$

Contact angles



Red: YSZ, Green: Ni/LSM, Blue: Pore

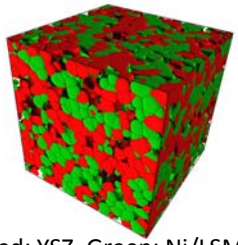
High energy interfaces

Anode: Ni surface & Ni-YSZ interphase boundary [2].

Cathode: LSM grain boundary [3].

Reference: All interfaces are the same.

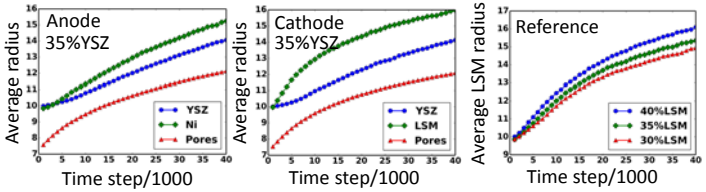
Microstructure evolutions



- 3D model, $128 \times 128 \times 128$ points.
- Three compositions:
  - 30%YSZ-40%Ni/LSM-30%Pore,
  - 35%YSZ-35%Ni/LSM-30%Pore,
  - 40%YSZ-30%Ni/LSM-30%Pore.
- Initial structure: ~2000 grains.

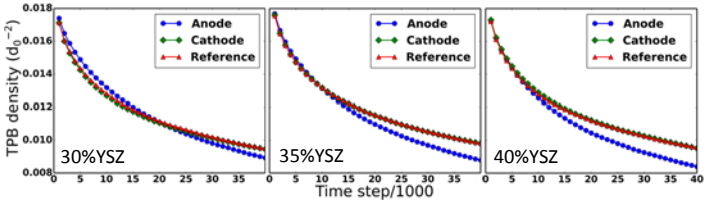
Red: YSZ, Green: Ni/LSM

Grain size



- Ni/LSM coarsened faster than YSZ.
- Coarsening rate depends on the volume fraction of each phase.

Triple phase boundary



- The degradation of TPB in anode is the fastest one.
- The degradation of TPB is insensitive to grain boundary energy.

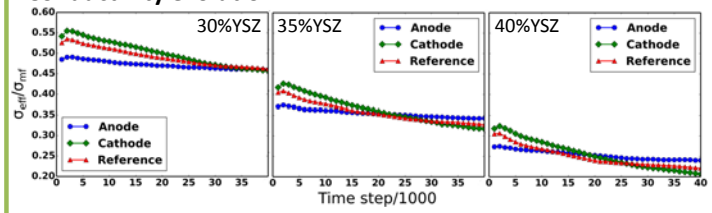
Conductivity calculations

Solving Poisson's equation

$$\nabla \cdot \left(\boldsymbol{\sigma}(\vec{r}) \vec{E} \right) = -\frac{\partial \boldsymbol{\rho}}{\partial t} = \mathbf{0}$$

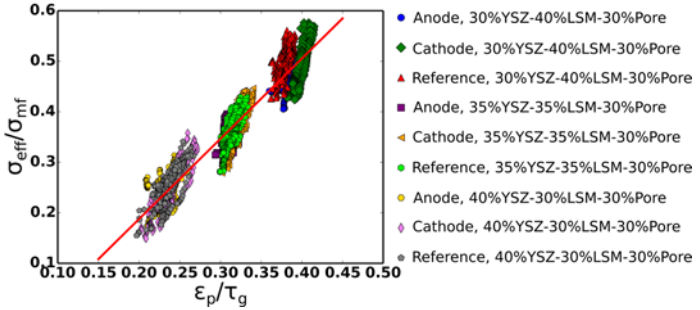
using Bound Charge Successive Approximation algorithm [4].

Conductivity evolution



- $\sigma_{mf} = \sigma_{YSZ} C_{YSZ} + \sigma_{Ni/LSM} C_{Ni/LSM}$
- σ_{eff} is greater with more Ni/LSM in the electrode.
- Conductivity degradation is slowest in anode.

Correlation between conductivity and geometric properties



ε_p: percolated volume fraction of Ni/LSM

τ_g: geometric tortuosity of Ni/LSM

Positive correlation between the conductivity and the ratio between the percolated fraction and the tortuosity of Ni/LSM.

Conclusions

- The new phase-field model can simulate microstructure evolution in real SOFC electrodes and extracting the "real-time" effective conductivity during coarsening.
- Coarsening rate and TPB density depend on the electrode composition and ratio of interfacial energies.

Acknowledgement:

The authors would like to thank Drs. Kirk Gerdes, Gregory Hackett, Harry Abernathy, Long-Qing Chen, Paul Salvador, William Epting and Tom Kalapos for valuable technical discussions.

This project was supported in part by an appointment to the Internship/Research Participation Program at the National Energy Technology Laboratory, U.S. Department of Energy, administered by the Oak Ridge Institute for Science and Education.

References

[1] Liang et al, *J. Appl. Phys.*, **117** (2015) 065105. [2] Nahor *et al*, *J. Mater. Sci.*, **49** (2013) 3949-3950.
[3] Helmick, PhD thesis, CMU 2010. [4] Cheng and Wen, *Phys. Rev. E*, **91** (2015) 053307.