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 (non-conserved)
• Free energy
  \[ F = \int \left( f_{bulk}(C_i, \eta_j) + \sum_{i,k} \frac{K_{ij}}{2} \left( \nabla \eta_k \right)^2 + \frac{\sum_{i,j} K_{ij}}{2} \left( \nabla C_i \cdot \nabla C_j \right) \right) d^3r \]
  • Bulk free energy density \( f_{bulk} \) keeps \( C_i, \eta_j \) around (0,0) or (1,1).
  • Crossing terms of parameter graditens improves the tunability of interfacial energies.
• Evolution of \( C_i \) (representing electrolyte and electrode phases): Cahn-Hilliard equation.
  \[ \frac{\partial C_i}{\partial t} = \nabla \cdot \left[ M_i \nabla \left( \frac{\delta F}{\delta C_i} \right) \right] \]
• Evolution of \( \eta_j \) (representing different polycrystalline grains): Allen-Cahn equation
  \[ \frac{\partial \eta_j}{\partial t} = -M_j \frac{\delta F}{\delta \eta_j} \]

Microstructure evolutions
• 3D model, 128 × 128 × 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.

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.

References

Conductivity calculations
Solving Poisson’s equation
\[ \mathbf{V} \cdot (\sigma(\mathbf{F})\mathbf{E}) = -\frac{\partial \rho}{\partial t} = 0 \]
using Bound Charge Successive Approximation algorithm [4].

Conductivity evolution

Correlation between conductivity and geometric properties

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.

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