Progressive Damage in Planar Solid Oxide Fuel Cell Electrode Materials

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Overview

Structural integrity of the cell layers dictate the performance and reliability of solid oxide fuel cells (SOFCs). The ceramic and cermet materials typically used in the state-of-the-art SOFCs exhibit quasi-brittle behavior within the operating temperatures of SOFCs (<850°C). Estimation of cell reliability based on statistical strength of brittle materials (Weibull theory) is a common practice which in our experience was found to be overly conservative as it estimates localized edge cracks in one of the cell components to be 100% cell failure, while in reality, the cell likely remains functional even with through-thickness cracks in the anode or cathode. An alternate method to simulate progressive damage in cell components due to operating loads and to predict whether localized damage can lead to cell failure and complete loss of function was investigated using a mechanistic continuum damage mechanics (CDM) model.

Technical Approach

1. Develop a mechanistic CDM model that captures the degradation of material stiffness resulting from the initiation, propagation and coalescence of microcracks, microvoids, and similar defects.
2. Implement the CDM model in a commercial finite element analysis software and validate the strain-strain behavior and stiffness variation with porosity.
3. Simulate progressive damage in simplified PEN layer and SOFC stack models using temperatures for realistic operating conditions obtained from the electrochemistry models solved by in-house SOFC MP-3D code.

Mechanistic CDM Constitutive Model

- The stiffness tensor components are very well fitted by an exponential expression of void and microcrack volume fraction p+α :

$$C_{ijkl}(p,\alpha) = C^{0}_{ijkl}\exp(-k_{ij}\,p)\,\exp(-k_{ij}\alpha)$$
$$= C^{\mathrm{I}}_{ijkl}(p)\exp(-k_{ij}\alpha)$$

This is the stiffness reduction law for a porous ceramic material subject to cracking.

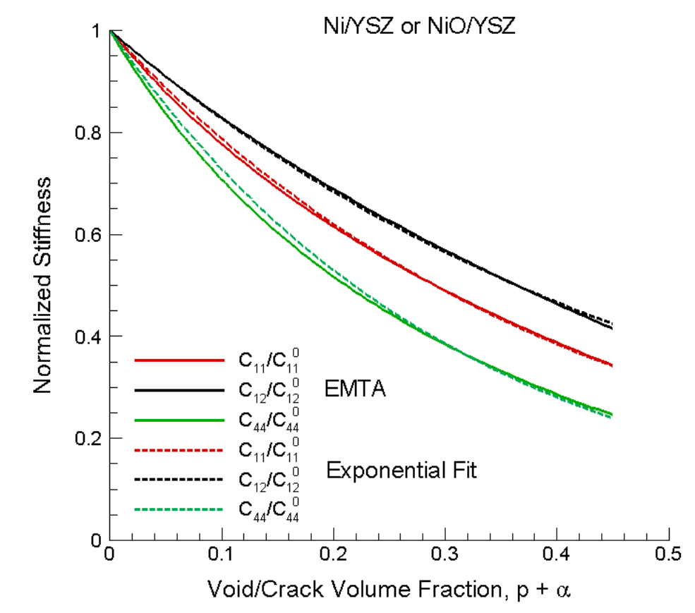


Figure 1: Stiffness Reduction in Porous Ceramics

- Constitutive relations and damage evolution laws are derived from the thermodynamics of continuous media.

Thermodynamic potential:

$$\Phi(\varepsilon_{ij},p,\alpha) = \frac{1}{2}C_{ijkl}(p,\alpha,T)\varepsilon_{ij}\varepsilon_{kl}$$
$$\varepsilon_{ij} = \varepsilon^{\mathrm{t}}_{ij} - \varepsilon^{\mathrm{th}}_{ij} = \varepsilon^{\mathrm{t}}_{ij} - \int_{T_0}^{T}\beta_{ij}(T)dT$$

Constitutive relation:

$$\sigma_{ij} = \frac{\partial\Phi}{\partial\varepsilon_{ij}} = C_{ijkl}(p,\alpha,T)\varepsilon_{kl}$$

Thermodynamic force = driving force for damage development:

$$F = \frac{\partial\Phi}{\partial\alpha} = \frac{1}{2}\frac{\partial C_{ijkl}(p,\alpha,T)}{\partial\alpha}\varepsilon_{ij}\varepsilon_{kl}$$

Damage evolution law:

$$d\alpha = -\frac{\dfrac{\partial C_{ijkl}}{\partial\alpha}\varepsilon_{ij}d\varepsilon_{kl}}{\dfrac{1}{2}\dfrac{\partial^2 C_{ijkl}}{\partial\alpha^2}\varepsilon_{ij}\varepsilon_{kl} - \dfrac{dF_c}{d\alpha}}$$

Microcrack volume fraction (damage variable, α) can evolve from an initial value to a critical one at which total failure occurs and is captured by a vanishing element method in FEA.

Stress-Strain Behavior & Porosity Effects

In view of the lack of stress-strain data, porous brittle materials are assumed to typically exhibit nearly linear stress-strain response till failure. The behavior of prominent SOFC materials and the effect of initial porosity on their strength have been validated using characteristic strength data from literature.

Figure 2: Stress-Strain Behavior Showing Reduction in Stiffness and Strength of (a) Ni/YSZ (b) YSZ and (c) LSM materials with Various Initial Porosities

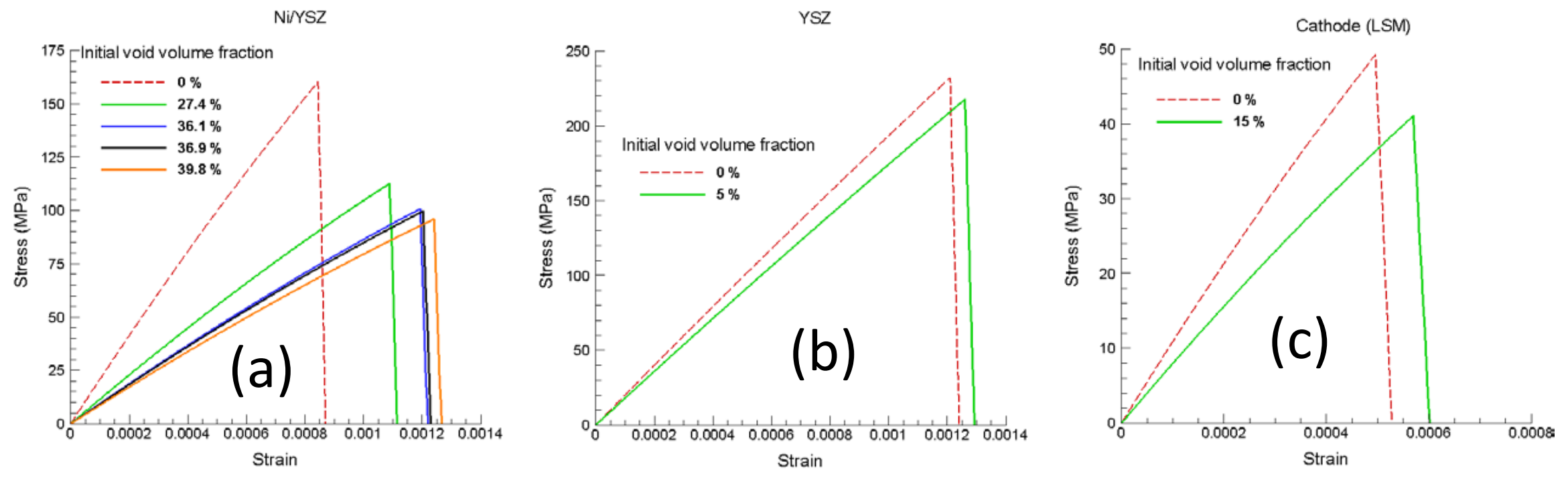


Figure 3 Evolution of Microcrack Volume Fraction Under Applied Stress in (a) Ni/YSZ (b) YSZ and (c) LSM materials with Various Initial Porosities

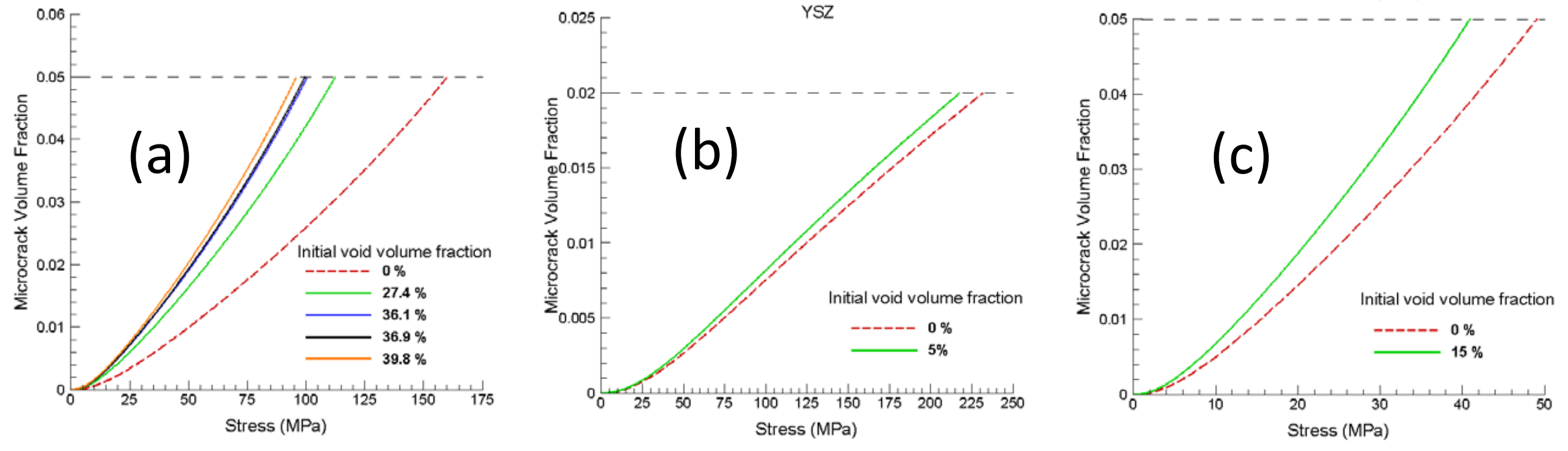


Table 1: Predicted vs. experimental strength for NiO/YSZ

Porosity (%)	Experimental (MPa)*	CDM Prediction (MPa)
6.6	127.4 ± 17.1	128.7
17.8	88.9 ± 23.7	111.6
19.8	86 ± 23.7	108.7
21.9	86 ± 21.5	105.8

Table 2: Predicted vs. experimental strength for Ni/YSZ

Porosity (%)	Experimental (MPa)*	CDM Prediction (MPa)
27.4	107.1 ± 19.7	112.6
36.1	74.3 ± 10.9	100.7
36.9	67.9 ± 13.9	99.7
39.8	50.7 ± 12.0	95.9

(*) M. Radovic, E. Lara-Curzio, Acta Materialia 52 (2004) 5747–5756

Damage in Simplified PEN Models

The progressive damage in a typical planar SOFC Positive electrode – Electrolyte – Negative electrode (PEN) layers was studied using a simplified quarter symmetric sandwich model (layers shown in Figure 4a) subject to various mechanical and thermal loads that a cell may encounter during operation. The loads include gravity, 0.2 MPa compressive load from a load frame, and operational (avg 750°C) and shutdown (25°C) temperatures. Figure 4b shows significant damage in PEN layers when the PEN assembly is only supported by an edge seal. Figure 5a shows the damage in the PEN layers under a uniform operating temperature of 750 °C and Figure 5b shows the damage under shutdown. The damage is localized to edges and is not progressive when the PEN assembly is properly supported in the out-of-plane direction.

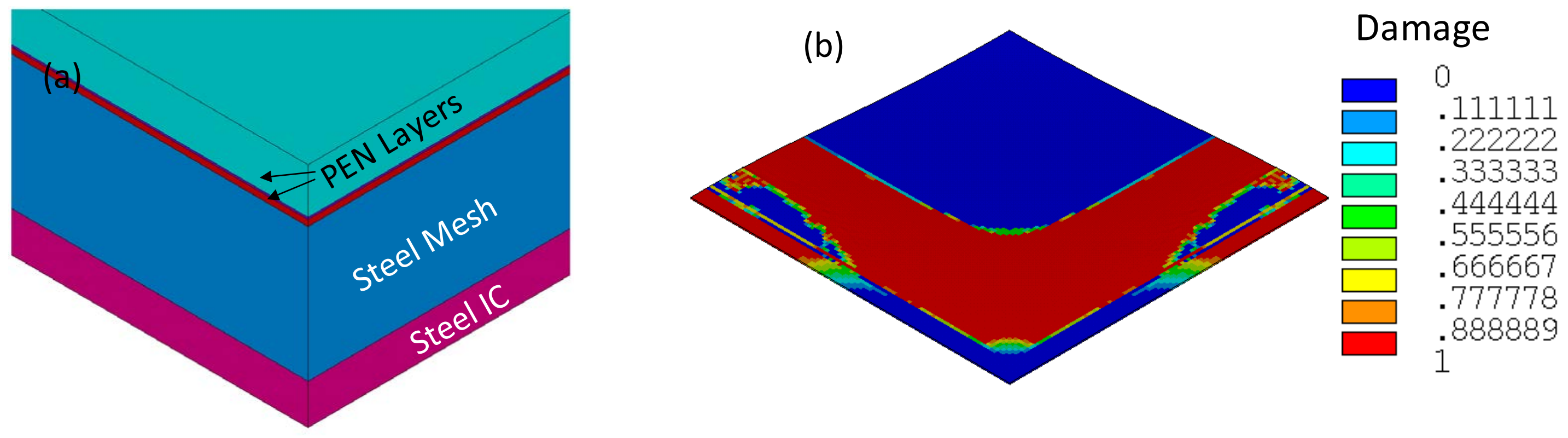


Figure 4: (a) Schematic of Simplified PEN Layer Model and (b) Damage in the PEN Without Steel Mesh Support

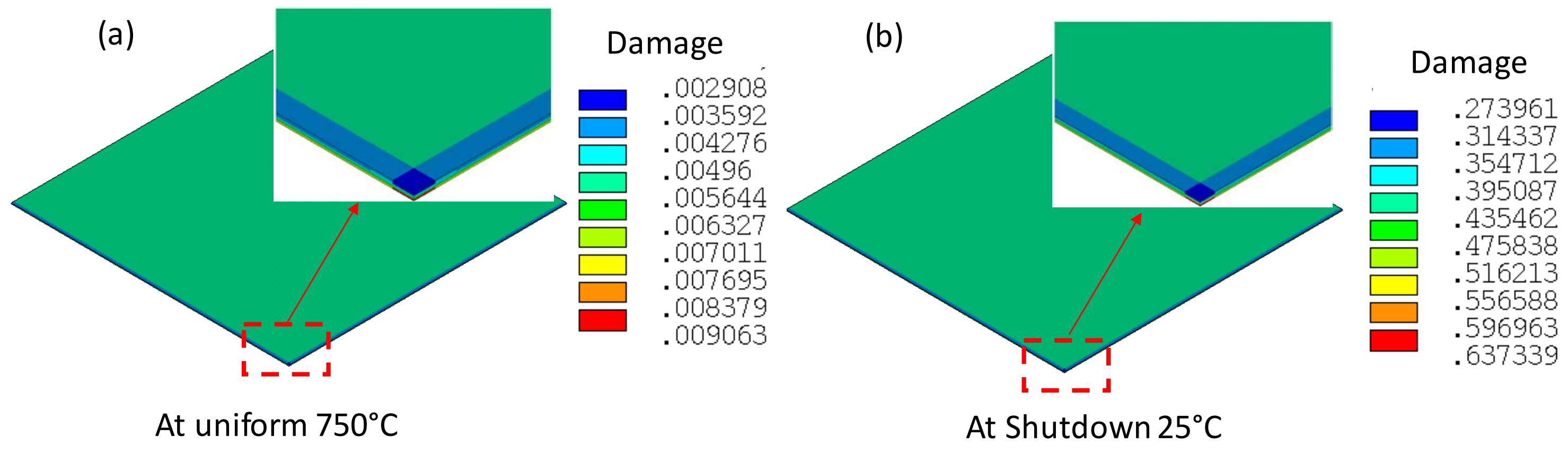
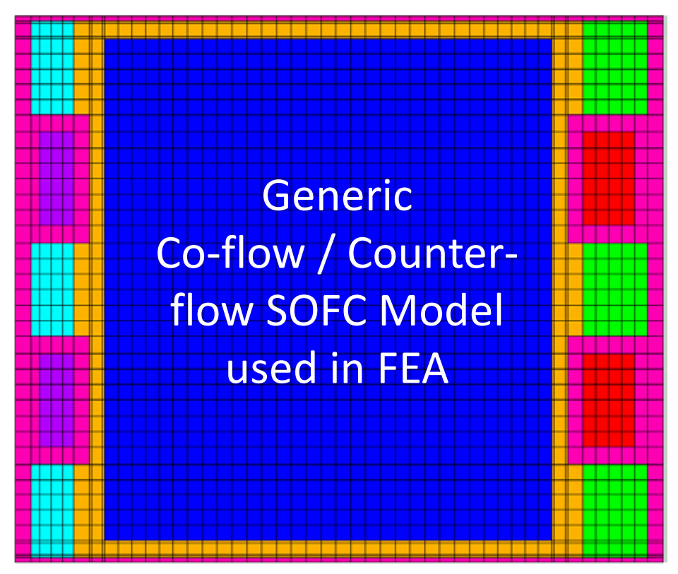


Figure 5: Damage in PEN Layers at (a) Uniform Operating Temperature of 750°C and (b) at Shutdown Condition with Stainless Steel Mesh Support Under the Cathode

Damage in Single Cell Stack Models

Figure 6 presents illustrates a generic planar SOFC model for co-flow/counter-flow configurations. The operating thermal contours obtained from SOFC MP – 3D for co-flow and counter-flow configurations are shown in Figures 7a and 7d respectively. The damage in PEN layers at operating and shutdown conditions under Co-flow configuration are presented in Figures 7c and 7d respectively. Figures 7e and 7f present similar results for counter-flow configuration. While similar damage was observed at operating condition, the counter-flow configuration showed slightly higher edge damage at shutdown.



Stack Average Performance

- T_{avg} ≈ 750°C
- FU ≈ 86%, AU ≈ 16.4%
- V ≈ 0.7908 per cell
- I_{dens} ≈ 0.4 A/cm² per cell

Figure 6: Generic Planar Single Cell SOFC Model for Co-flow and Counter-flow Configurations

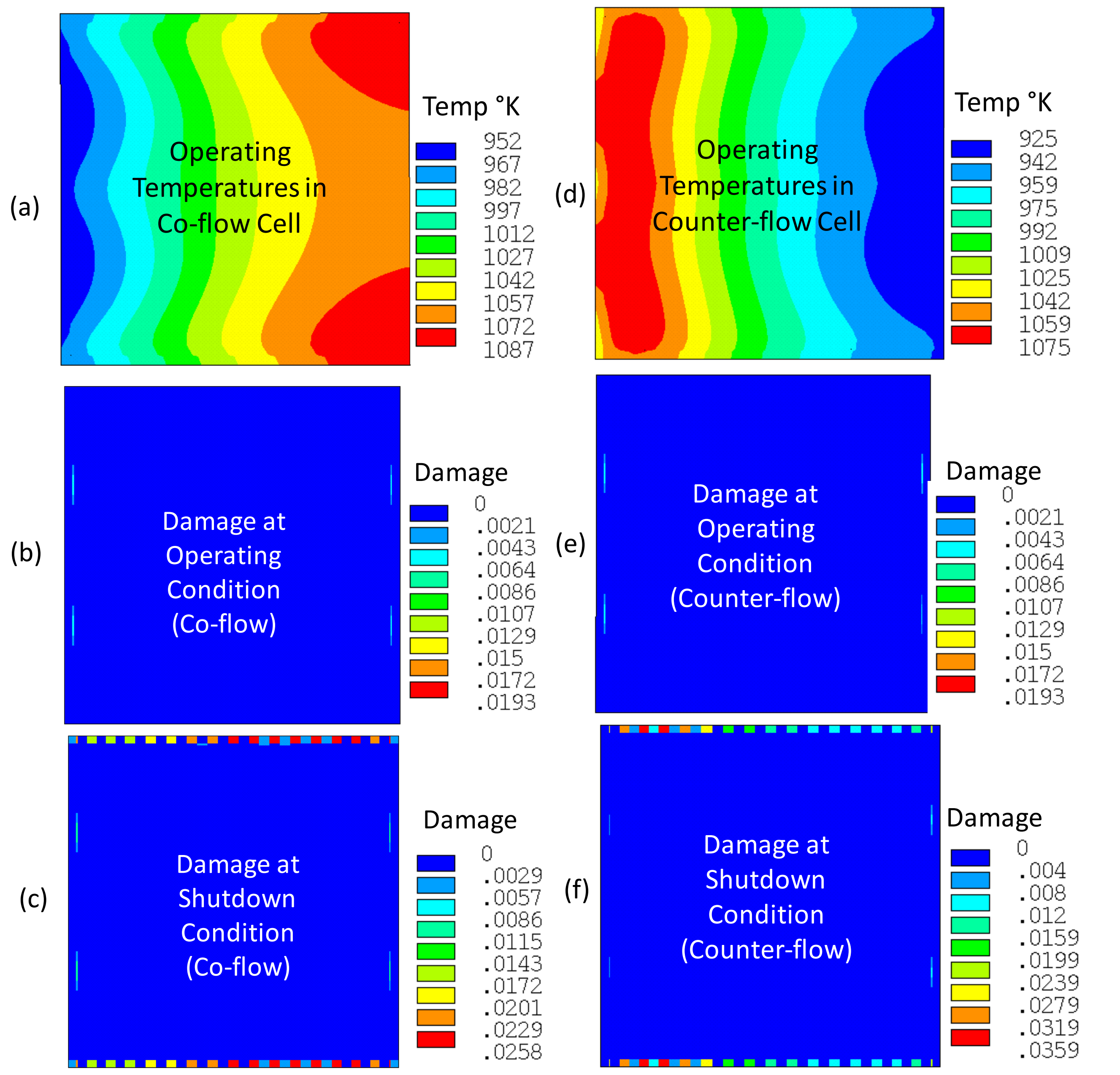


Figure 7: Co-flow Operational Temperatures (a) and Damage at Operating (b) and Shutdown (c) Conditions (Figures d, e, and f Show Similar Results for Counter-flow configuration)

Summary and Future Work

- ❖ A mechanistic continuum damage mechanics models was implemented in commercial FEA software to study progressive damage in SOFC cell materials.
- ❖ Localized edge damage was observed in single cell stacks under both co-flow and counter-flow operations when proper out-of-plane support for the PEN assembly exists (may not exist for middle cells in a multicell stack).
- ❖ Future work will investigate model mesh sensitivity and damage in multicell stacks under various flow configurations (counter-flow, cross-flow) and boundary conditions (adiabatic, furnace environments).

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