Performance degradation modeling of solid oxide fuel cells using a multiphysics framework

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Research & Innovation Center

NATIONAL ENERGY TECHNOLOGY LABORATORY

Motivation / Project Objective

According to SOFC system pathway studies performed by NETL, lowering the cell degradation rate is one of the most significant ways, on the cell level, to reduce system costs. Extending cell life reduces the number of times a stack needs to be replaced during the planned system's lifetime. To obtain this goal, modeling and characterization efforts at NETL focus on the following broad objectives:

- **To identify and quantitatively rank the major degradation mechanisms** of solid oxide fuel cells electrodes and electrolytes as a function of cell materials set, operating conditions, and expected system contaminants.
- **To develop analytical methods and toolsets** to characterize more fully the performance and degradation mechanisms of SOFCs. The tools are to be used by NETL's partners to provide extra quality control, to help establish stack maintenance schedules, and to guide future research by identifying the specific areas that will have the greatest impact on system costs.
- **To improve SOFC system performance and lifetime** by optimizing cell composition, microstructure, and operating conditions using high throughput cell performance degradation simulations. In conjunction with electrode engineering efforts at NETL, the loading level and distribution of infiltrated nanoparticles into SOFC electrodes will also be tailored to meet this goal.

Button Cell Multiphysics Model [1]

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:

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

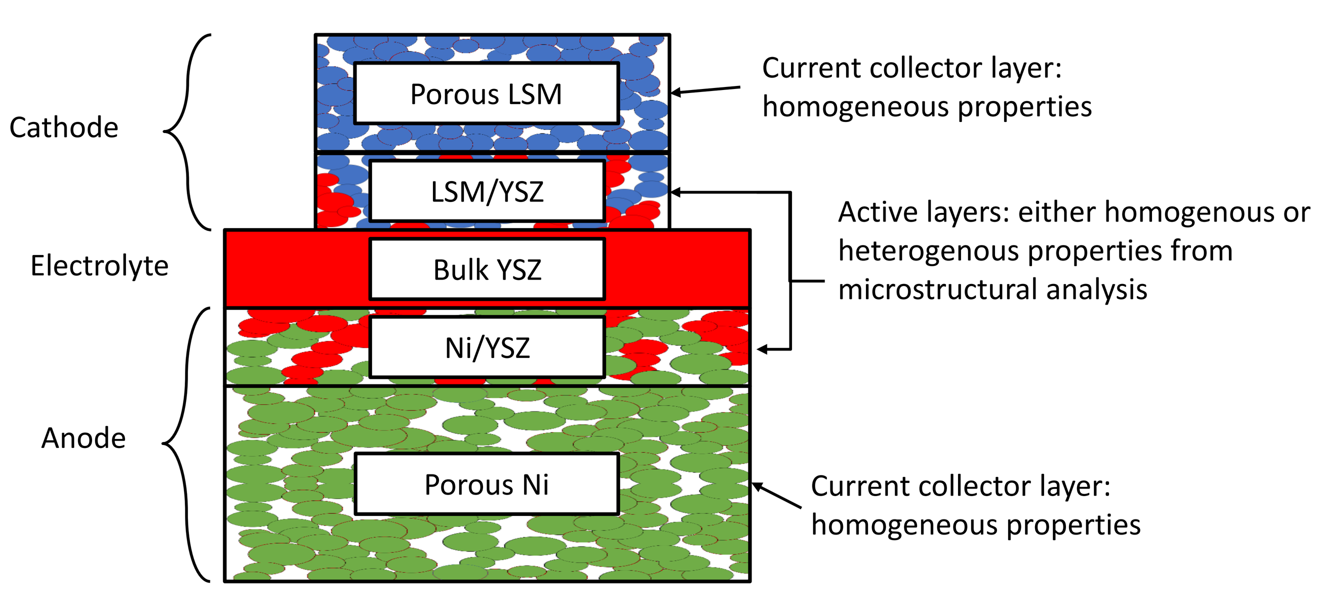
$$i_{0a}^{eff} = i_{0a} l_{TPB,a} \left(P_{H_2}\right)^a \left(P_{H_2O}\right)^b$$

Cathode:

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

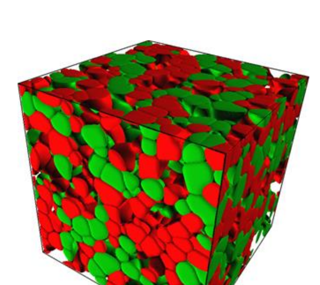
$$i_{0c}^{eff} = i_{0c} l_{TPB,c} \left(P_{O_2}\right)^m$$

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

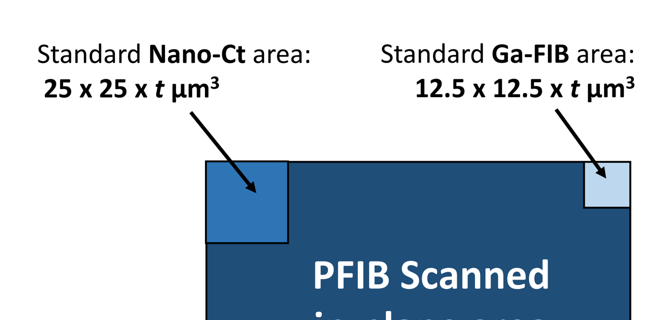


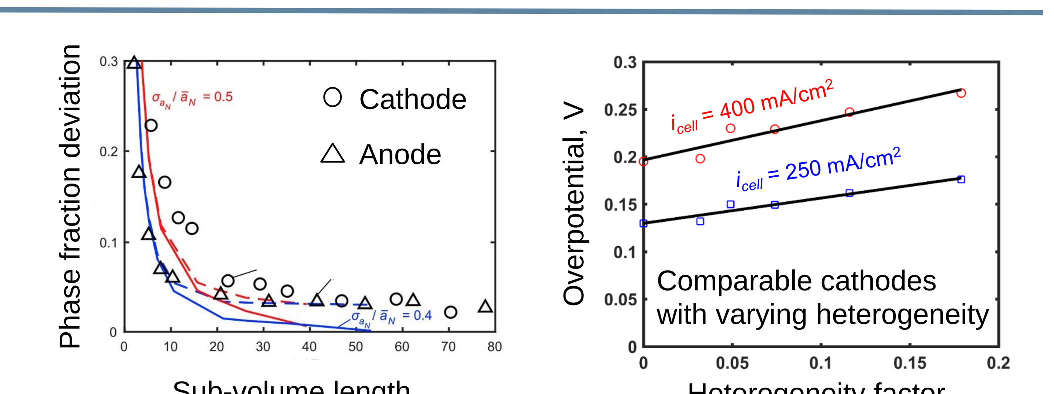
Heterogeneous microstructures

NETL uses x-ray tomography (μ-CT) and focused ion beam SEM (pFIB-SEM) to generate **large volume, high resolution** 3D reconstructions of commercial SOFC electrodes. The large volumes allow for statistical analysis of distribution in microstructure parameters within a cell. This heterogeneity contributes to cell degradation by generating hotspots and changing local degradation behavior. NETL uses real and synthetic microstructures in our multiphysics models to simulate electrode performance and long-term degradation.



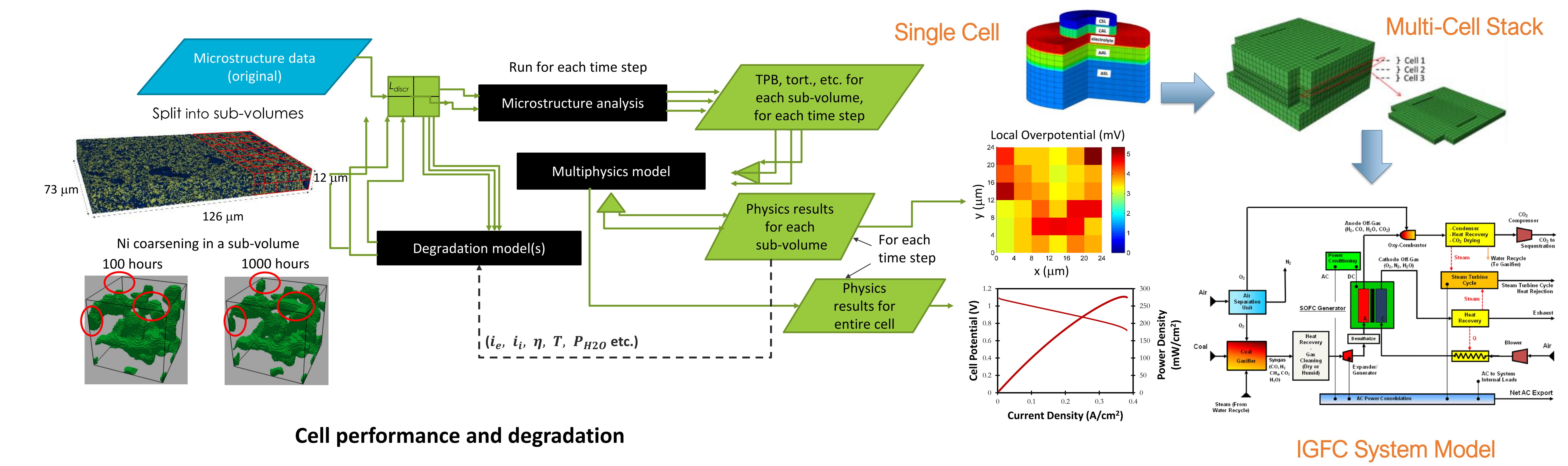
A synthetic electrode created using Dream3D software.





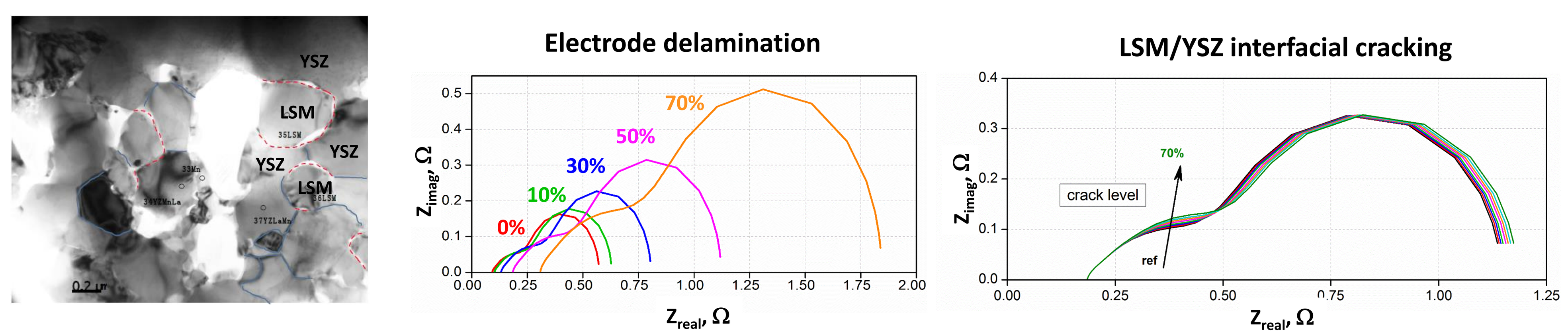
Heterogeneity in real electrodes

NETL Integrated SOFC Degradation Modeling Framework

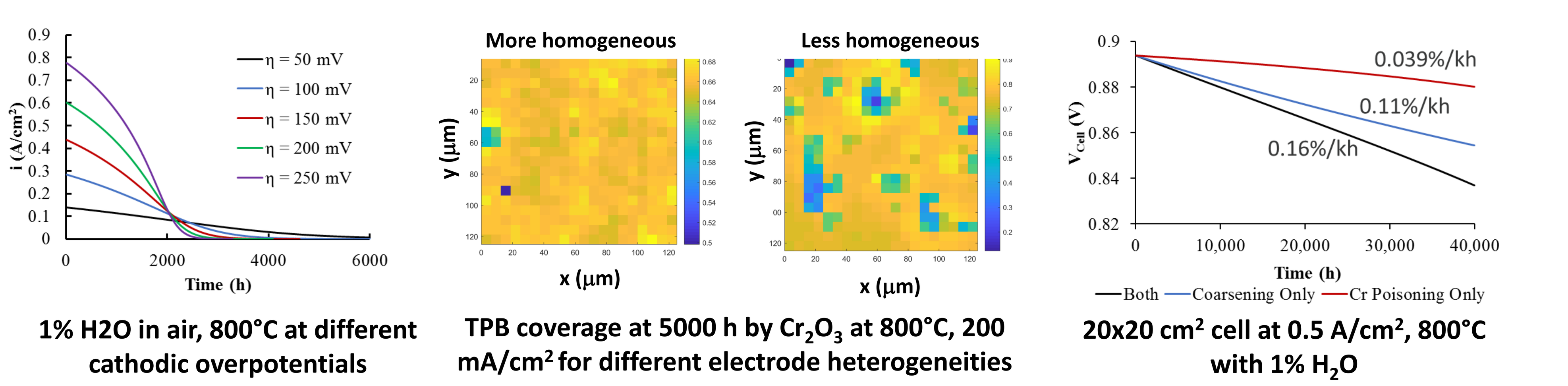


Cell performance and degradation

NETL combines cell testing with detailed chemical/structural analysis to identify degradation mechanisms (e.g., interdiffusion, secondary phase formation, void formation, cracking). These degradation modes are then incorporated into our performance models. Statistical methods are used for scale-bridging efforts to pass data from single cell simulations to stack- and system-level models. Our single cell simulations now include particle coarsening, chromium poisoning of the cathode, anode poisoning from fuel contaminants, cracking/delamination, and interactions between infiltrated nanocatalysts and the electrode backbone.



Observation and simulation of delamination and cracking along LSM/YSZ interfaces for cathodes operated in humidified air. Delamination occurs at the electrode/electrolyte interface. Cracking occurs within the electrode active layer.



1% H2O in air, 800°C at different cathodic overpotentials

TPB coverage at 5000 h by Cr_2O_3 at 800°C, 200 mA/cm² for different electrode heterogeneities

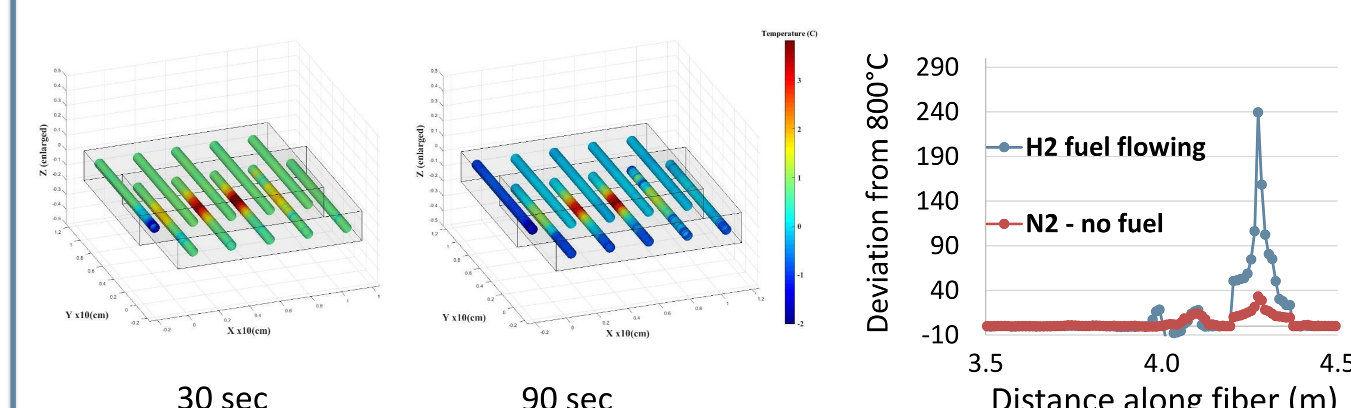
20x20 cm² cell at 0.5 A/cm², 800°C with 1% H_2O

Simulation of chromium poisoning at triple phase boundaries (TPBs) of LSM/YSZ cathodes. The deposition rate of Cr_2O_3 at TPBs is assumed to be dependent on overpotential. Heterogeneity within the cathode accelerates chromium poisoning. In a collaboration with PNNL, the relative degradation rates of chromium poisoning and particle coarsening are being compared.

Optical sensing of large area SOFC performance[2]

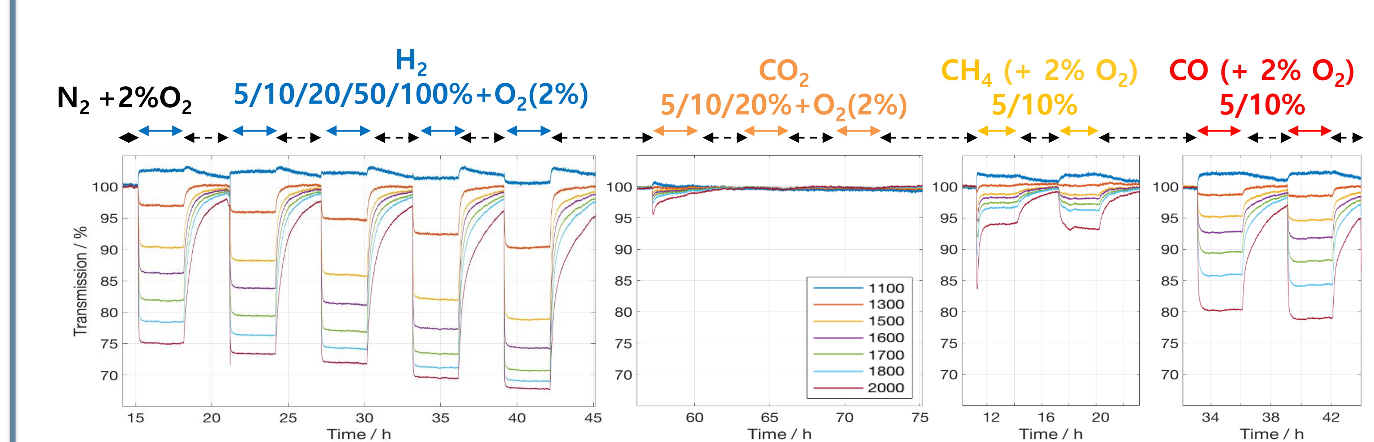
NETL has developed an optical fiber sensor for collecting distributed temperature measurements along the fiber. By applying a functional coating to the fiber, it is also possible to simultaneously measure the anode fuel composition and the temperature. Research continues to improve the selectivity and stability of the functional coating.

The sensor can reduce stack instrumentation, allow for **real-time** monitoring of **inlet-to-outlet** temperature and fuel utilization in individual cells, and collect data to calibrate and validate stack and cell models.



Thermal transients from 25 cm² cell at 750°C as current was switched from 0 to 2 A.

Failure detection: Temperature spike from cracked cell



Optical response of ITO-coated sensor to different gas compositions

References:

[1] T. Yang, et al, "Prediction of SOFC Performance with or without Experiments: A Study on Minimum Requirements for Experimental Data", Int. J. Electrochem. Sci., 12, 6801 (2017).

[2] Y. Jee, et al, "Plasmonic Conducting Metal Oxide-Based Optical Fiber Sensors for Chemical and Intermediate Temperature-Sensing Applications", ACS Appl. Mater. Interfaces, 10(49), 42552 (2018).

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