# SECA Core Technology Program and Small Scale SOFC Test Platform

J. Hardy, B. Koeppel, Y. Chou, J. Choi, C. Coyle, Z. Xu, N. Karri, J. Bao, B. Kirby, G. Whyatt, J. Davis, C. Fischer, C. Lowrey, N. Canfield, J. Fitzpatrick, T. Droubay, B. Nguyen, C. Mason, D. Wang, X. Yang, J. Kim, M. Prange

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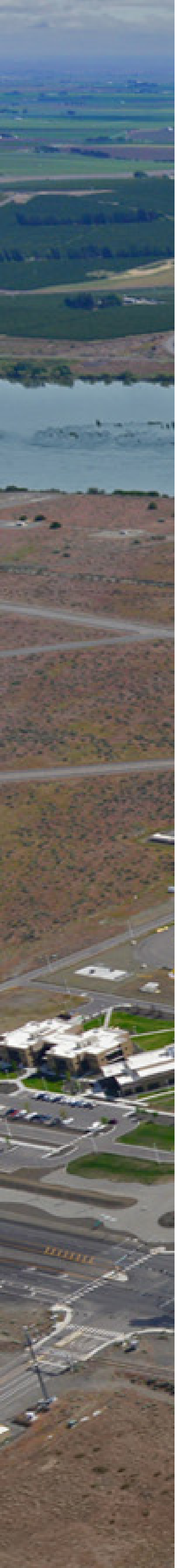
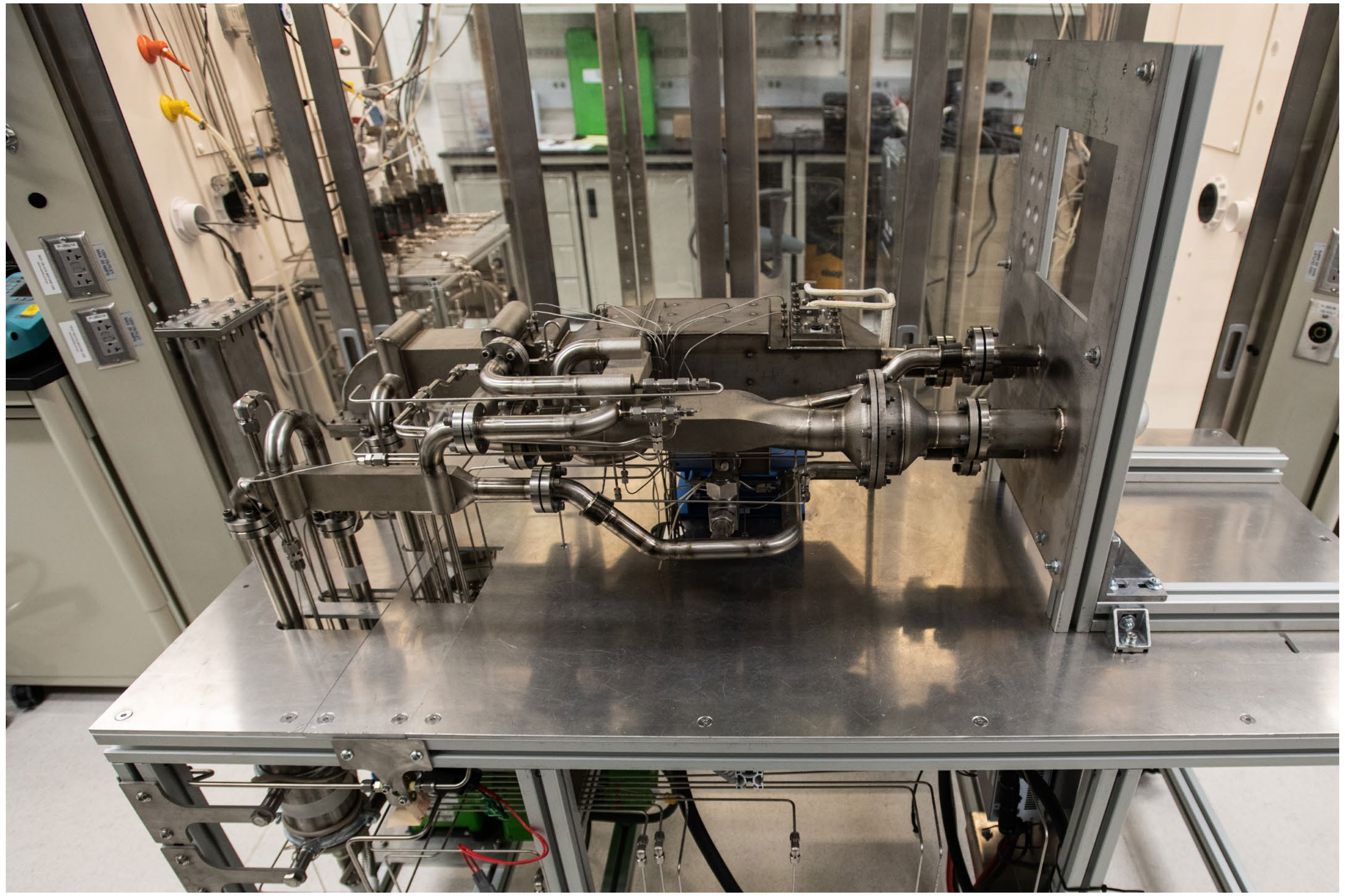


# Small-Scale SOFC Stack Test Platform

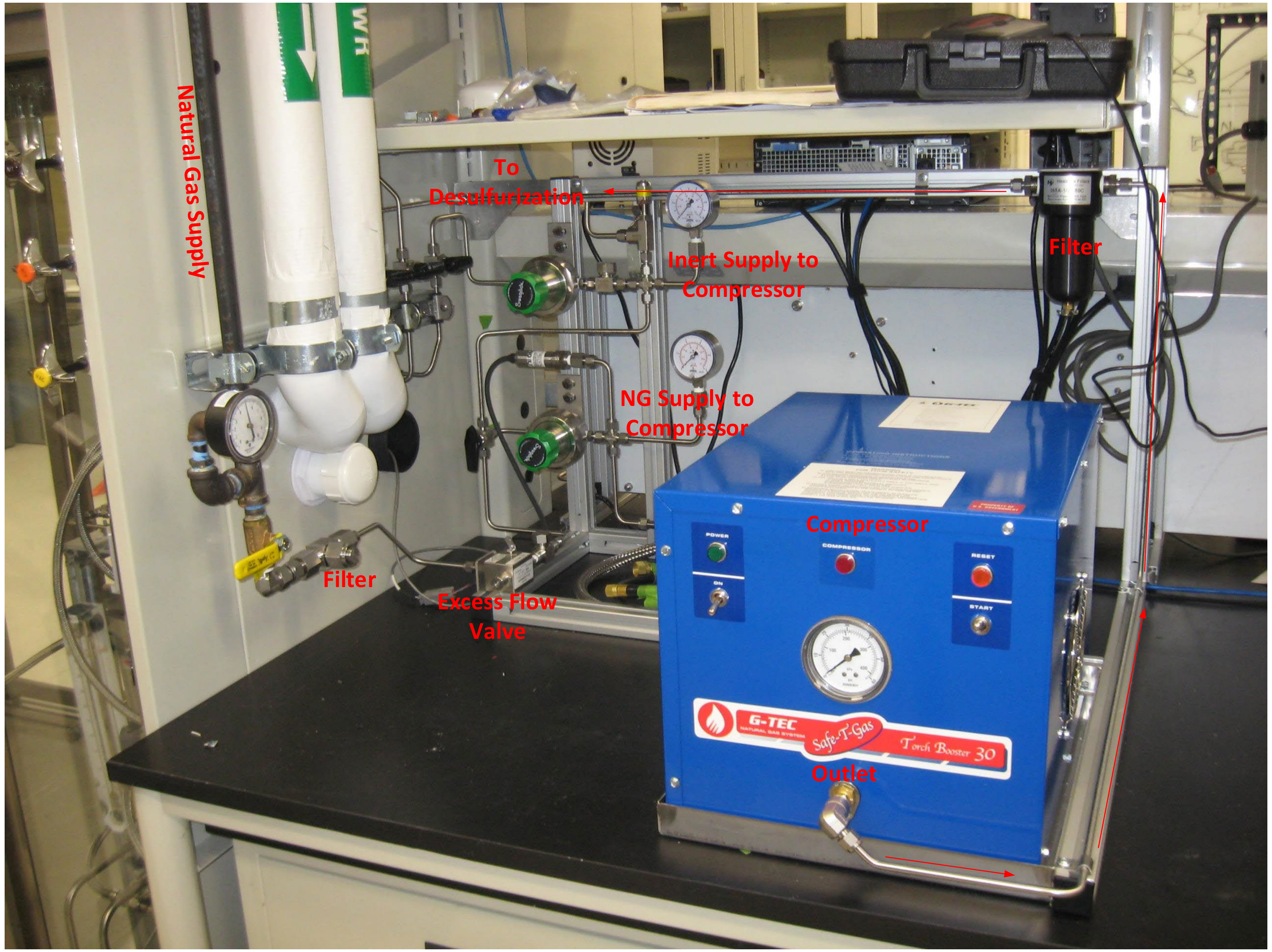
- Commissioned by DOE for independent evaluation of performance and reliability of emerging stack technologies (2-7 kW) under realistic operating conditions
- Demonstrated test stand capabilities:
  - Steam-reformed methane or natural gas
  - Steady-state isothermal tests
    - ✓ Variables: temperature, current, voltage, fuel
  - Thermal cycling
  - E-stop cycles (redox tolerance)
  - Variable anode recycle rates
  - **Gross efficiency: 56% HHV, 62% LHV**



- Recent efforts have been dedicated to upgrading the platform for use with commercial natural gas, including addition of sulfur traps and automated sulfur gas sampling/analysis.

# Added Natural Gas Supply And Compression

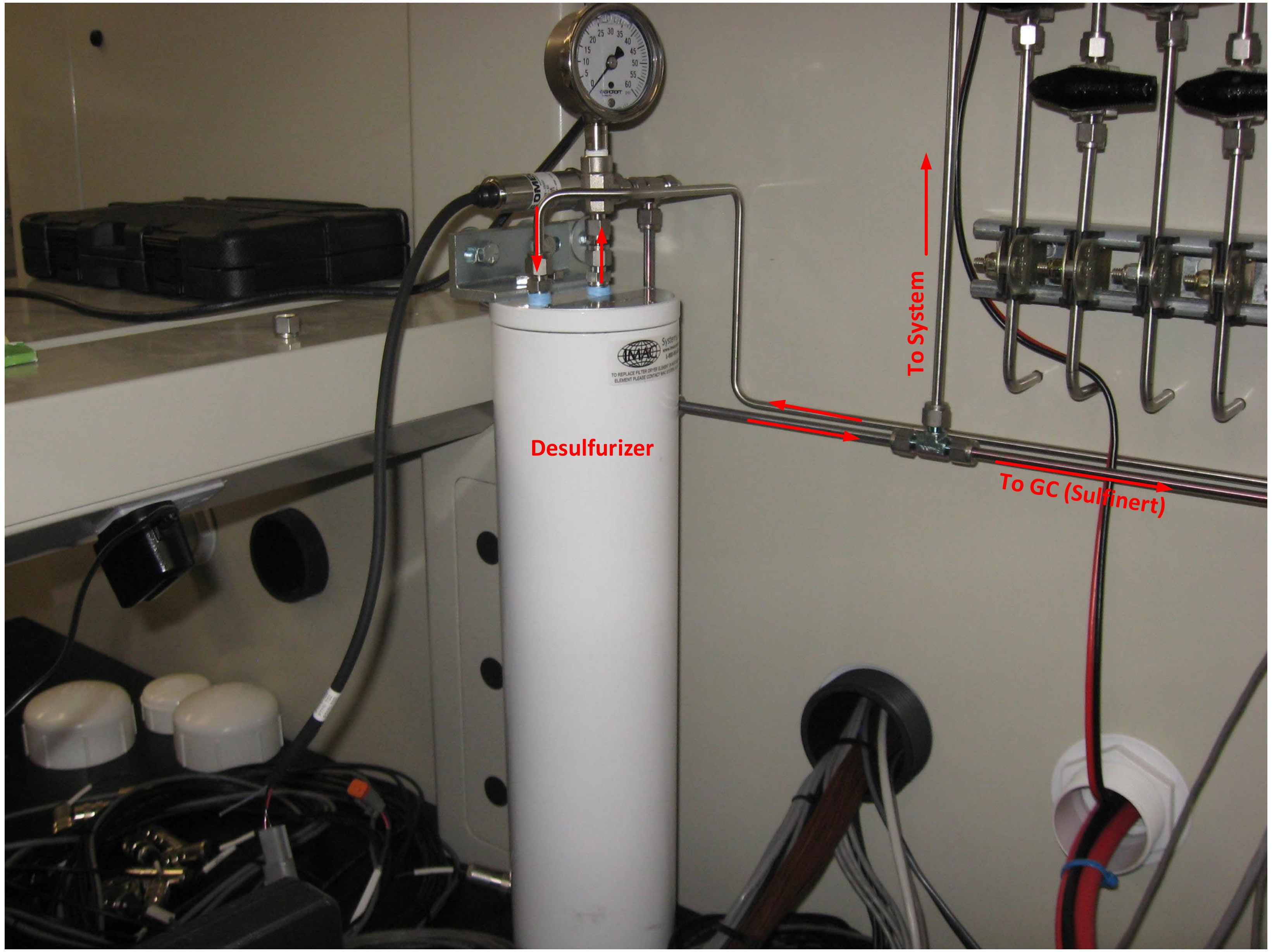
- Compress natural gas to 20 -30 psig to allow mass flow controller operation
- Safety Features
  - Excess flow valve protection
  - Shuts down for loss of downstream pressure
  - Can be inerted prior to receiving natural gas




Natural Gas Supply and Compression

# Natural Gas Desulfurization

- Provided by SulfaTrap, LLC, consisting of combination of X1 and X5 materials
- 20 slpm flow
- Outlet <10ppbv
- 12,000 h life
- Replaceable cartridge




Natural Gas Supply Desufurization

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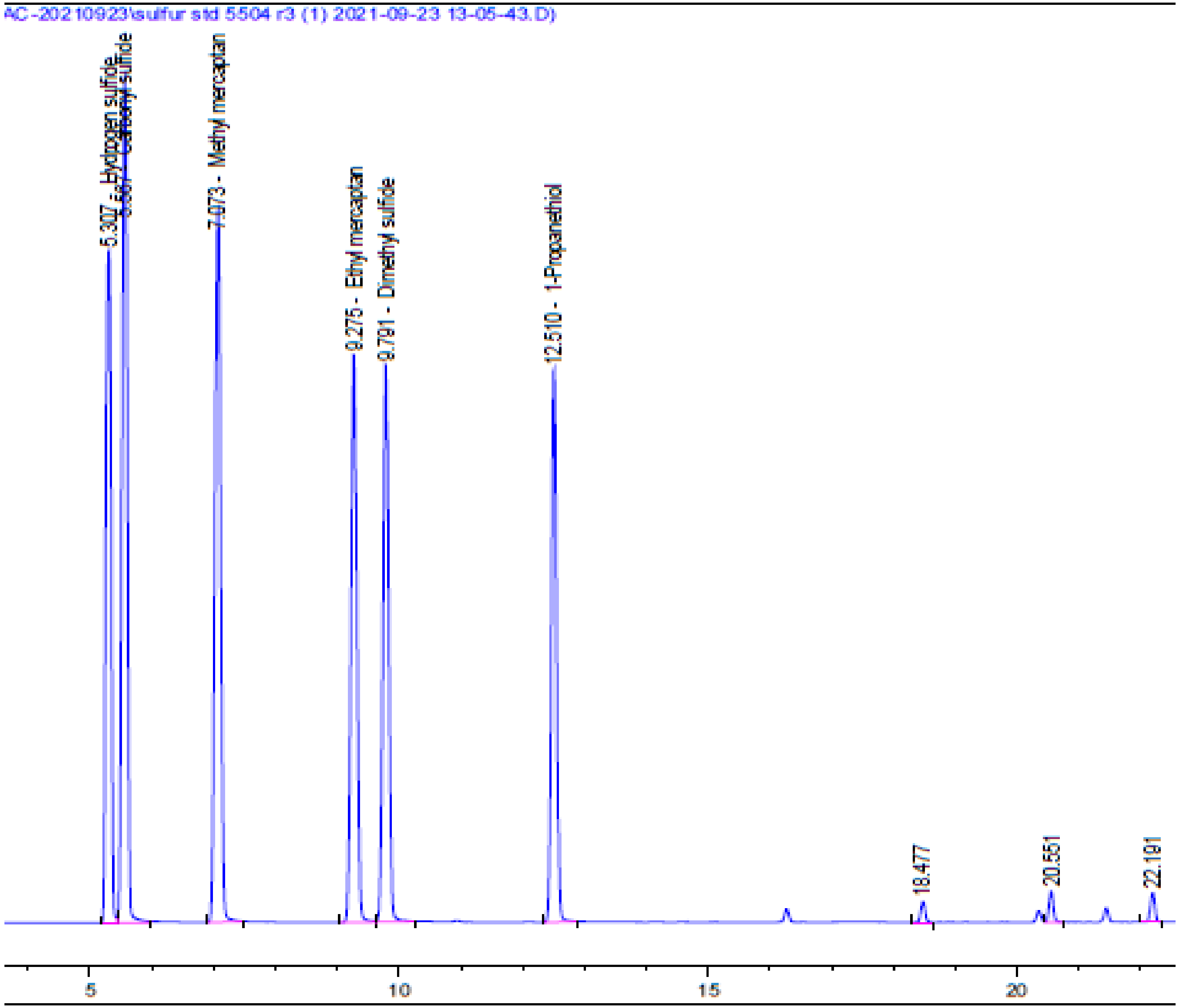
# Natural Gas Analysis for hydrocarbons and trace sulfur

- 2 channel analysis
  - FID: 0.01 mol % detection of hydrocarbon species
  - Chemiluminesence: 10 ppb detection of sulfur species

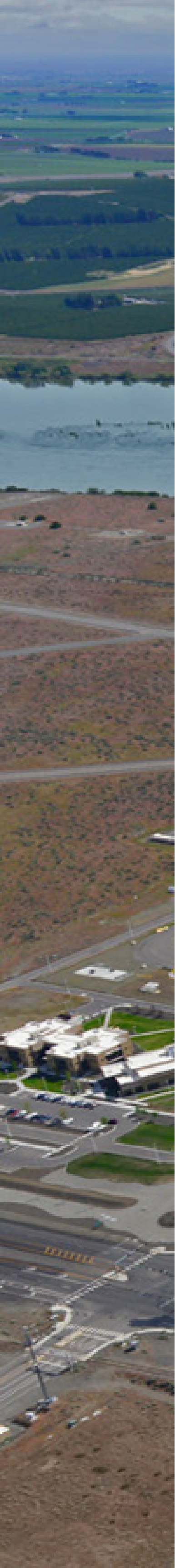

Natural Gas Supply Analysis For HC and trace sulfur

# Sulfur Analysis

- Sample chromatogram showing analysis of standard with ~1 ppm spikes of 6 different sulfur species

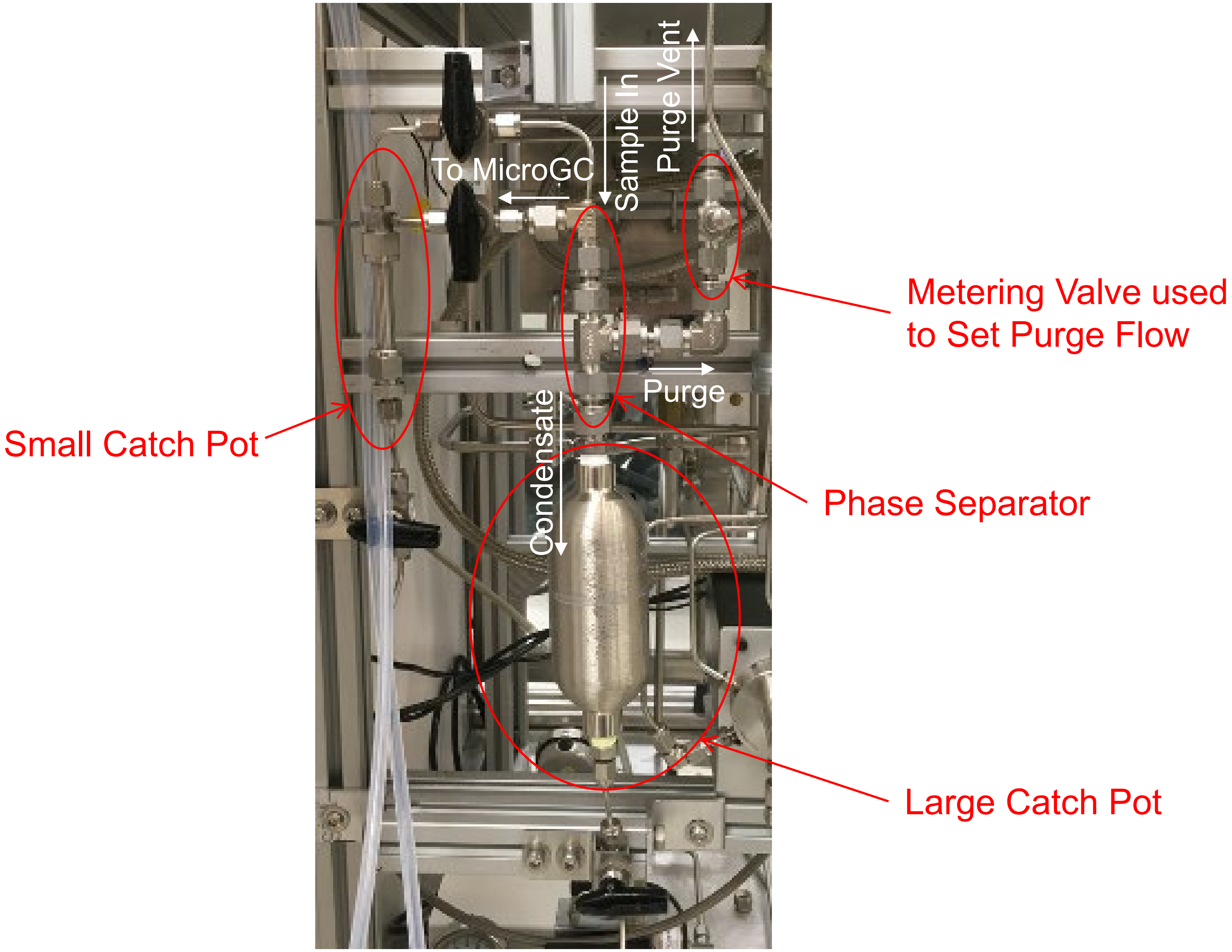



Chemiluminescence Detector Chromatogram



# MicroGC Sampling System – Large Catch Pot Modification

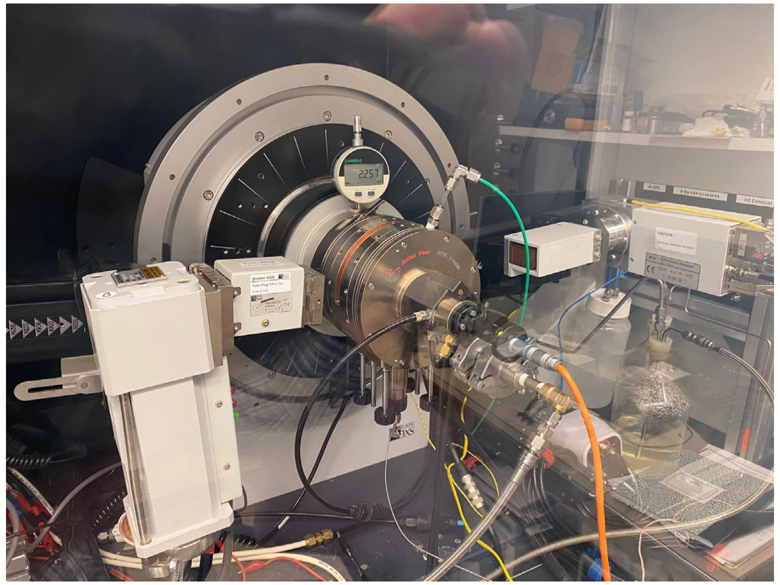
- Split large catch pot sample flow to continuously purge phase separator region.
- Purge prevents gases in catch pot from contaminating MicroGC samples.
- Sample quality same small catch pot.

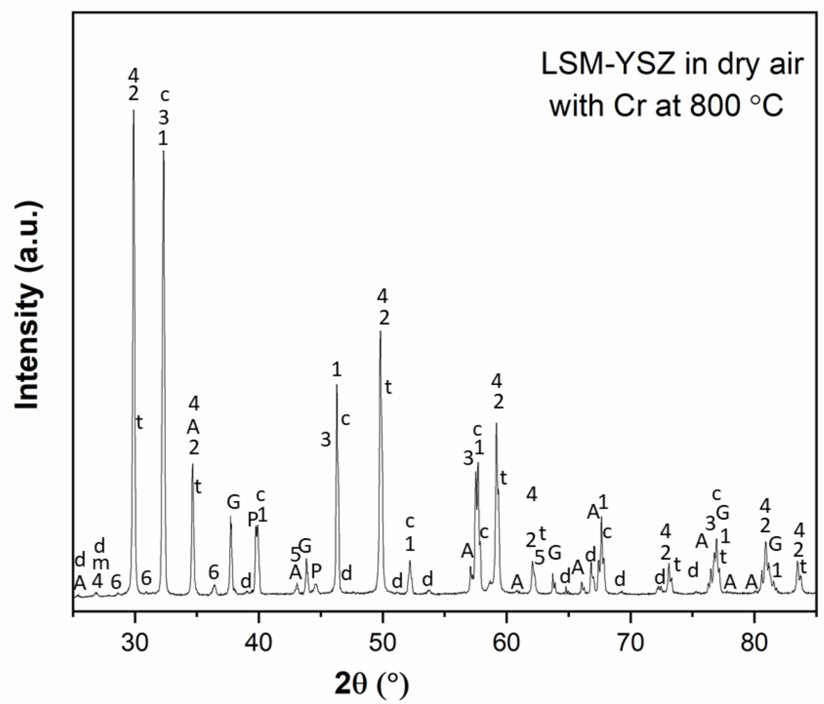


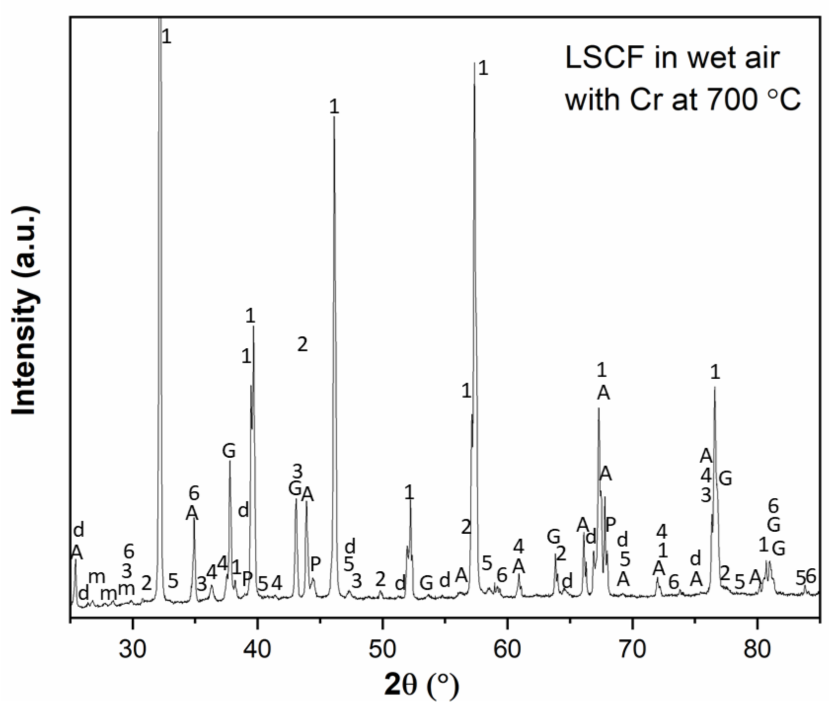

*Modified large catch pot installed on MicroGC sampling system*

# Core Technology Program
# Cathode Task Highlights

## Cr Poisoning, In-operando XRD



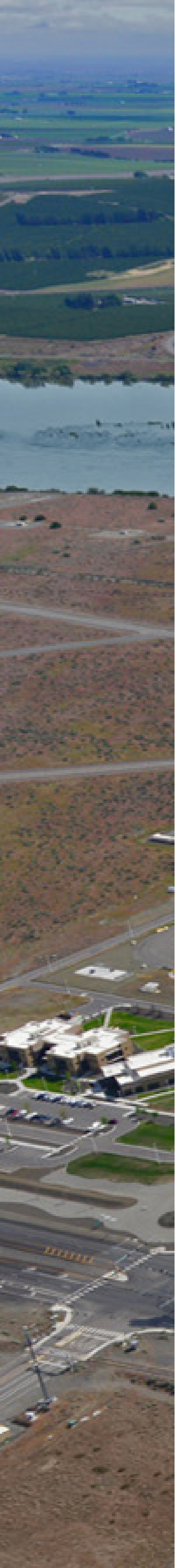


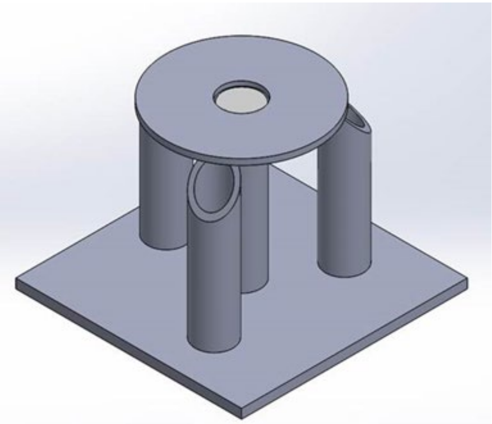

- Experimental matrix completed in 2021
  - LSCF and LSM/YSZ cathodes
  - Dry and humidified air
  - With and without Cr dosing
- Evaluated XRD patterns for changes in cathode structure

Integrated patterns representing the summation of hundreds of hours of XRD patterns were able to distinguish the formation of trace amounts of $SrCrO_4$ (***d*** in patterns above) in tests with Cr exposure

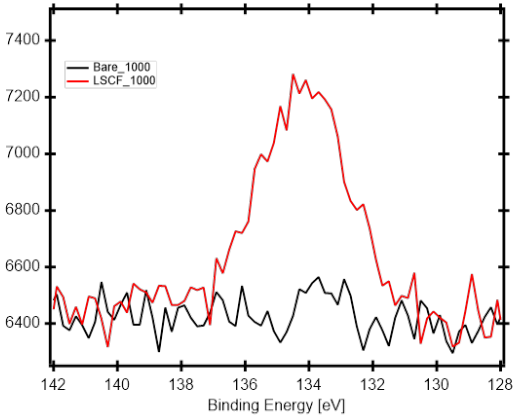
# Cathode Task Highlights



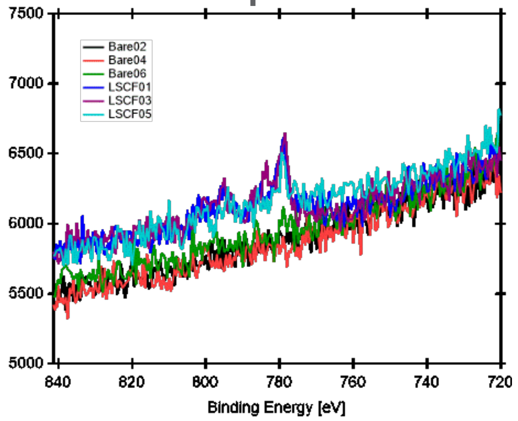
## Vapor Transport from LSCF Cathodes



Sr peak

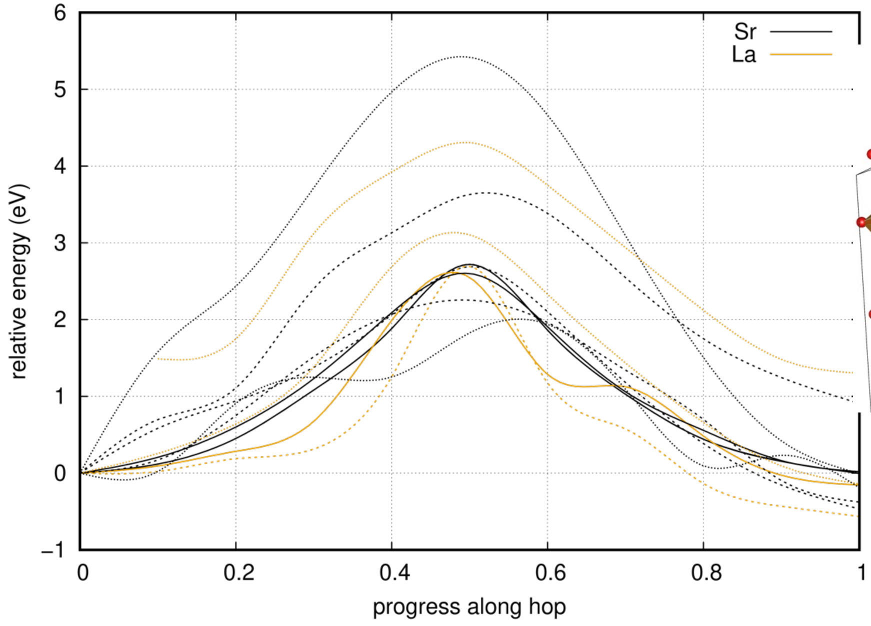


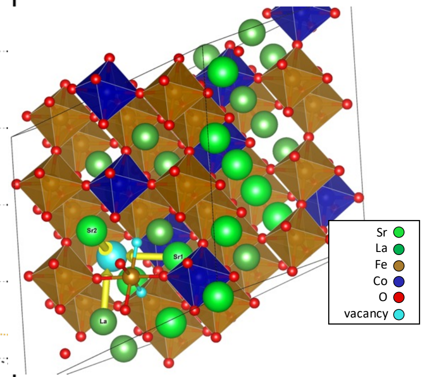

Co peaks




- Test fixtures designed with 2-mm air gaps and very long surface pathways
- Sr and Co transport across air gap from LSCF on GDC to YSZ target.
  - 1000-1100°C
  - Measured using XPS
- Evidence suggests Sr and Co vapor species emanate from LSCF cathode during sintering

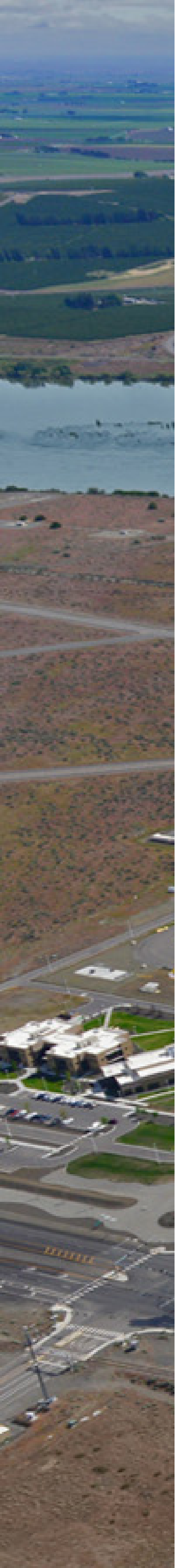
## Modeling Sr Transport in LSCF



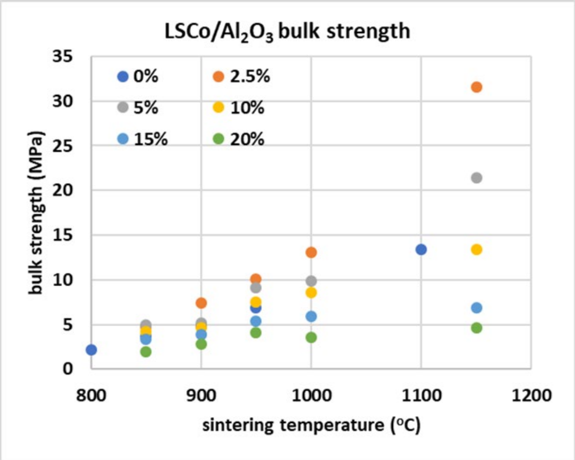




- DFT modeling of 198-atom LSCF model
- Hopping barriers shown for A-site cations
  - No nearby O vacancies (solid lines)
  - One nearby O vacancy (dashed lines)
  - Two nearby O vacancies (dotted lines)
- Nearby O vacancies facilitate Sr diffusion, but not La
- Results to be submitted to Solid State Ionics

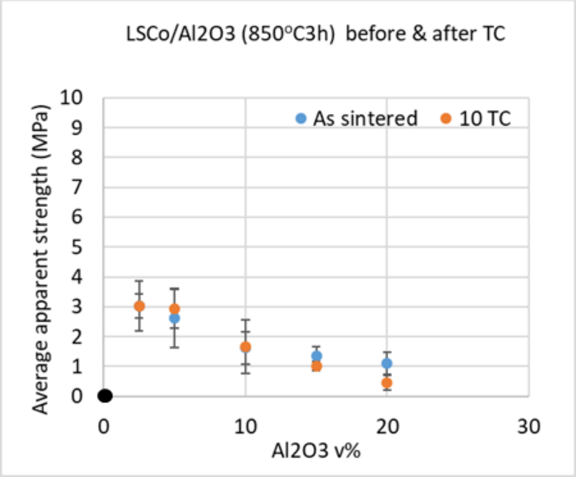
# Cathode Contact Development of LSCo/$Al_2O_3$



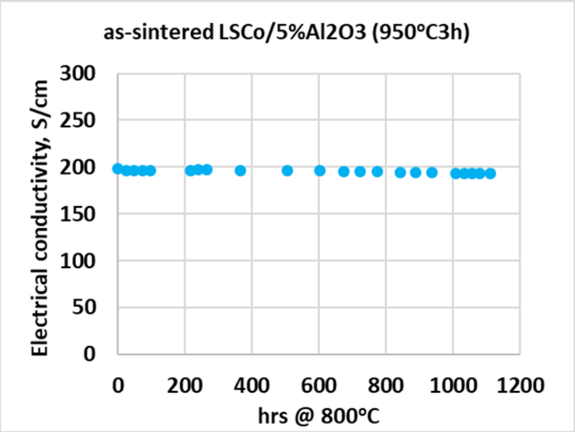
Alumina short fiber (0-20 v%) was evaluated to improve the strength and thermal cycle stability of LSCo cathode contacts.




Adding small amounts (≤5v%) of alumina fiber increased the bulk strength; however, the strength was poorer at higher loadings due to constrained sintering. Sintering was severely hindered at high alumina loadings.

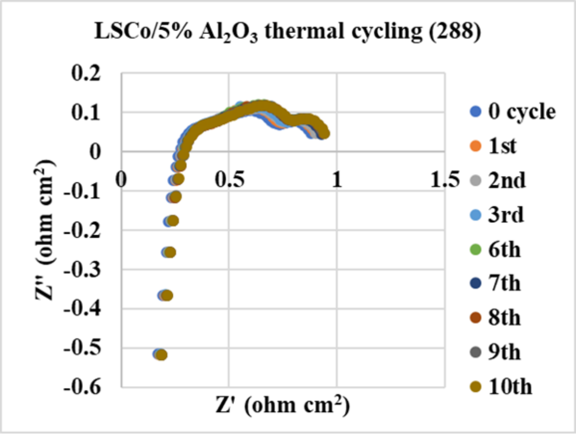



Contact strength tests showed great improvement in thermal cycle stability where plain LSCo contact materials would all spall off after sintering.




LSCo/$Al_2O_3$ composite showed very stable behavior of electrical conductivity over 1000h at 800°C.

- XRD found no reaction of alumina fiber with LSCo matrix, indicating chemical compatibility.
- SEM/EDS analysis near electrolyte interface found no trace of alumina.




Successfully validated LSCo/5%$Al_2O_3$ contact in a stack fixture test where the impedance versus thermal cycles was comparable to ductile Ag contact. Cell showed similar degradation as plain LSCo in standard 1000h stability test, implying no “poisoning” effect of alumina fibers.

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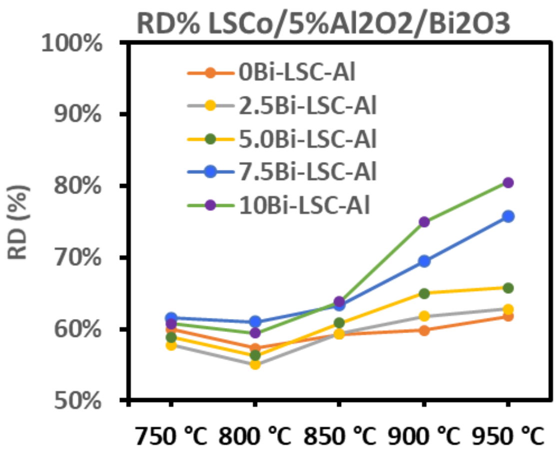
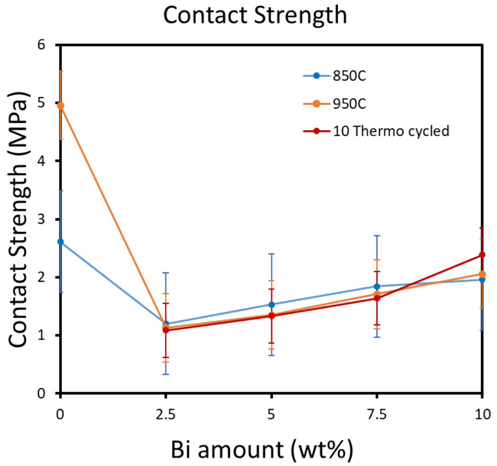
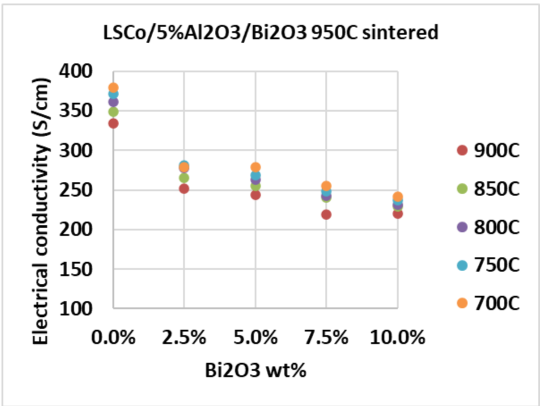
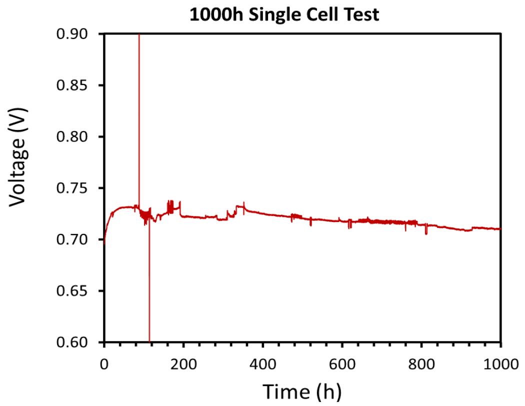
# Cathode Contact Development of LSCo/$Al_2O_3$/$Bi_2O_3$

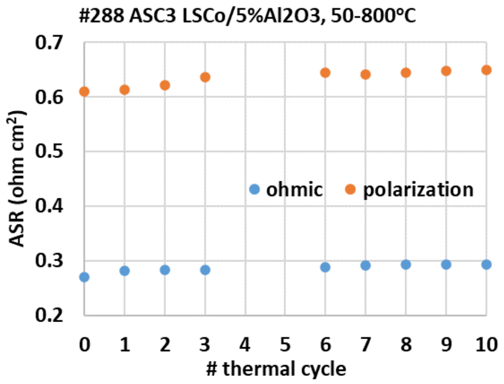
0 to10wt% $Bi_2O_3$ was investigated as sintering aid for LSCo/5v%$Al_2O_3$ contacts.

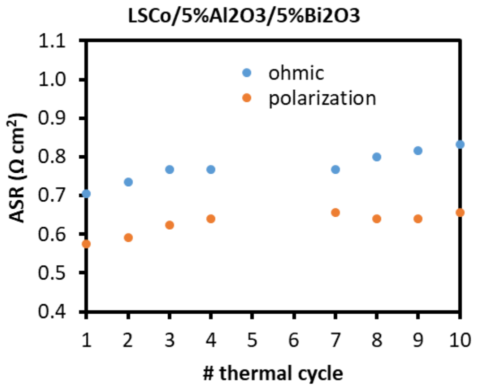


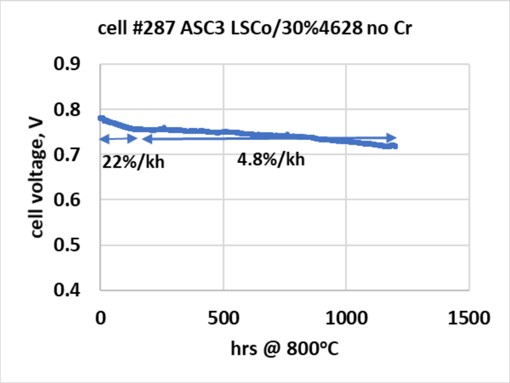



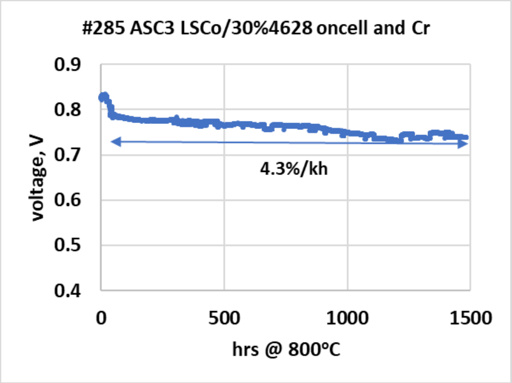

- Addition of $Bi_2O_3$ improved densification, especially at higher loadings (≥ 7.5%).
- Adding sintering aid appeared to generally decrease contact strength.
- No significant change in contact strength after 10 deep thermal cycles for 950$^o$C sintered samples, indicating good thermal cycle stability.
- Electrical conductivity decreased with increasing $Bi_2O_3$, likely due to the low conductivity of $Bi_2O_3$.
- LSCo/5%$Al_2O_3$/5%$Bi_2O_3$ was validated in a stack fixture test for 1000h at 800$^o$C, followed by 10 deep thermal cycles. Cell showed comparable degradation rate as plain LSCo and LSCo/5%$Al_2O_3$, implying no "poisoning" effect.
- Impedance after thermal cycles indicated that $Bi_2O_3$ did not improve the thermal cycle stability, likely due to bismuth oxide's low modulus and strength.
- XRD of LSCo/5%$Al_2O_3$/10%$Bi_2O_3$ sample sintered at 950$^o$C showed no other crystalline phases, suggesting good chemical compatibility.

# Fiber-reinforced On-cell LSCo/LSCF Composite Cr-getters

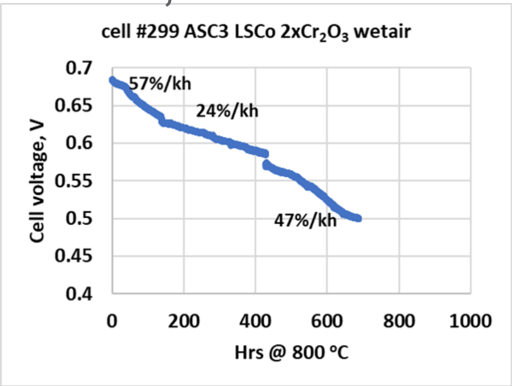
No Cr



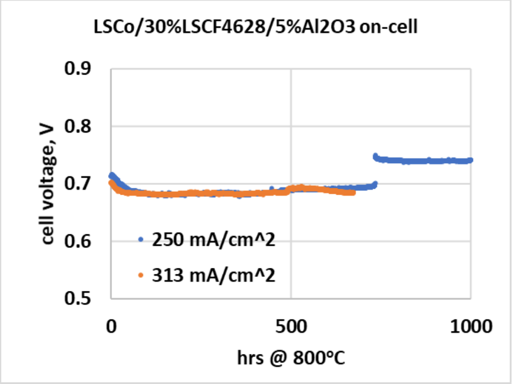

Cr + Getter

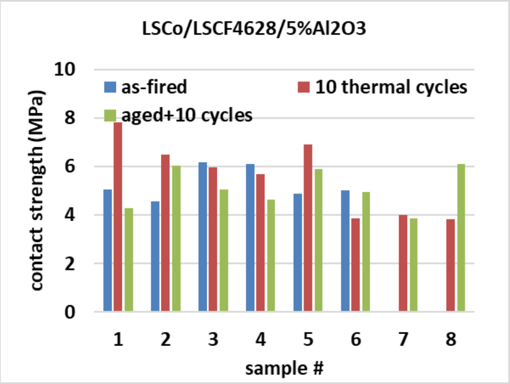



Cr, No Getter



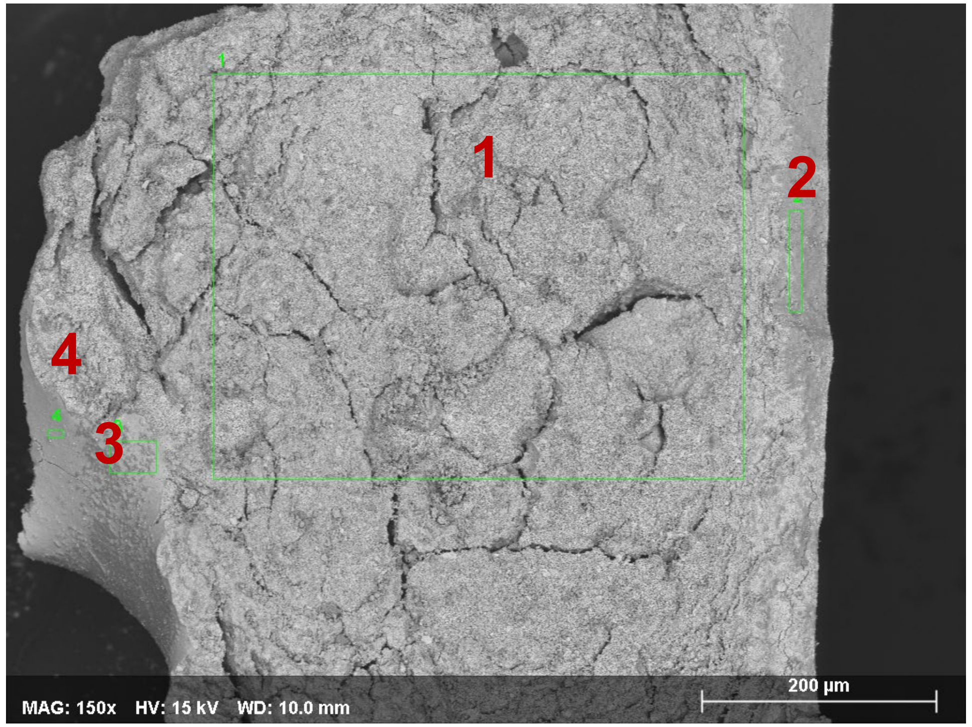

Cr + Getter w/ fiber reinforcement




- LSCo/30%LSCF4628 reinforced with 5%$Al_2O_3$ fibers tested in **dual-purpose Cr-getter and cathode contact** functionality.
- When tested in an intermediate (5 cm x 5 cm) cell test for stability at 800°C/1000h with volatile Cr sources and moisture, the degradation was comparable to or less than cells without Cr sources, suggesting effective Cr gettering.
- Adding 5v% $Al_2O_3$ fibers resulted in great improvement in contact strength after thermal cycling and 800°C/1000h isothermal ageing.
- Post-mortem fractography showed on-cell LSCo/30%LSCF4628 getters with fibers still bonded to cell, while without fibers it all spalls off due to large CTE mismatch.

# Evidence of Cr capture by LSCo/30%LSCF for on-cell application




**Cell after 800°C 1000h stability test with LSCo/30%LSCF4628 applied on-cell as both Cr-gettering and cathode contact. SEM shows a broken part of the gettering/contact material where Cr were mostly concentrated near the exposed surface.**

| Spectrum | O | Si | Cr | Mn | Fe | Co | Sr | La |
|---|---|---|---|---|---|---|---|---|
| 1 | 53.89 | 3.32 | 1.37 | 0.83 | 5.11 | 12.36 | 6.74 | 16.36 |
| 2 | 57.85 | 1.96 | 5.21 | 1.25 | 3.29 | 6.81 | 12.40 | 11.22 |
| 3 | 51.36 | 1.68 | 13.24 | 1.12 | 1.86 | 4.15 | 19.25 | 7.34 |
| 4 | 90.08 | 1.30 | 1.57 | 0.05 | 0.14 | 1.40 | 3.42 | 2.05 |

# Co-free Spinel Interconnect Coatings

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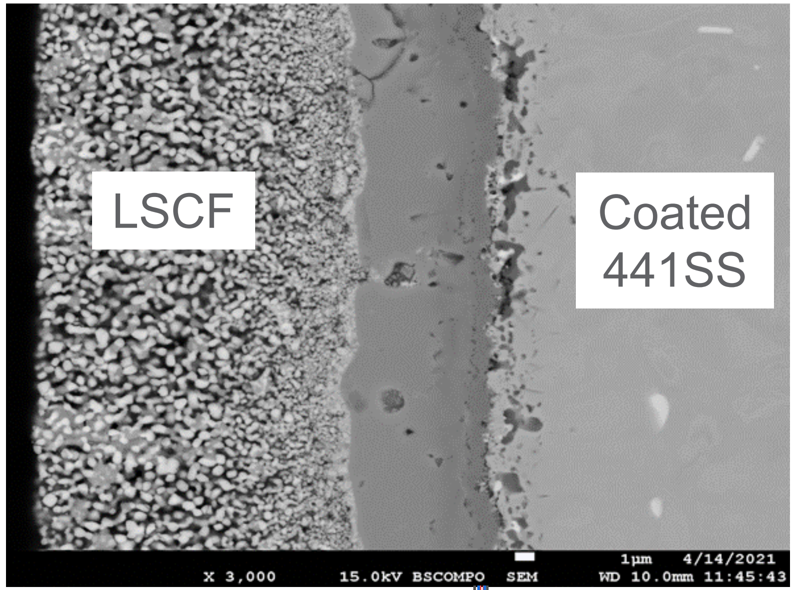
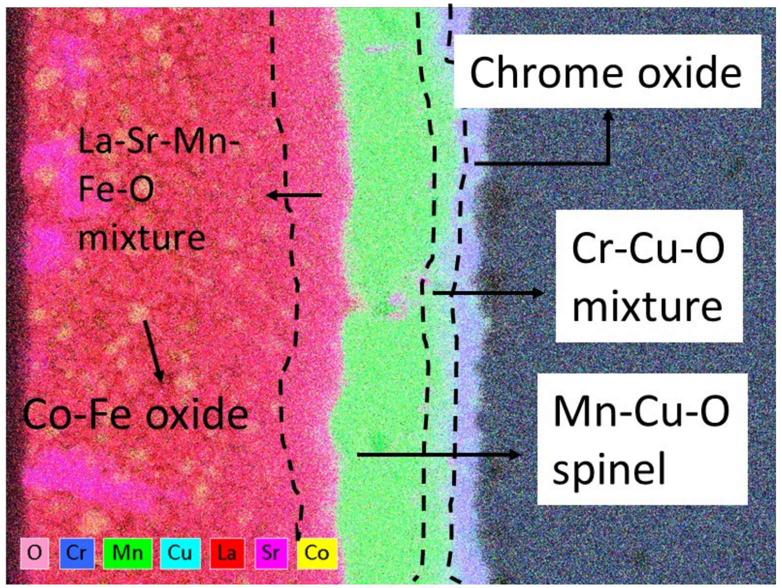
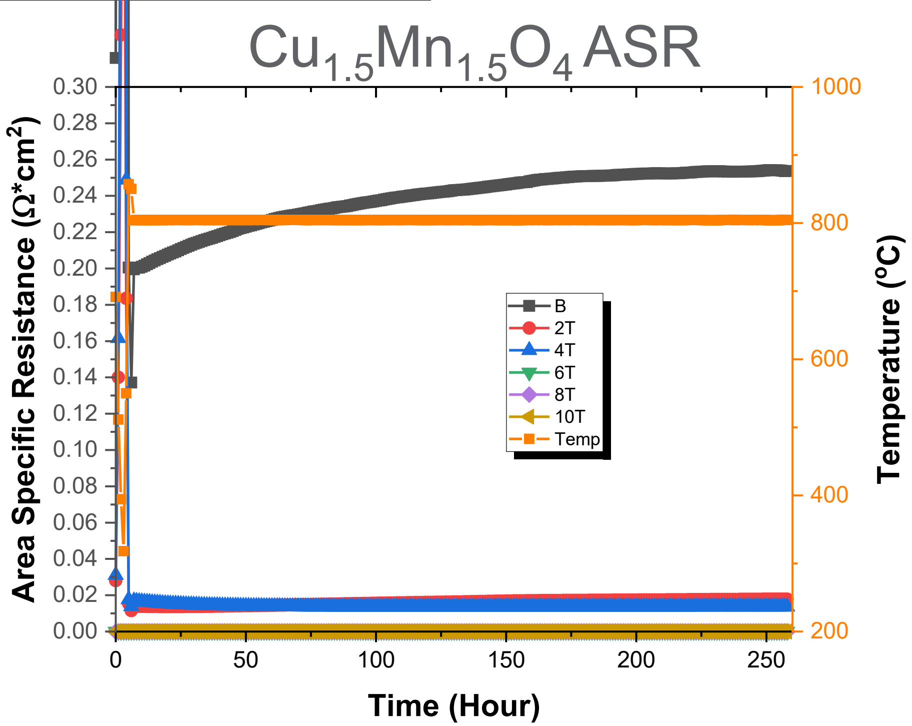
## Sample heat-treated at 800°C for 1,000 hours




After 800°C/1,000h with the (Cu, Mn)$_3$O$_4$ coating:

- Cu-Cr-O and $Cr_2O_3$ layers form between the substrate and spinel.
- No significant Cr diffusion through the spinel
- Mn diffused from the spinel to the LSCF
- Sr from LSCF segregates at interface.

**During over 250 h of testing, thicker layers (6 – 10 coats or ~45 to 75 μm) of $Cu_{1.5}Mn_{1.5}O_4$ resulted in very low ASR (on the order of 10s of μΩ*cm²).**

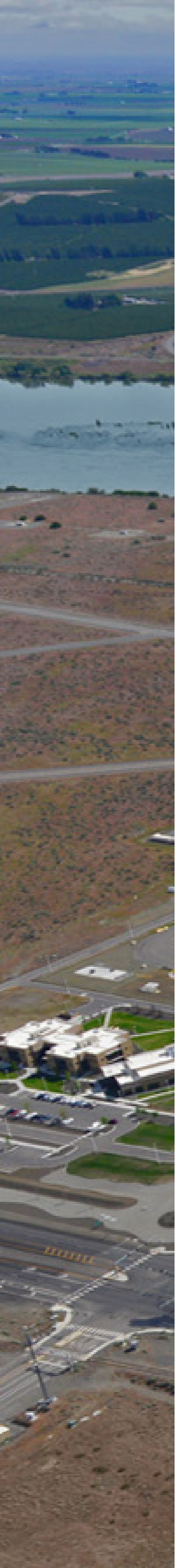
# Modeling Task Overview

## Objective

- Develop numerical models (primarily at the cell and stack scale), analysis methods, and software tools to improve the thermal-mechanical performance, reliability, and stability of SOFC materials.

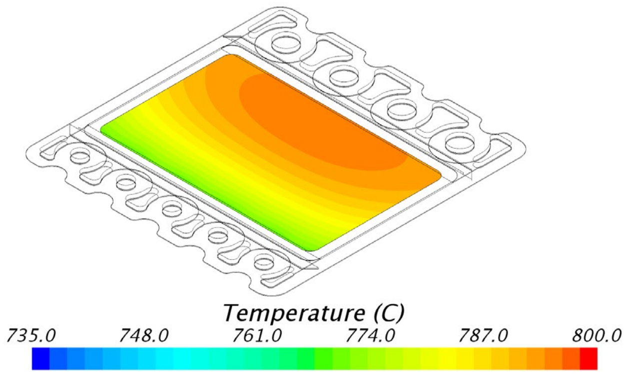
## FY21 Accomplishments

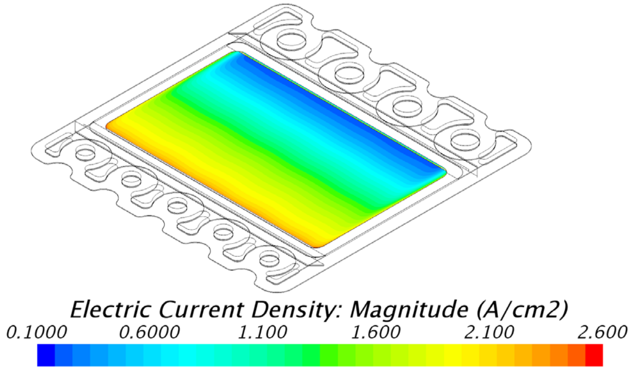
- Adapted SOFC modeling tools for SOEC operation.
- Developed user interface for automated generation of SOFC reduced order models (ROMs).
- Used machine learning (ML) to enhance ROM accuracy.
- Developed constitutive model to characterize damage to ceramic cell components due to thermal-mechanical stresses from assembly, operating, shutdown, and transient thermal conditions.
- Used damage model to evaluate stresses due to anode reduction-oxidation (RedOx).
- Obtained Weibull strength for reinforced cathode contact material.



# Simulation of Electrolyzer Operation

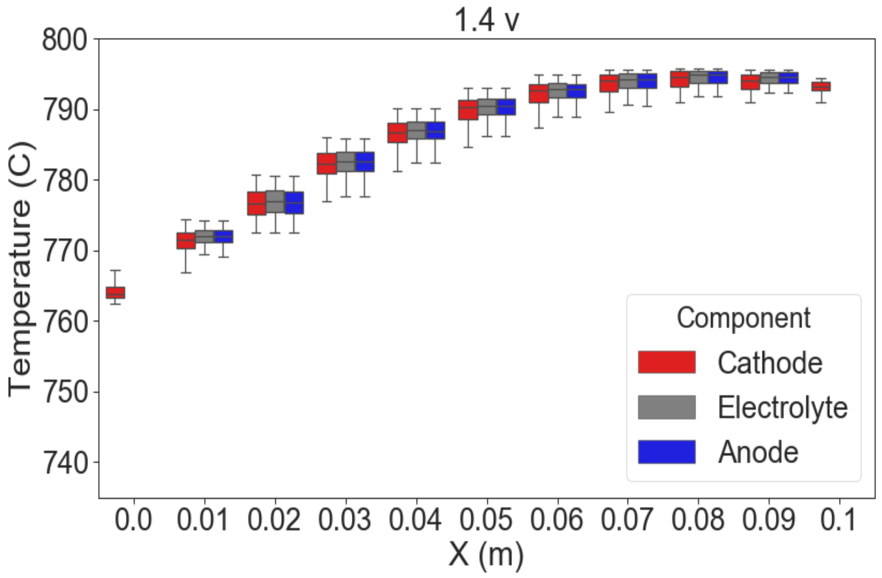
- Adapted existing 2D and 3D SOFC-MP algorithms and modeling tools for evaluation of single or multicell stacks operating in electrolysis mode[1].
- Updated current-voltage approach to incorporate Knudsen diffusion in the electrodes.



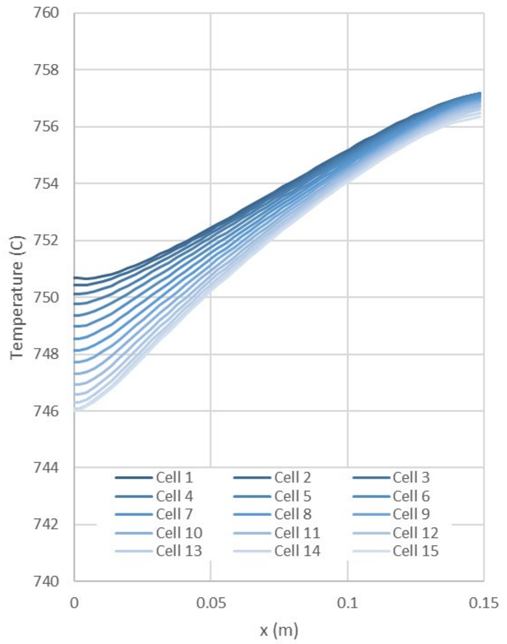




300 cm$^2$ 15-cell SOEC stack (11000 A/m$^2$)

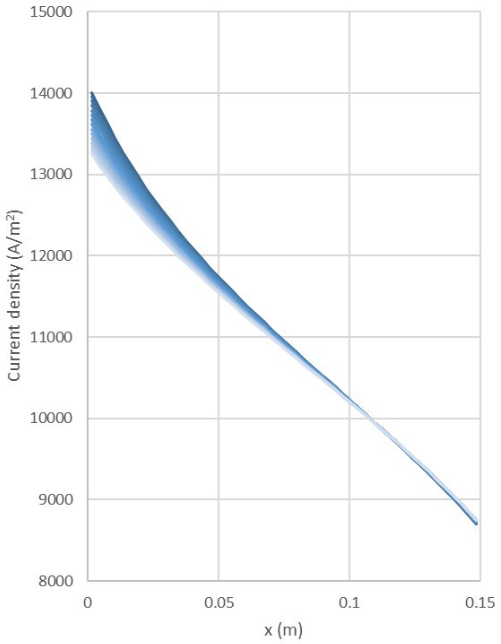
## Temperature Variation



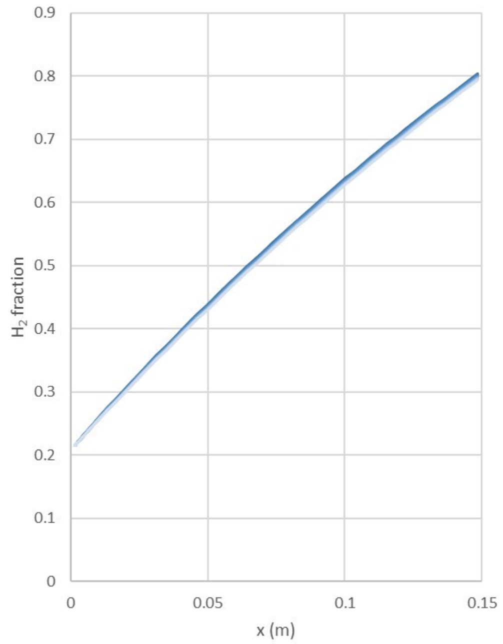

## Temperature




## Current Density



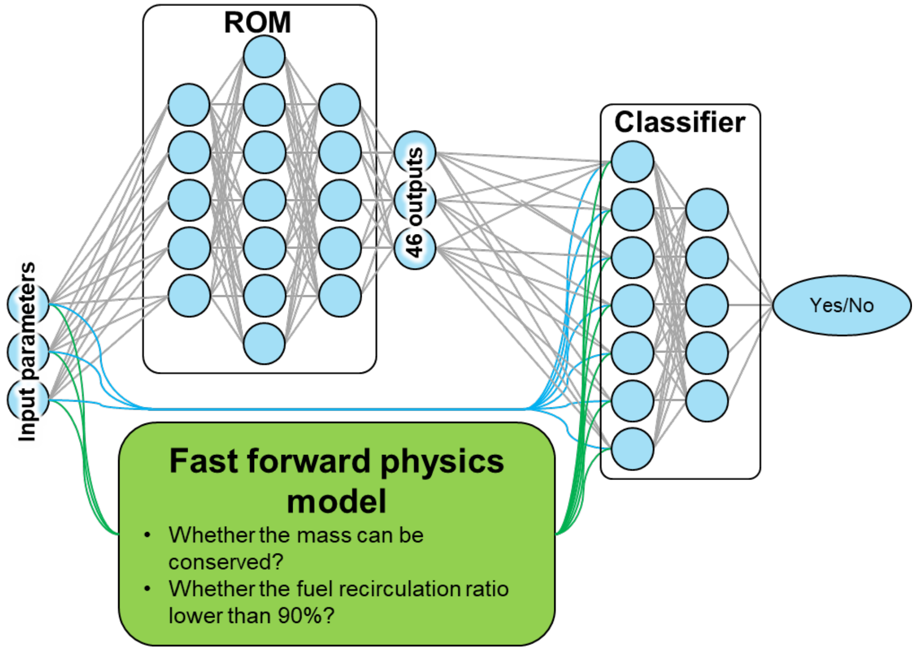

## $H_2$ Fraction

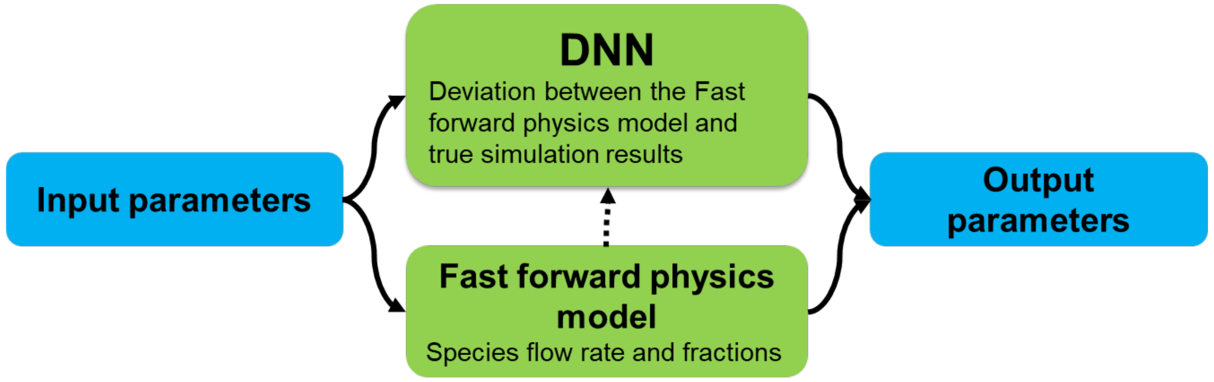



*1Application of code to actual SOEC stacks and modeling results obtained with funding from DOE EERE HFTO, award number AOP-73263 and DOE FECM, award number FWP-77108.*

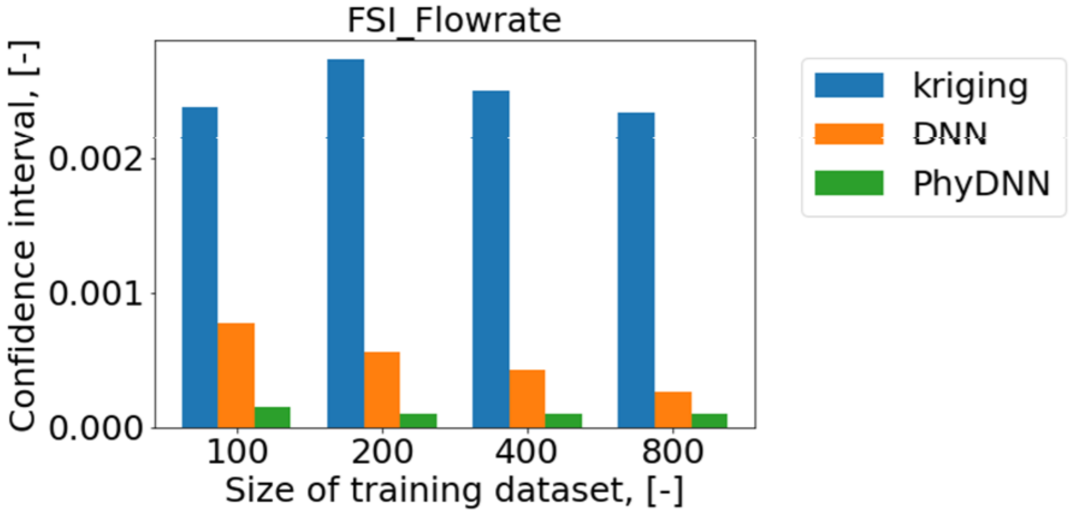
# Use of Machine Learning Techniques to Improve ROM Accuracy

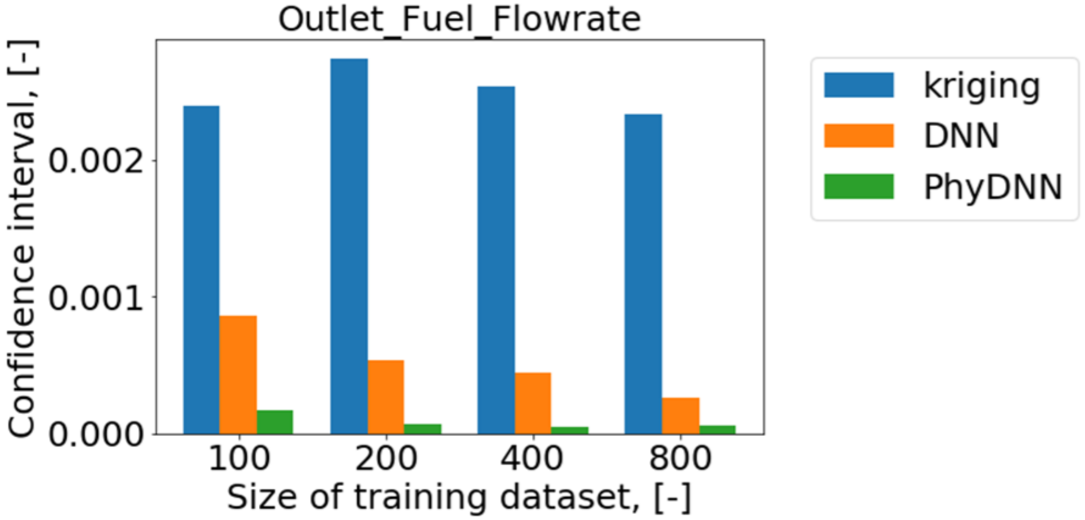
- ROM accuracy improved (or less training samples required)
  - Deep neural network (DNN)
  - Classifier of case viability
  - Physics-informed DNN




Confidence Interval Improvement for ROM Predictions



# Automated ROM Construction Tool/GUI

- Automated ROM construction tools were developed with Jupyter Notebook
  - Generates ROMs for different NGFC and IGFC power system designs with options for carbon capture and vent gas recirculation
  - Runs/controls case submission on HPC.

| | | |
|---|---|---|
| .. | | |
| Test_NW | ROM GUI PNNL | 2 months ago |
| Test_WW | ROM GUI PNNL | 2 months ago |
| source | ROM GUI PNNL | 2 months ago |
| InstallPackages.ipynb | Add files via upload | 2 months ago |
| Readme.txt | Update Readme.txt | last month |
| WSL_Instruction.pdf | ROM GUI PNNL | 2 months ago |
| pySOFC_v12_Release_v1.1.ipynb | v1.1a | last month |
| pySOFC_v12_Release_v1.py | Add files via upload | 2 months ago |

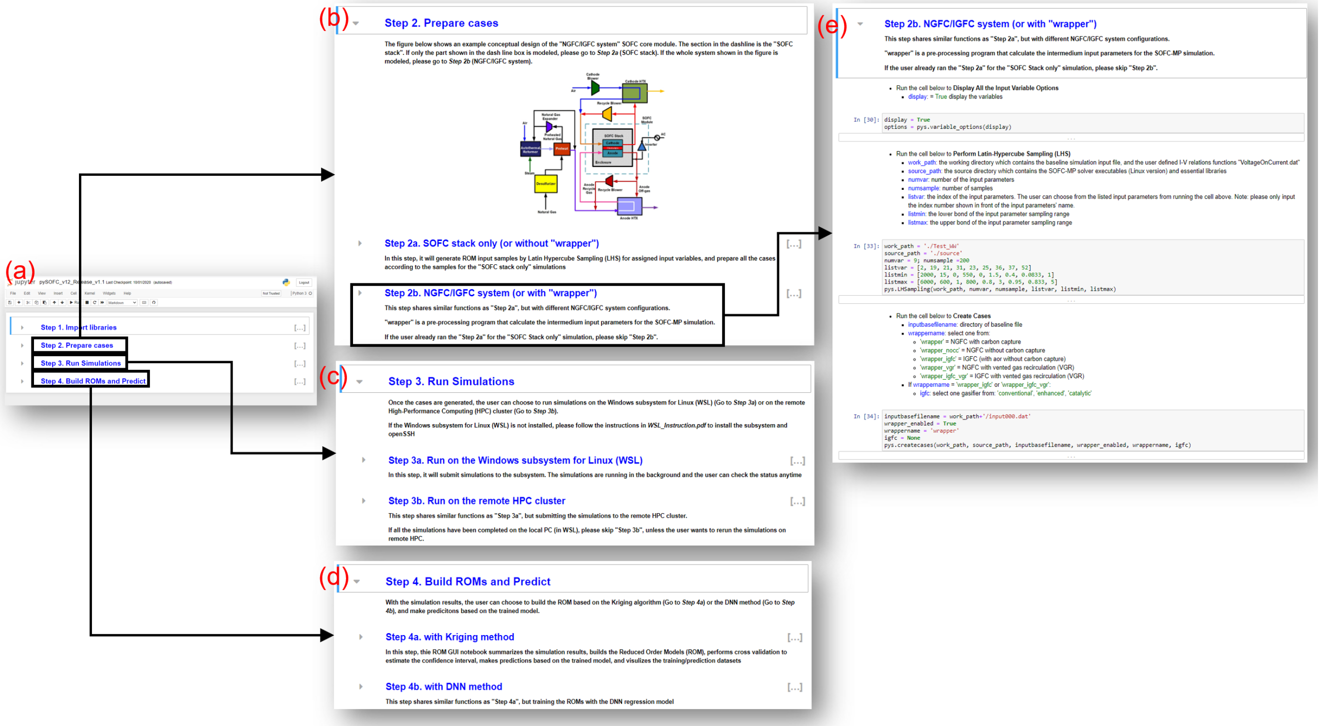
User interface

Tool package

Readme.txt

```
The universal ROM GUI can be used for SOFC-MP simulation:
    1. For using this ROM GUI, the user needs to download the "pySOFC_v12_Release_v1.ipynb", "pySOFC_v12_Release_v1.py" and the
"source" folder to the same directory.
    2. The user also needs to install essential packages to the Jupyter Notebook, and also the windows subsystem for linux if the
```

Screenshots of Graphical User Interface (GUI)




```
class DNN():
    def __init__(self, work_path, ↔
    
    #%% The DNN function for ROM, save the trained DNN
    def DNNROM(self,maxiteration,trainX_nrm,trainY_nrm,testX_nrm1,input_num,output_num,DNN_save_file):↔
    
    #%% The DNN function for ROM, load in a trained DNN, and continue training
    def DNNROM_restore(self,maxiteration,trainX_nrm,trainY_nrm,testX_nrm1,input_num,output_num,DNN_load_file,DNN_save_file):↔
    
    #%% The DNN function for ROM, load in a trained DNN, and do prediction
    def DNNROM_prediction(self,testX_nrm1,input_num,output_num,DNN_load_file):↔
    
    #%% DNN classification      one layer, train DNN classifier, and save DNN
    def DNNCls(self,maxiteration,trainX_nrm,trainY_nrm,input_num_units,DNNcls_save_file):↔
#        return(test_p0)
    
    #%% DNN classification      one layer, load in a trained DNN, and continue training
    def DNNCls_restore(self,maxiteration,trainX_nrm,trainY_nrm,input_num_units,DNNcls_load_file,DNNcls_save_file):↔
#        return(test_p0)
    
    #%% DNN classification      one layer, load in a trained DNN, and do preidction for classification
    def DNNCls_prediction(self,testX_nrm,input_num_units,DNNcls_load_file):↔
    
    def summarize_SimuResult(self, source_path, indcase, exclude_case = 1, display_detail = False):↔
```

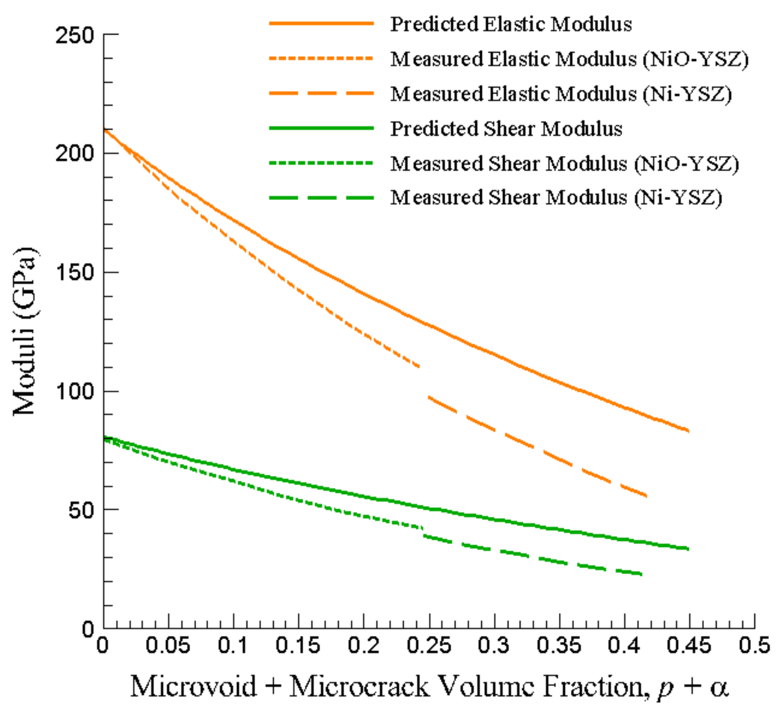
Screenshot of the Package Source Code

# A Mechanistic Damage Model Developed for SOFC Ceramics

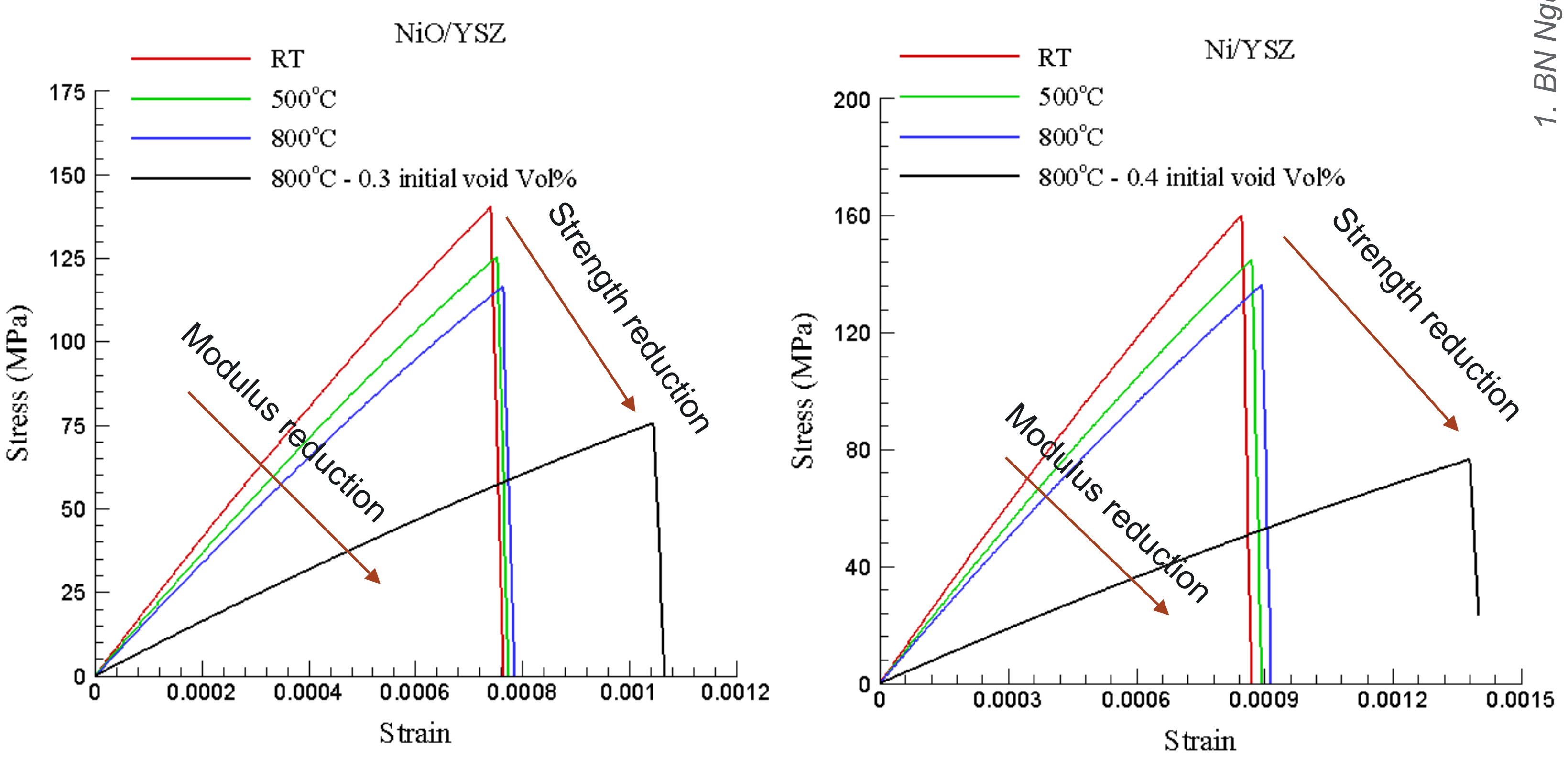
- A mechanistic damage model for SOFC ceramics was developed[1] and applied to predict material response and damage accumulations in SOFCs
  - Micromechanics to establish stiffness reduction relation as a function of pore and microcrack volume fractions.
  - The constitutive relation and damage evolution law established using thermodynamics of continuous media.[2]
  - Redox-induced swelling treated in the same manner as thermal expansion but irreversible.[3]
  - Model predictions consistent with experimental observations in trends and values.

## Microvoids + Microcracks Effect on Elastic Moduli

(Measured data from M Radovic, E Lara-Curzio, 2004, Acta Materialia, 52:5747.)




## NiO/YSZ & Ni/YSZ Strength Reduction Due to Damage[1]





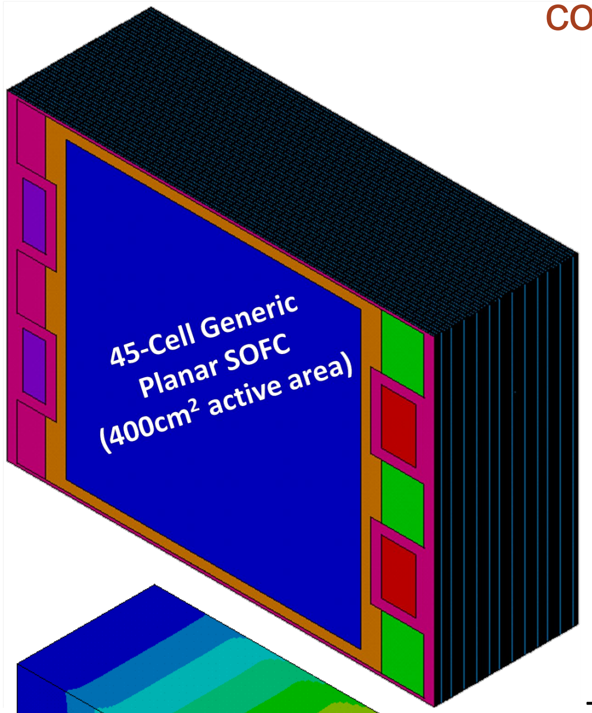
1. BN Nguyen et al., Int. J. Hydrogen Ener., 2021, in press.
2. BN Nguyen et al, J. Amer. Ceram. Soc., 89 (2006):1358–1368)
3. BN Nguyen et al. J. Nucl. Mater., 495 (2017): 504-515)

# Damage Analysis of an SOFC Multicell Stack

- Evaluated damage in 45-cell, anode supported, large area stacks in co-flow and counter-flow configurations.
- Realistic operating temperatures were obtained by solving electrochemistry with in-house SOFC Multiphysics code (SOFC MP-3D).
- Stacks were subject to various mechanical and thermal loads to represent realistic loading.
- Load Sequence: 6 load steps simulated in FEA
  - **1.** Uniform 850 °C → **2.** 0.2 MPa Compression → **3.** Uniform 750°C → **4.** Realistic operating condition → **5.** RedOx cycling at 750°C → **6.** Shutdown (25°C)
- Counter flow stacks generally had higher power and peak temperature but also higher temperature difference for similar operating states and average cell temperature.

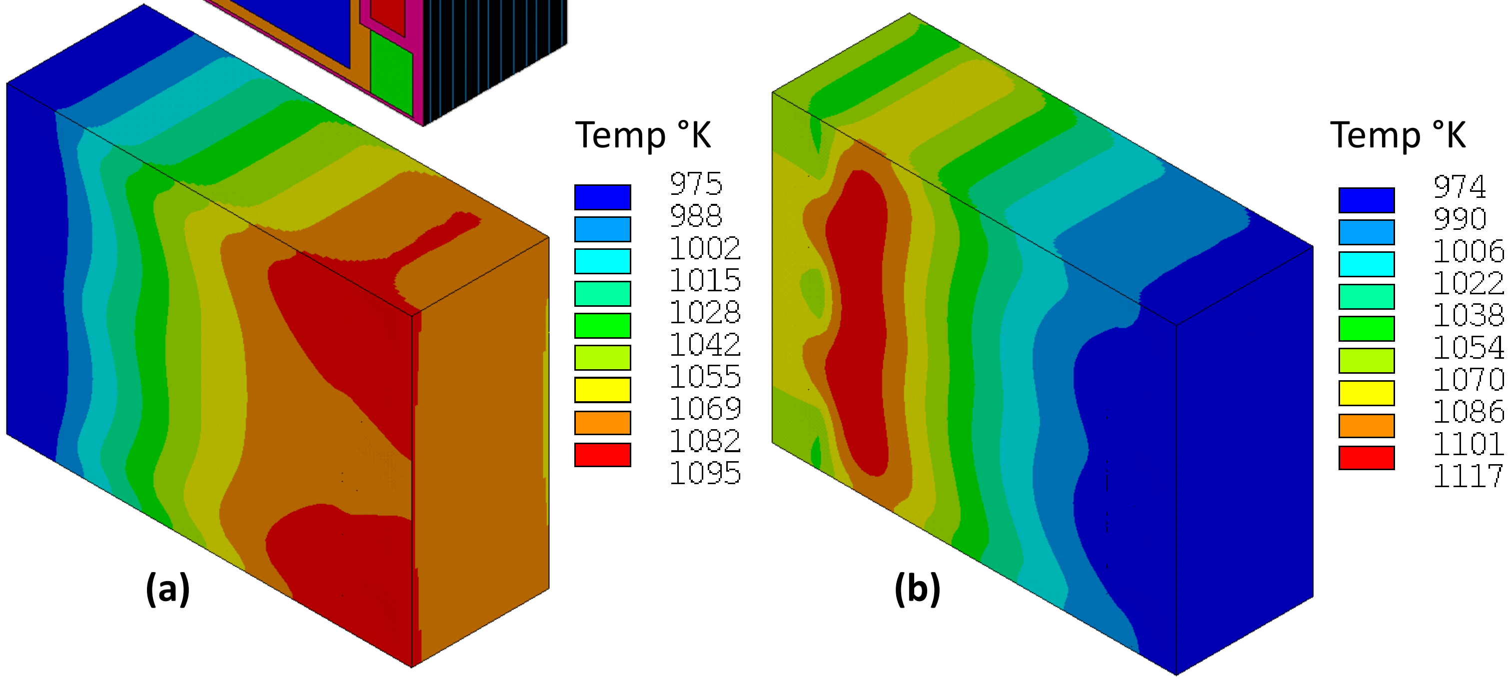
*BN Nguyen et al., 2021. "Damage Modeling of Solid Oxide Fuel Cells Accounting for Redox Effects," J. Electrochem. Soc. (submitted).*

Generic planar SOFC for co-flow and counter flow configuration simulations




**45-Cell Stack Target Performance**

- NGFC Fuel composition with 60% IR and 2.1 OCR
- $T_{avg} \approx 750°C$
- FU ≈ 86%, AU ≈ 16.4%
- Voltage ≈ 0.791 per Cell
- $I_{dens} \approx 0.4 A/cm^2$ per Cell




Temperature in 45-cell stacks for (a) co-flow and (b) counter flow configurations under similar operating conditions of a NGFC system

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# Damage in Cells: Influence of Redox Cycling

*BN Nguyen et al., 2021. "Damage Modeling of Solid Oxide Fuel Cells Accounting for Redox Effects," J. Electrochem. Soc. (submitted).*

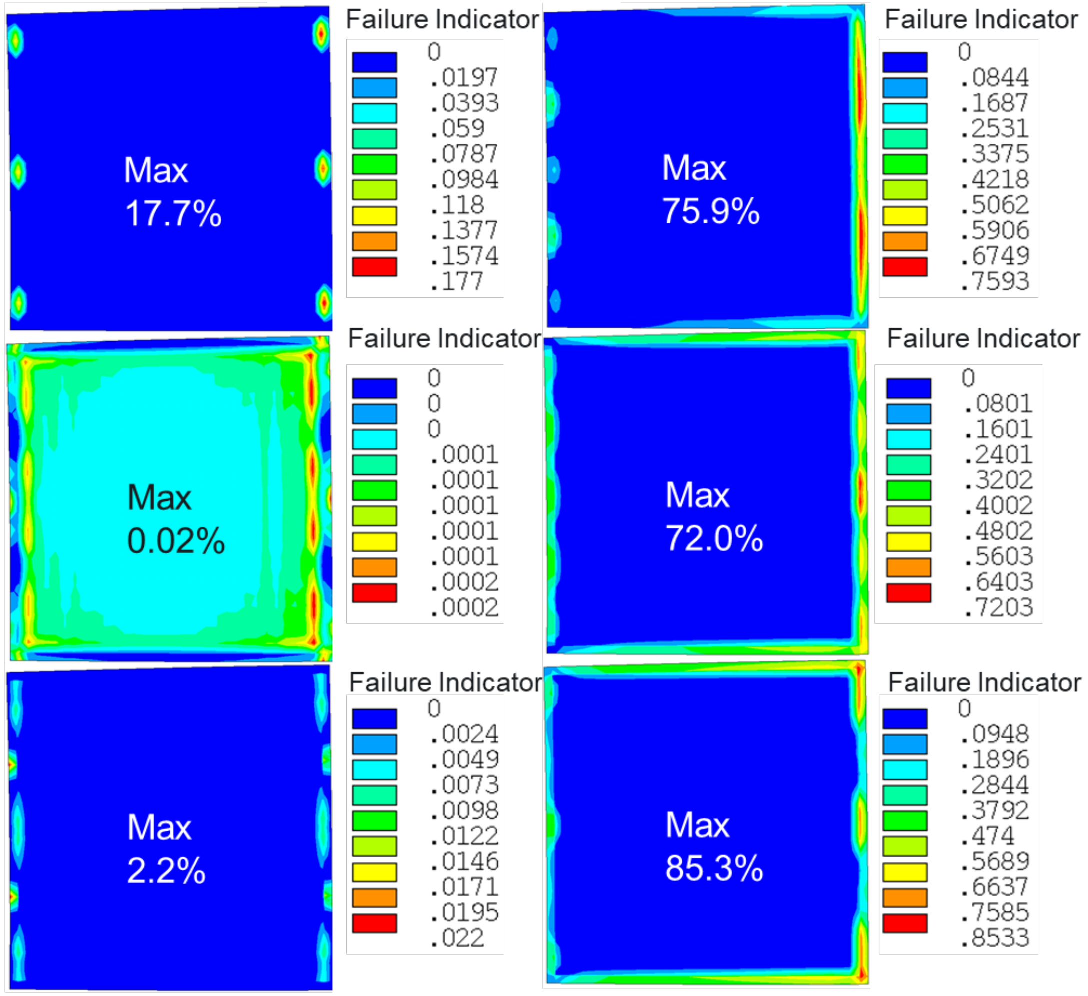
- Significant local damage observed in the electrolyte after redox cycling along the edges (near the glass-ceramic perimeter seals).
- Damage in the anode is mostly localized near air/fuel inlets and outlets. No significant damage observed before and after redox cycling.

Before RedOx **Electrolyte** After RedOx

Cell #1 (Bottom)

Cell #23 (Middle)

Cell #45 (Top)

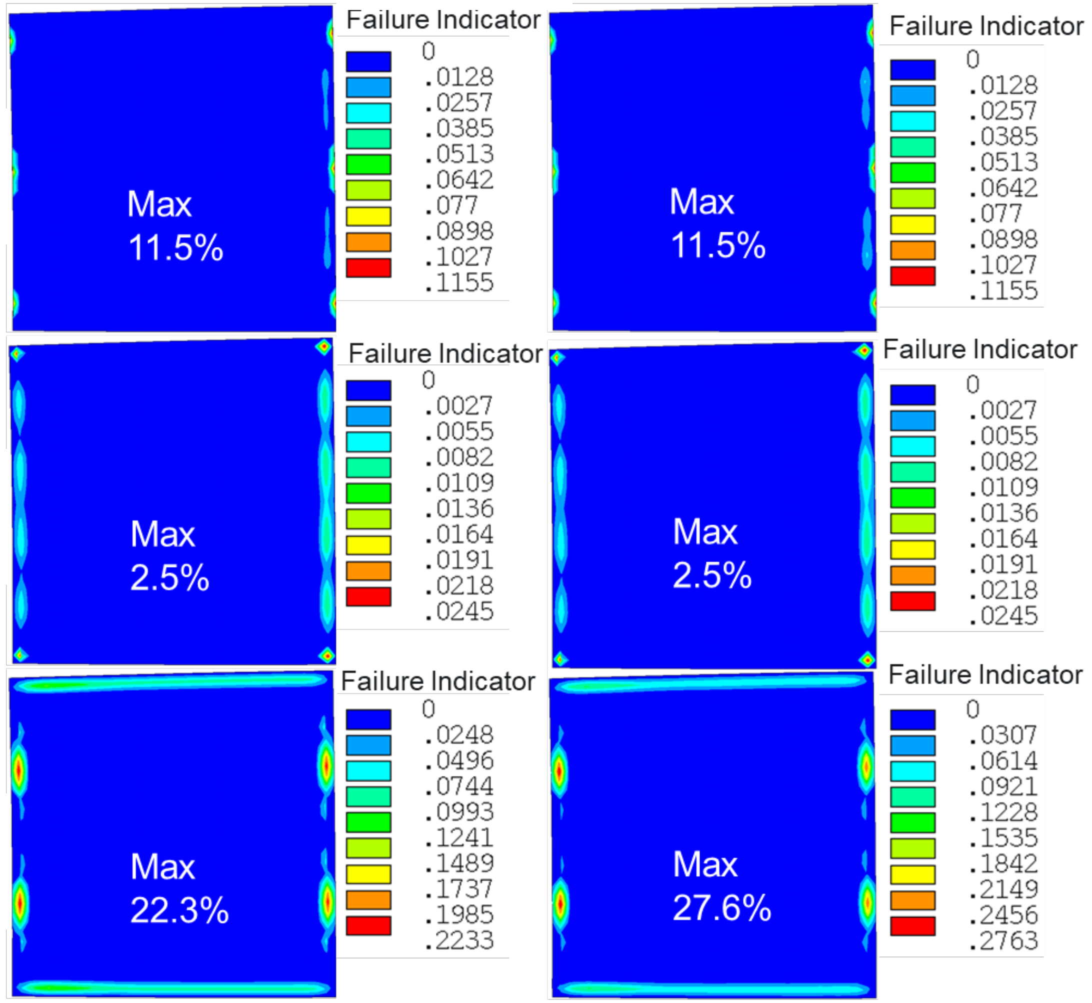



Before RedOx **Anode** After RedOx

Cell #1 (Bottom)

Cell #23 (Middle)

Cell #45 (Top)



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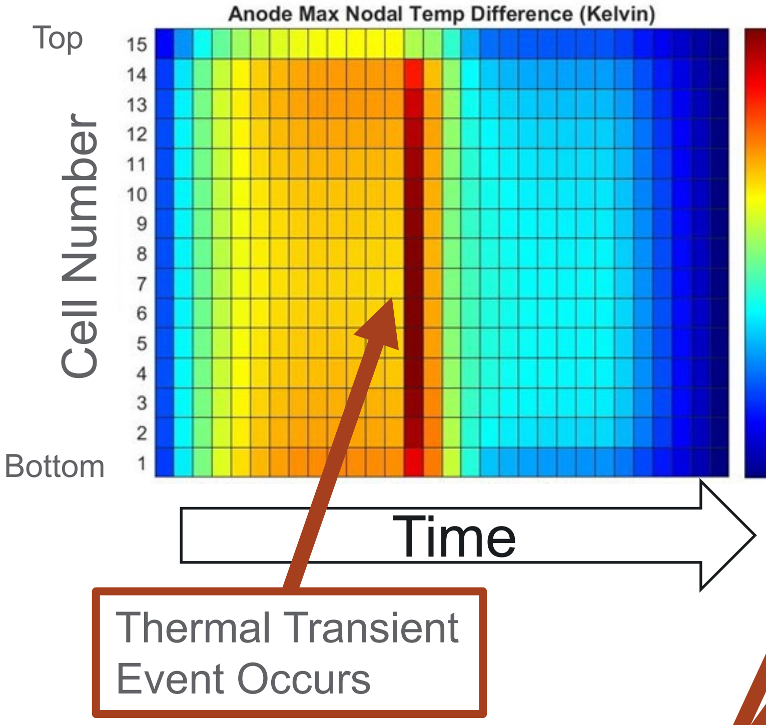
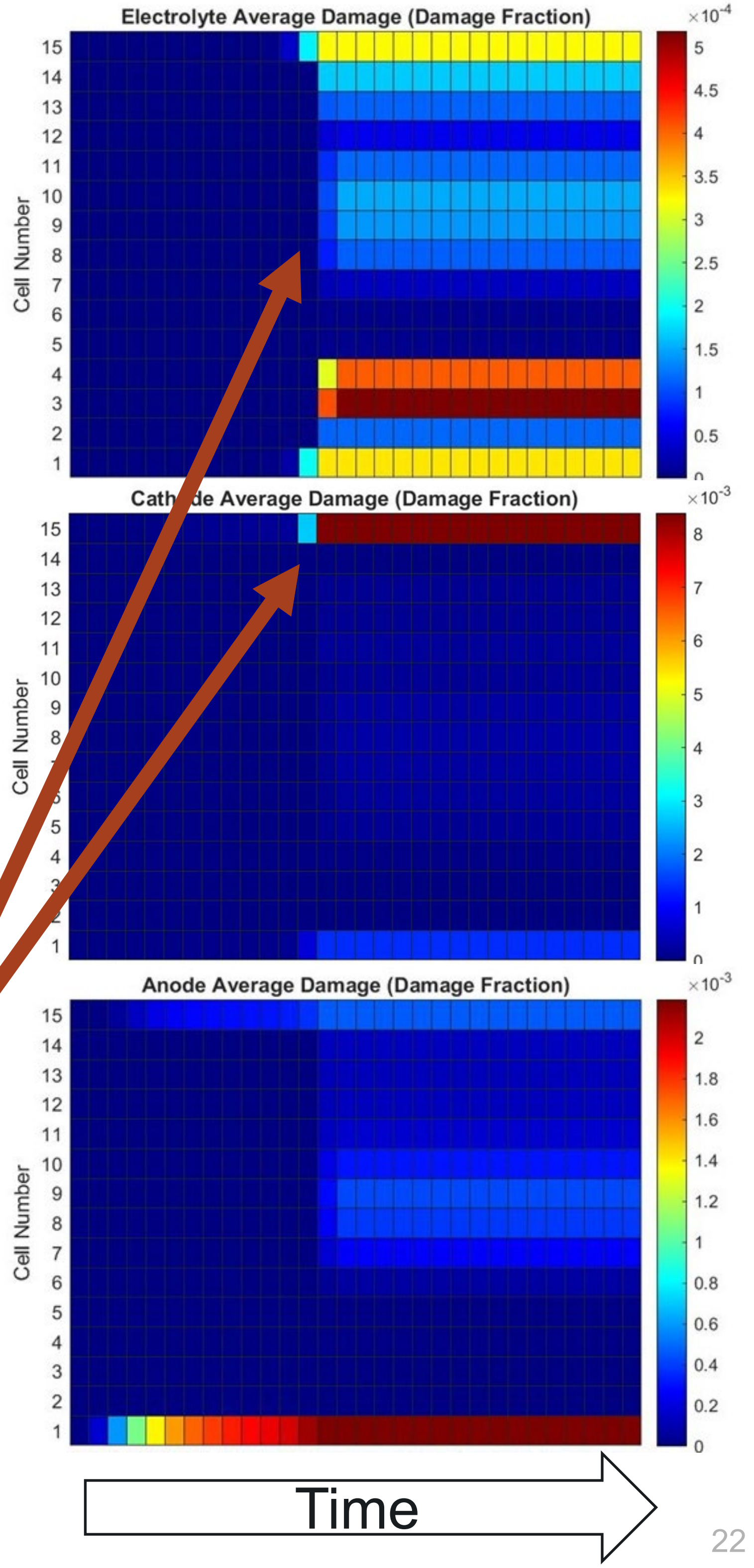
# Damage in Cells: Influence of Thermal Cycling

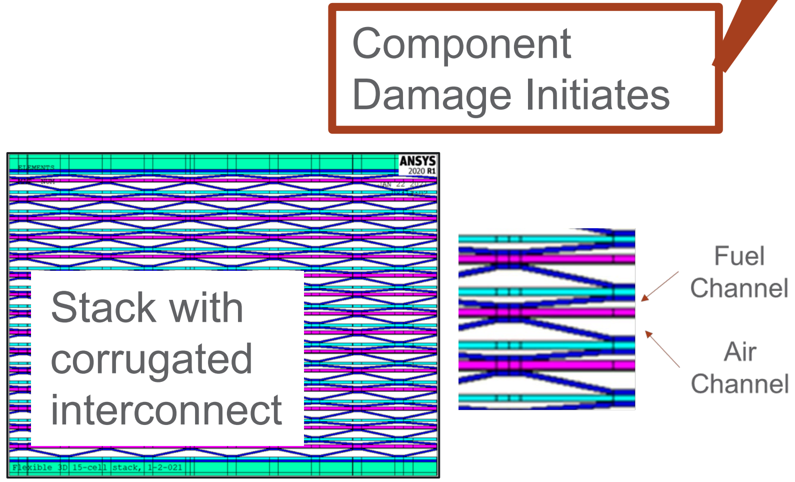
- Simulated transient thermal behavior of stack start-up and unplanned transient events in a 15-cell stack
  - Model internal flow with convection effects.
  - Unplanned events:
    - ✓ Loss of air/fuel heat source
    - ✓ Loss of blower
  - Unplanned event example: 50% reduction in air inlet temperature (loss of heater).
    - ✓ High air-side flow rate dominates the stack thermal response.
  - Generates thermal gradients in the cell.
- Transient thermal temperature profile used in pseudo-static structural simulation
  - Thermal gradients cause onset of damage in the cell.
  - Greater damage in cells at bottom and top of stack indicate end effects due to stiffness of the mechanical load frame.

## Cell Temperature Difference




## Cell Maximum Damage



# Acknowledgments


- This work has been funded by the SOFC Program of the US DOE Office of Fossil Energy and Carbon Management

- The NETL management team, including Debalina Dasgupta, Rin Burke, and Shailesh Vora, provided much helpful guidance and discussion

- Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the US Department of Energy