Tuning Surface Stoichiometry of SOFC Electrodes at the Molecular and Nano-Scale for Enhanced Performance and Durability

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Project Objectives

- Control the surface stoichiometry of electrodes (cathode and anode)
- Correlate the catalytic activity with the surface defect chemistry
- Develop surface modification techniques to modify the surface stoichiometry of electrodes
- Prevent the phase segregation such as strontium carbonate / strontium oxide formation in common cathodes and advanced ceramic anodes
- Develop novel approaches utilizing different cost-effective and mass producible surface modification techniques
- Identify the optimal surface modification process that yields the best initial performance and long-term stability on the modified electrodes
- Quantify degradation rates/performance and reveal the underlying mechanisms on tuned stoichiometric electrodes
- Integrate the optimized cathode and anode to full cell level

Project Schedule

		YR1				YR2			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1	Project management								
Task 2	Develop surface modification process								
MS 2.1	Develop ALD coating techniques	Completed							
MS 2.2	Develop solution-based infiltration techniques		Completed						
Task 3	Apply and test developed process on conventional cathodes								
MS 3.1	Determine the performance of modified cathodes			Completed					
MS 3.2	Identify optimized surface modification process				Completed				
Task 4	Apply and test developed process on anodes								
MS 4.1	Determine the performance of modified anodes					Completed			
MS 4.2	Determine the performance of modified anodes in methane						Completed		
Task 5	Adapt the developed techniques to full cells								
MS 5.1	Complete performance characterization of button cells integrated with modified anodes and cathodes							In progress	
MS 5.2	Complete post-testing characterization on surface modified SOFCs								In progress

Achievements (Oct. 2018~Jul. 2020)

- Determined Factors that Control Cation Segregation on Cathodes

- Developed Surface Modification Technique

    -Developed ALD Coating Technique

    -Developed Solution Infiltration Technique

- Enhanced SOFC Cathode Performance/Durability

- Enhanced SOFC Ceramic Anode Activity

Control Surface Cation Segregation

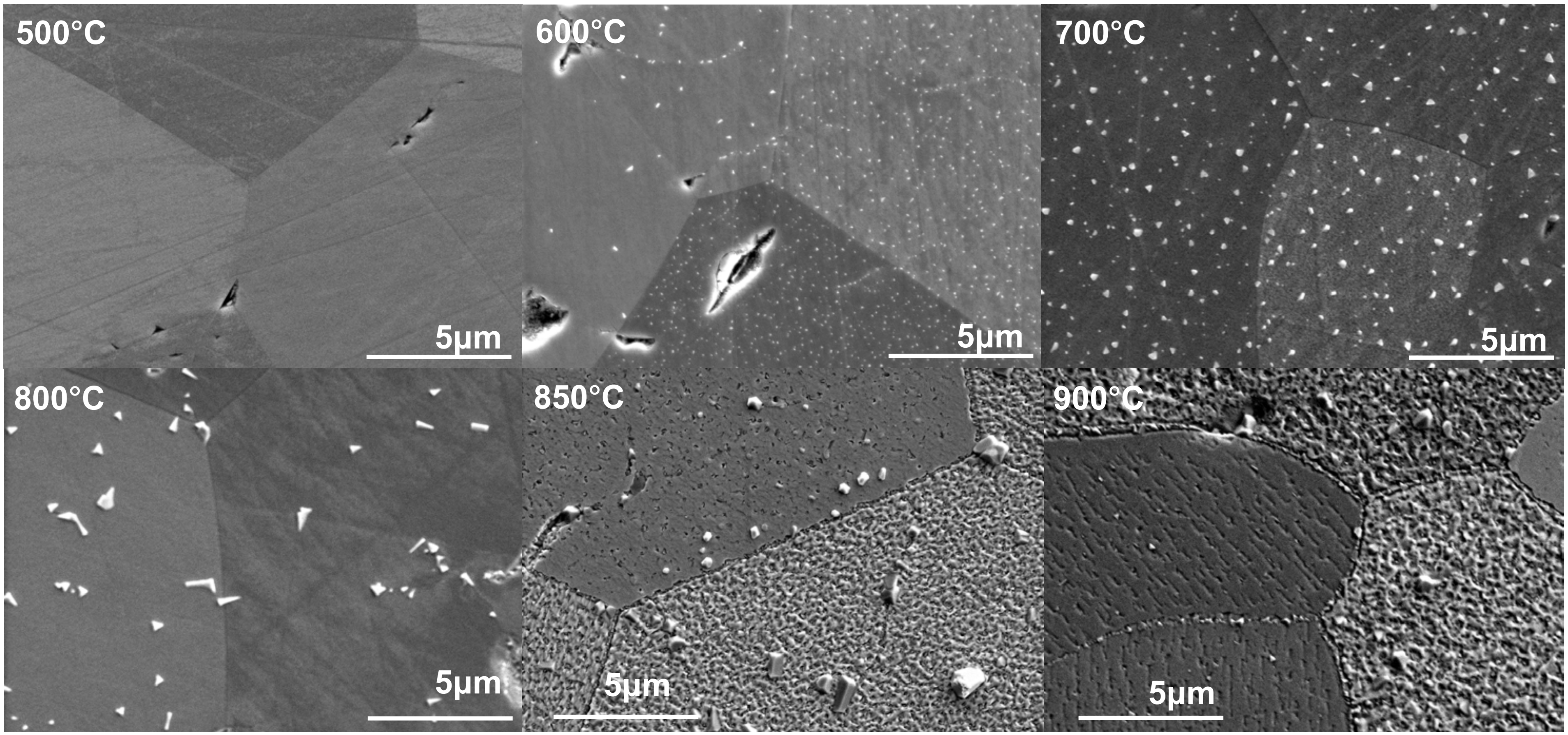
Surface Segregation is Driven by Thermodynamics and Kinetics

Determined key factors that control surface cation segregation

1. Temperature
2. Aging time at different temperature
3. Oxygen partial pressure (chemical potentials)
4. CO_2
5. A-site Stoichiometry
6. Different perovskite compositions

Temperature Effect on Surface Segregation of LSCF

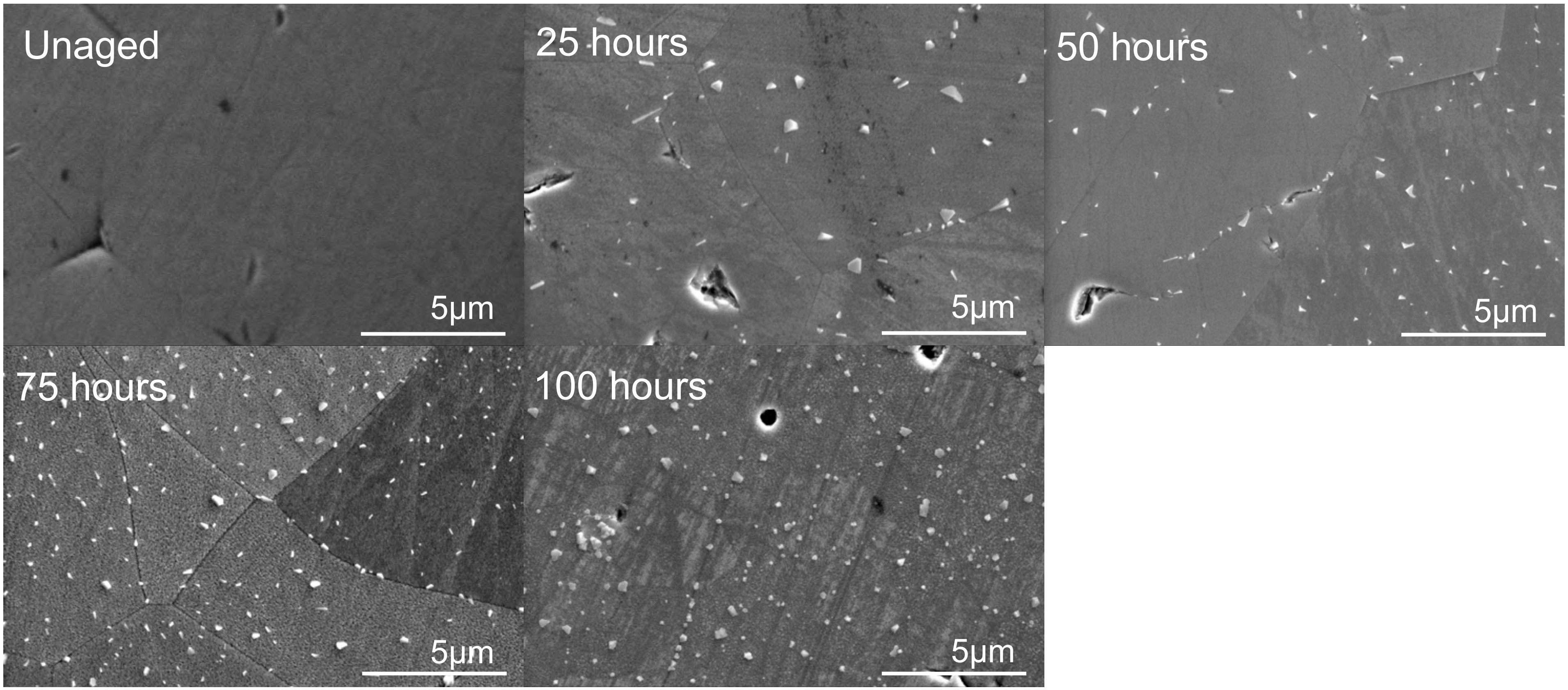
Aging of Dense LSCF Surface in Synthetic Air for 25 hrs



- The increase in temperature promotes surface cation precipitation (size, numbers)
- Temperature activates SrO segregation
- Different mechanism is observed at higher temperatures (> 850 °C), porous surface and grain orientation dependence.

Time Effect on Surface Segregation of LSCF

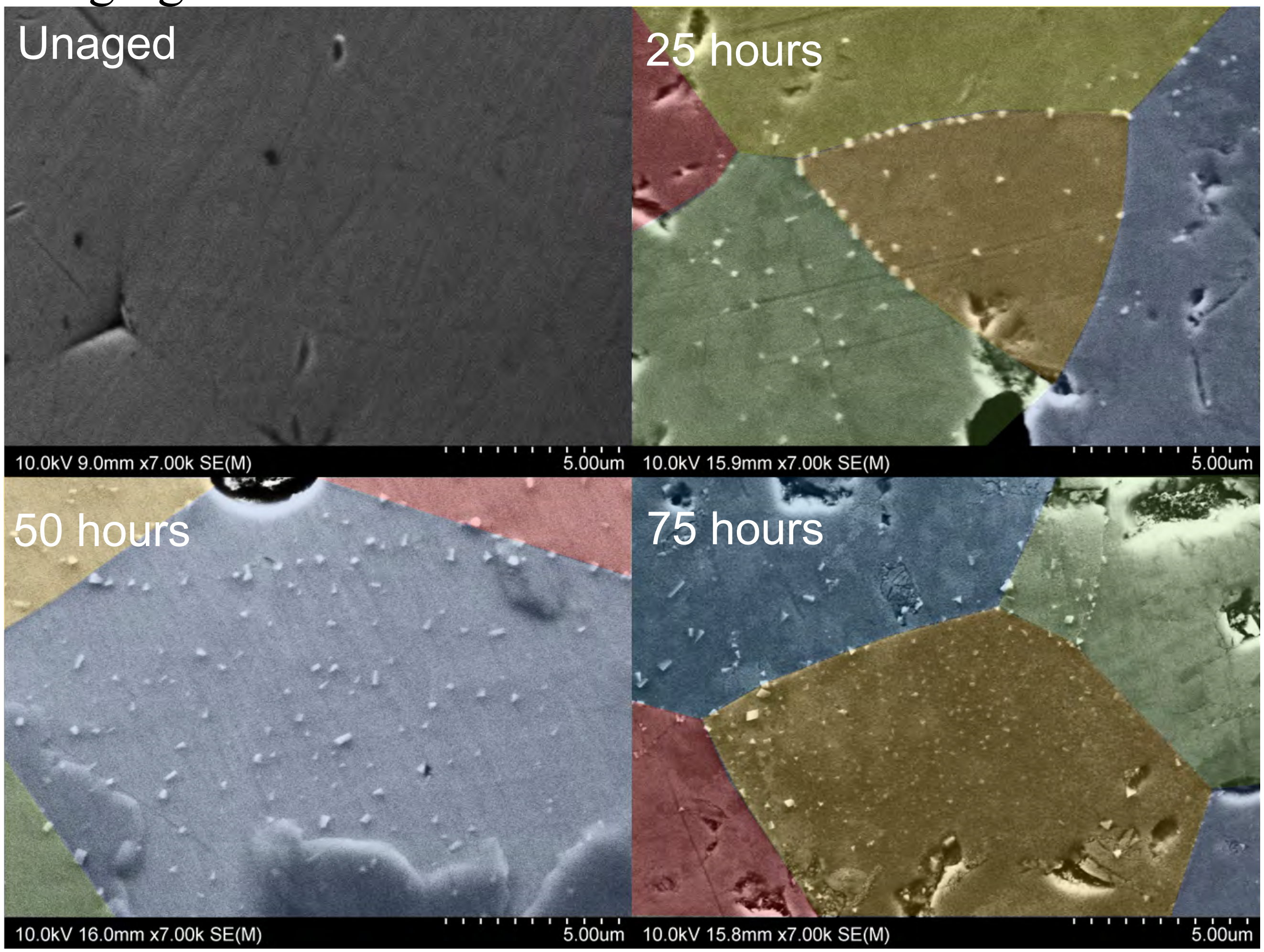
Aging of Dense LSCF Surface at **700 °C** in Synthetic Air



Aging time increases SrO particle nucleation and growth at 700 °C

Time Effect on Surface Segregation of LSCF

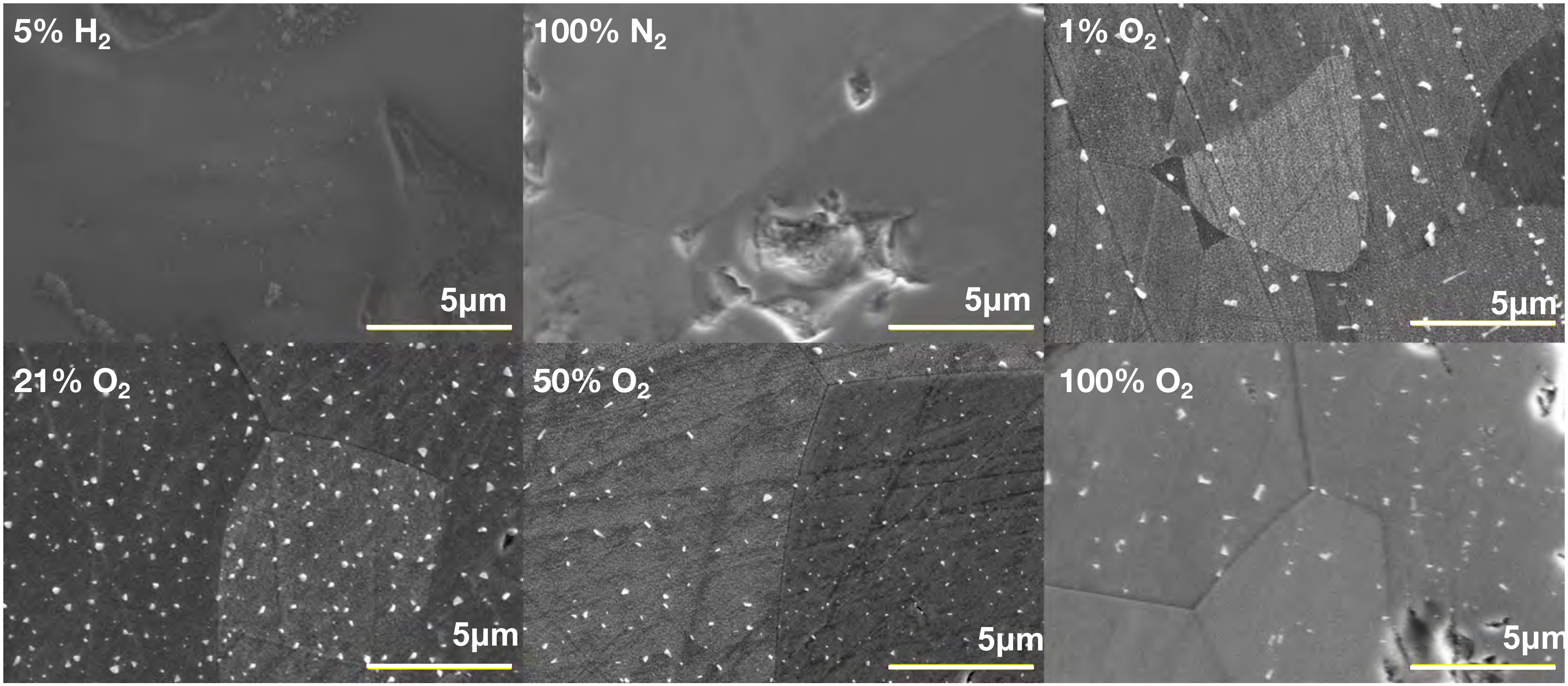
Aging of Dense LSCF Surface at **800 °C** in Static Air



- Different grains are highlighted using different colors
- Segregation Process: Likely to nucleate at grain boundaries and then migrate to the grain center.

pO_2 Effect on Surface Segregation of LSCF

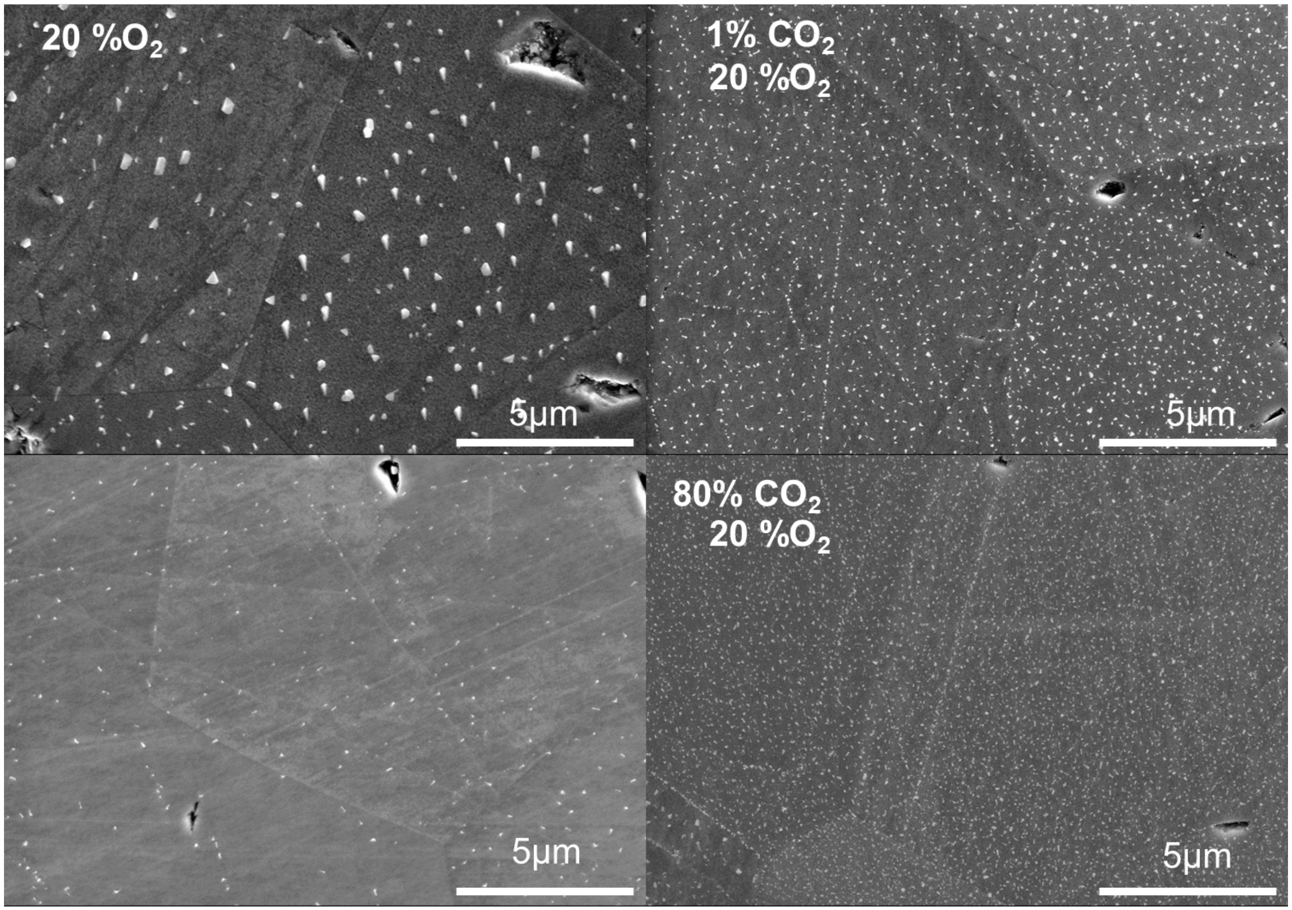
Aging of Dense LSCF Surface at **700 °C** for 25 hrs



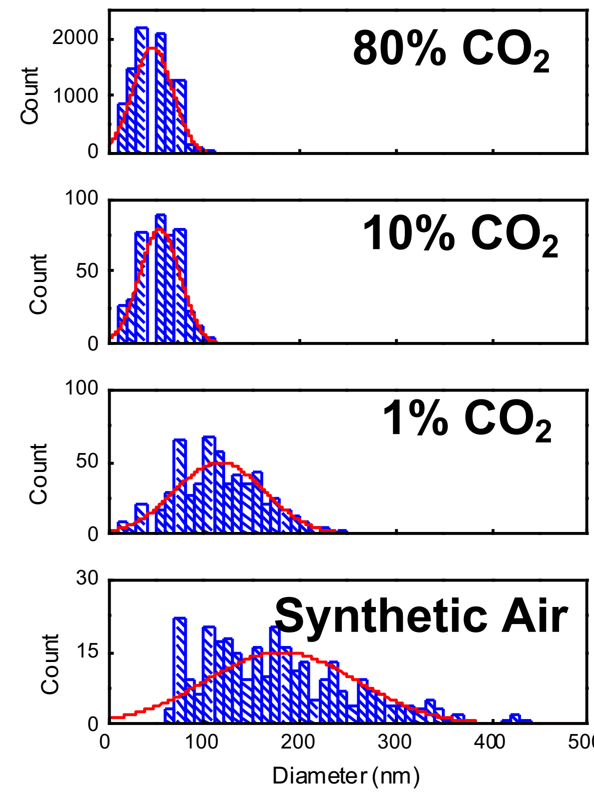
- The increase in pO_2 first promotes SrO segregation.
- Above 21% further increase in pO_2 supresses SrO segregation.
- Likely correlates to defect chemistry of LSCF

$p\mathrm{CO_2}$ Effect on Surface Segregation of LSCF

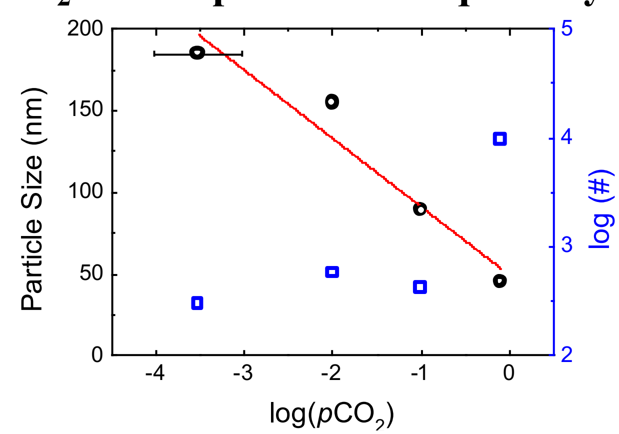
700 ° C for 25 hrs, balanced with N_2



Particle Size Distribution



$p\mathrm{CO_2}$ versus particle size/quantity

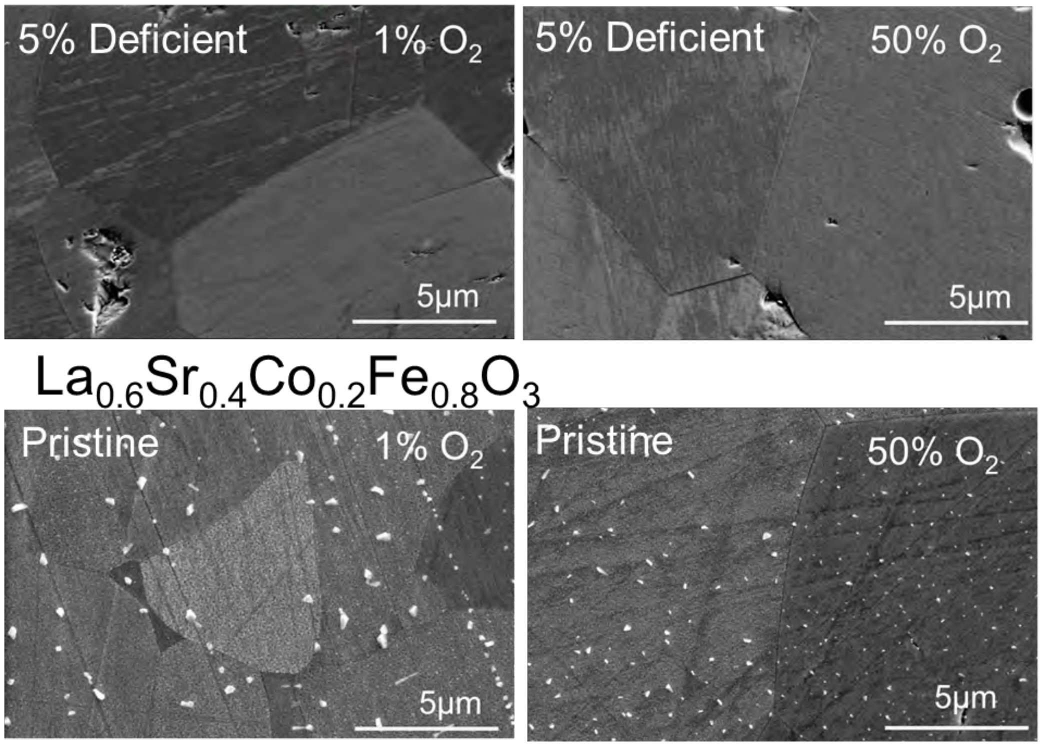


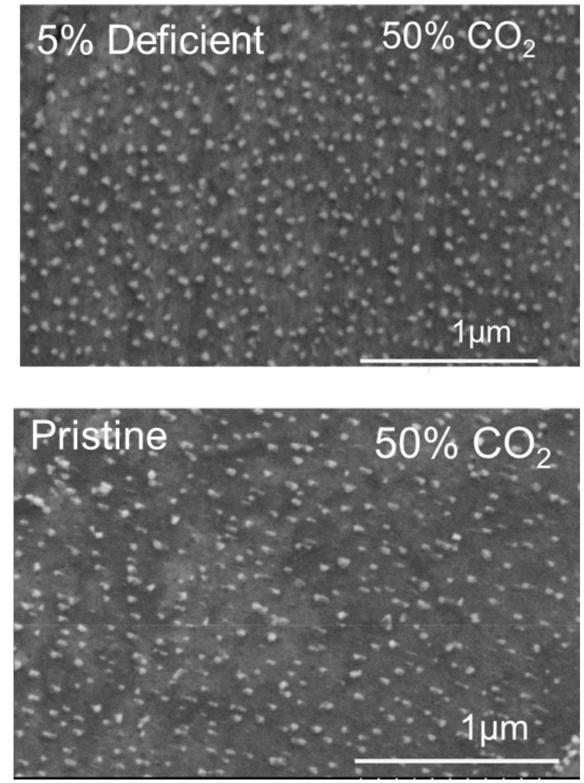
- Increase in $p\mathrm{CO_2}$ decreases the precipitated particle size and increases particle number.
- CO_2 promotes nucleation and suppress particle migration/growth.

A-site Stoichiometry Effect

$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_3$ **In N_2/O_2 Mixture**

In 50% CO_2 (20%O_2, 30%N_2)





- A-site deficient suppresses SrO segregation
- A-site deficient does **NOT** help prevent CO_2 induced SrO segregation

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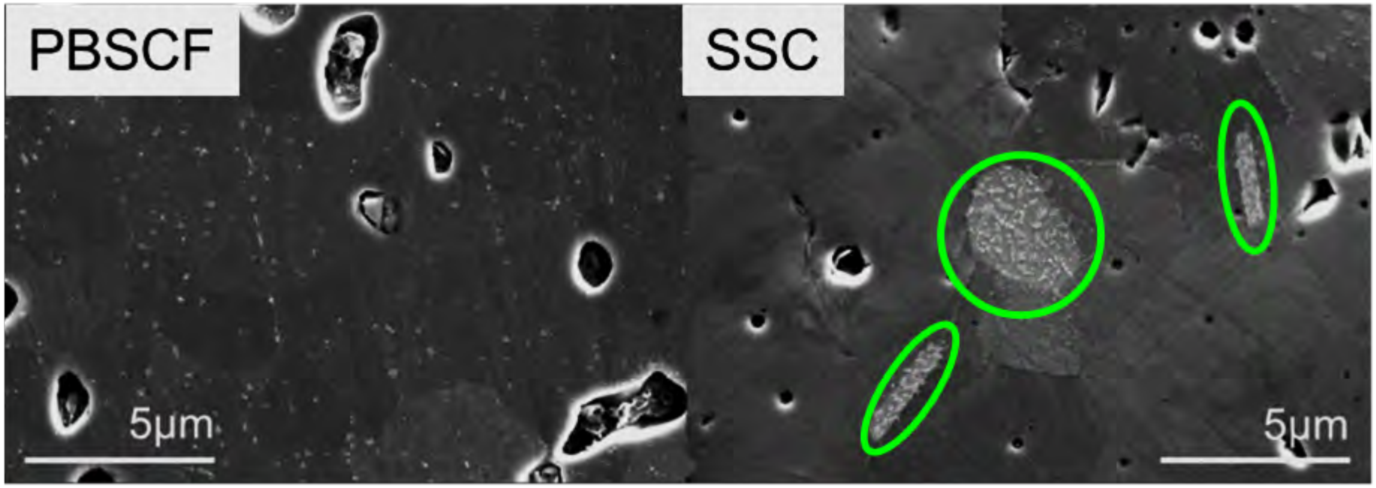
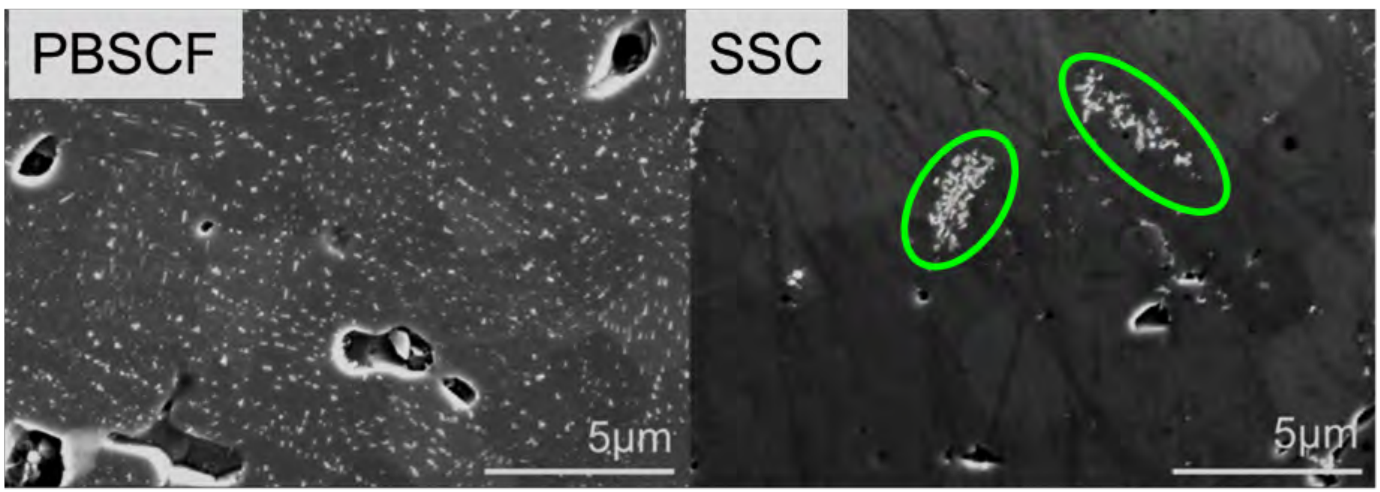
Different Surface Segregation Mechanism on Different Cathodes

Surface Segregation of PBSCF and SSC

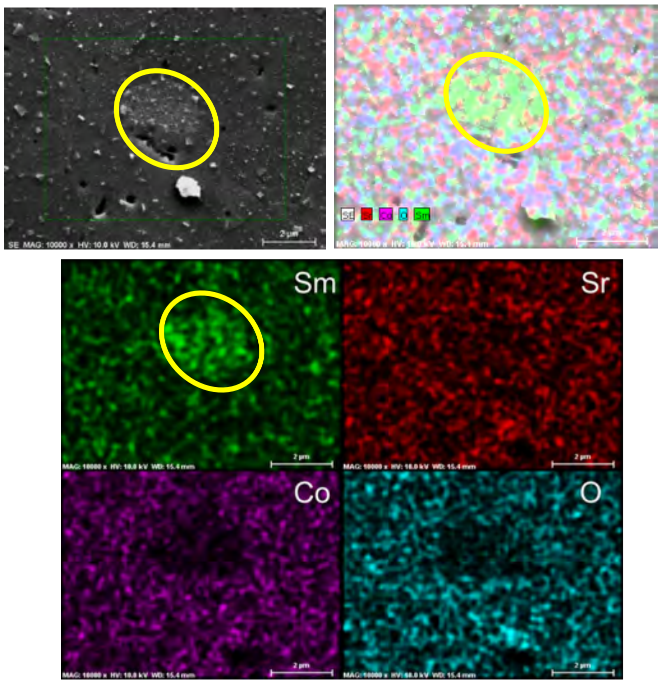


10% CO_2

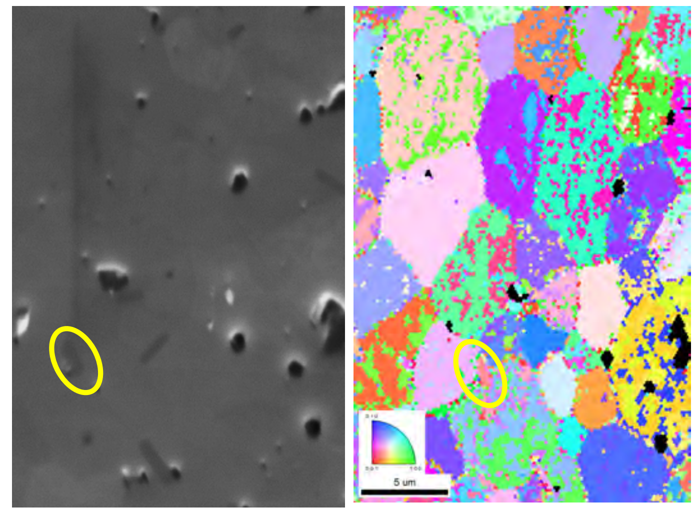


Composition Analysis on Surface Segregation of $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC)

Observed Sm segregation
(EDS)



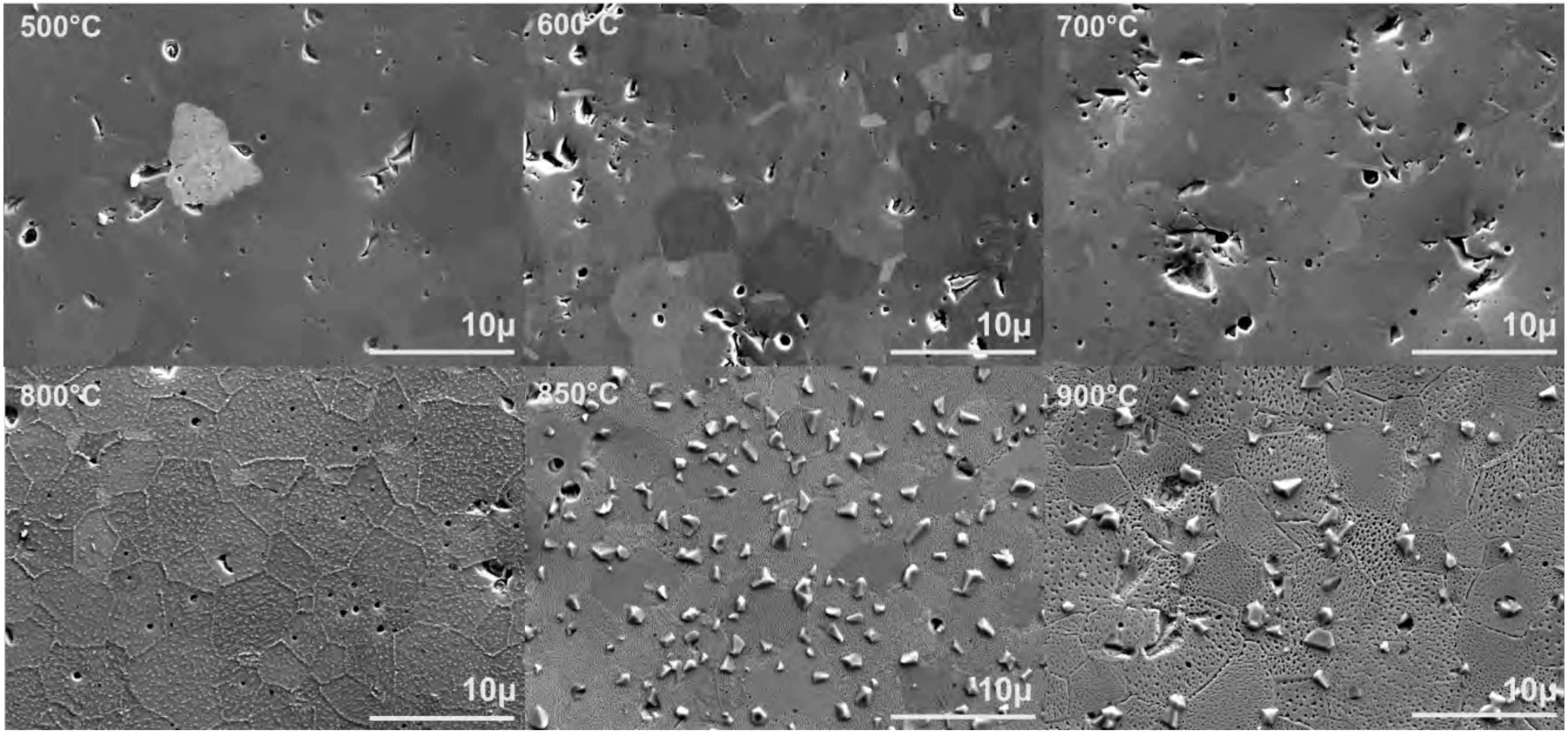
Strong Crystal Orientation Dependence
(EBSD)



- Study of the light-colored grains indicates they were rich in Sm instead of Sr.
- This was unexpected and is further evidence of a different cation segregation mechanism in SSC.

Temperature Effect on Cation Segregation in SSC

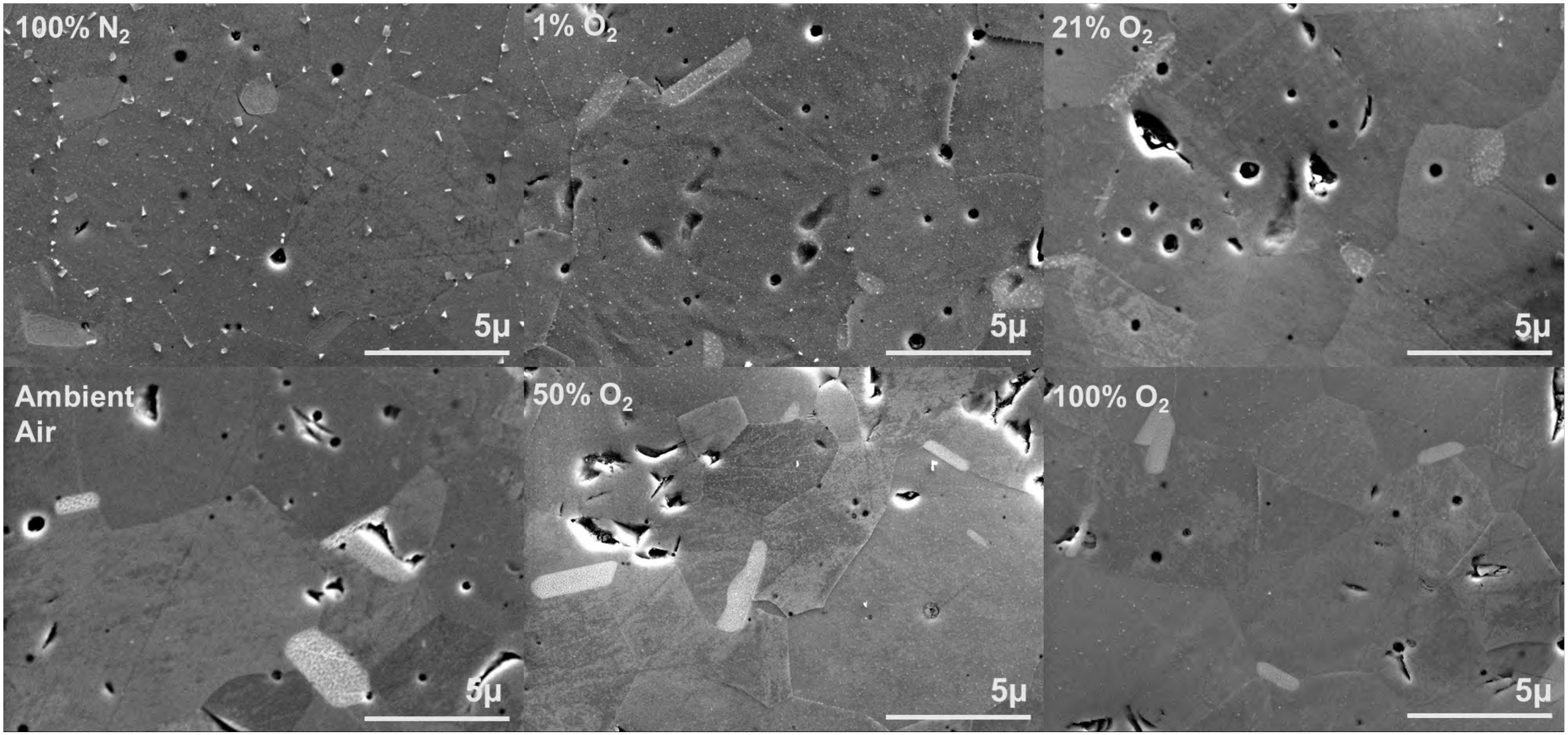
Aging of Dense SSC Surface in Synthetic Air for 25 hrs



- As with LSCF, when SSC undergoes cation segregation, there is also nucleation of distinct particles that seem to start at the grain boundaries and agglomerate.
- Unlike LSCF, SSC exhibited discolored grains prior to particle segregation. These grains appear in multiple aging conditions.

Oxygen Effect on Cation Segregation in SSC

Aging of Dense SSC Surface at 700°C for 25 hrs



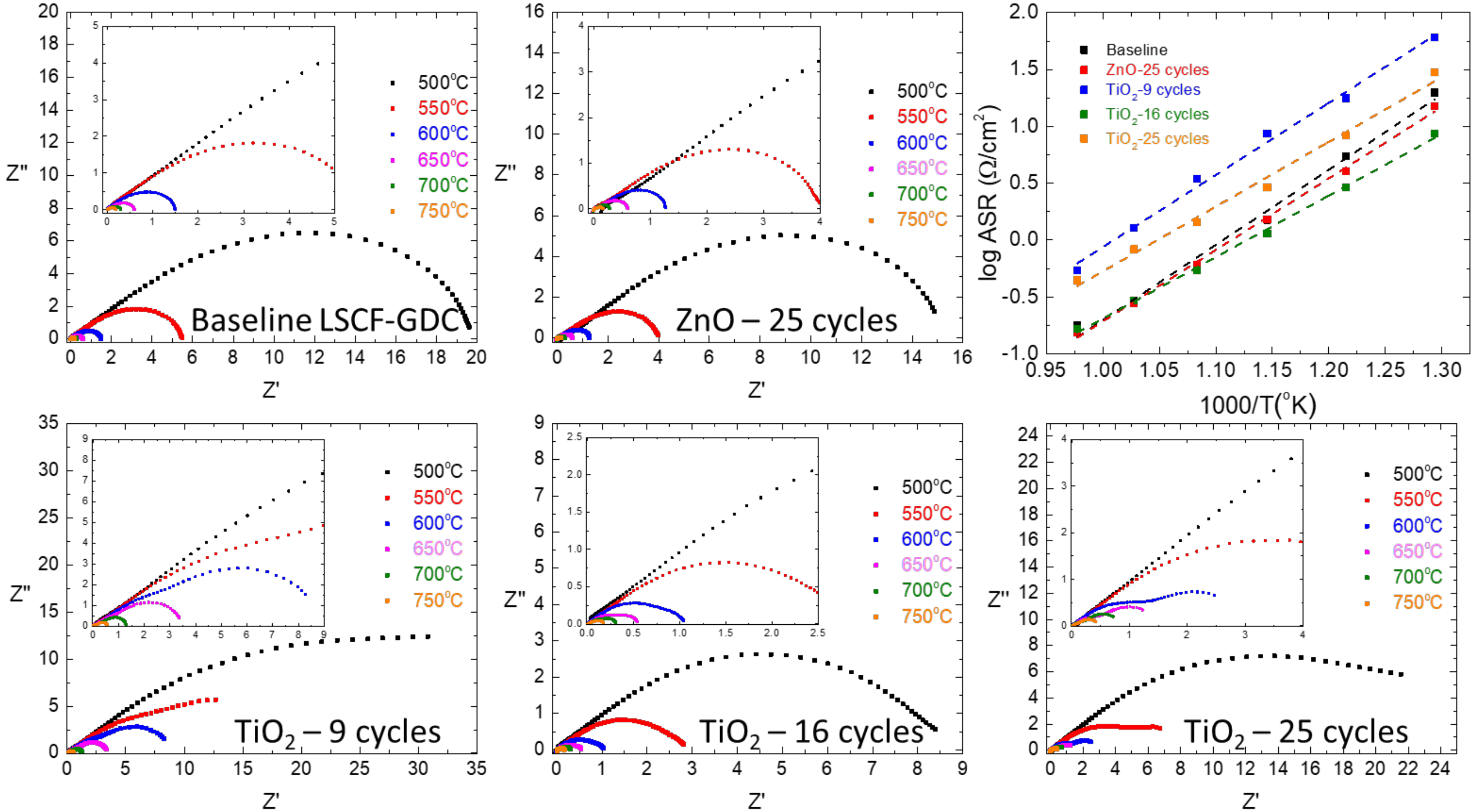
- SSC appears to be more stable in higher pO_2 environments.
- Light-colored regions appear to be the first step in cation segregation in SSC.
- These observations suggest a different mechanism for cation segregation in SSC compared to LSCF.

Cathode Surface Modification

1. Development of ALD coating technique
2. Development of solution infiltration technique
3. Performance/Durability Enhancement of Surface Modified Cathode

Electrochemical Performance of ALD Modified LSCF-GDC

Temperature Dependence - ALD Modified and Unmodified Symmetric Cells



- ALD films of TiO_2 and ZnO were found to improve electrochemical performance of LSCF-GDC cathode symmetric cells.
- 16 cycles of TiO_2 ALD was found to be optimum for enhancing performance.

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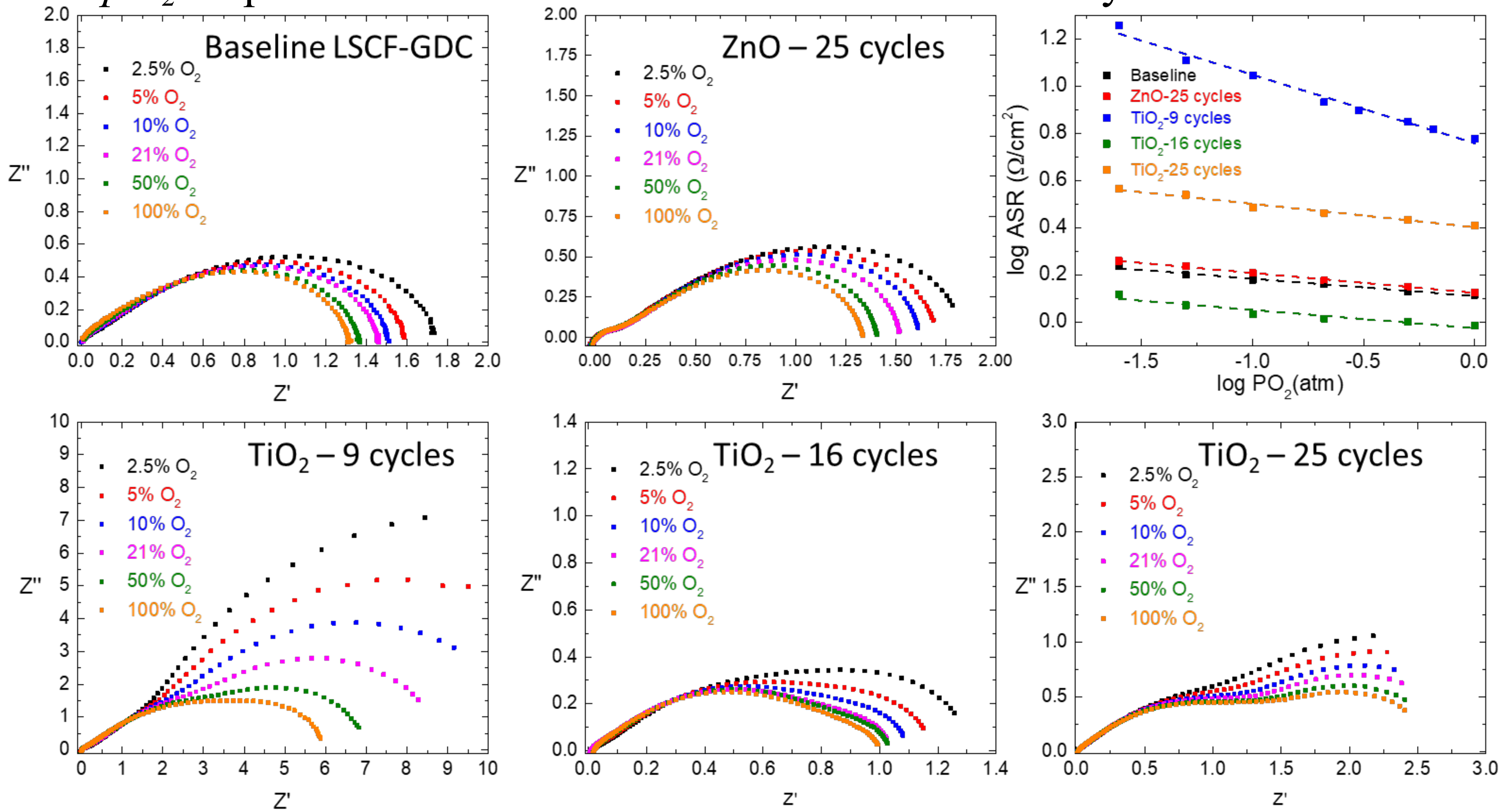
Electrochemical Performance of ALD Modified LSCF-GDC

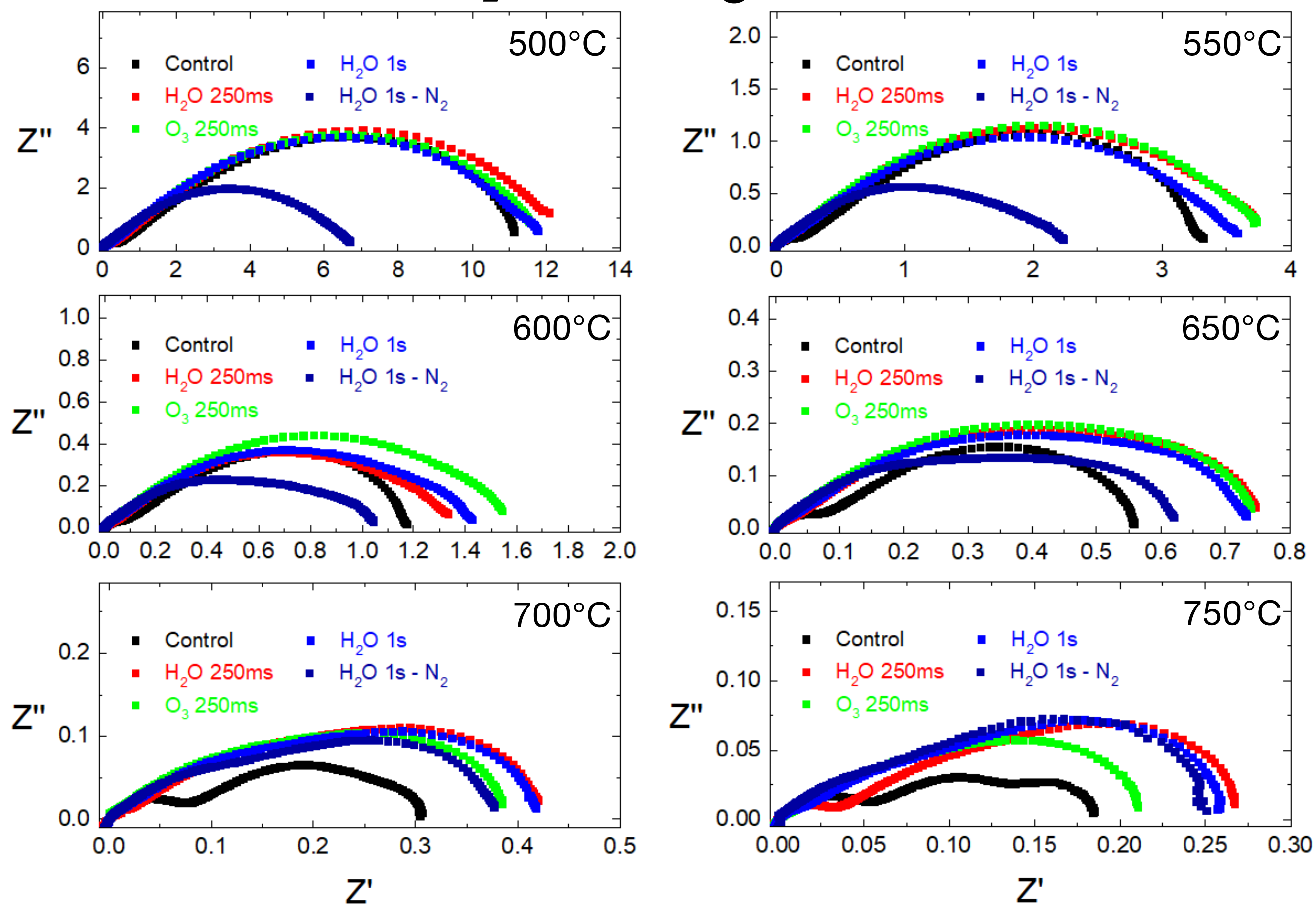
pO_2 Dependence - ALD Modified and Unmodified Symmetric Cells



- All ALD modified samples had similar pO_2 dependence except for 9 cycles of TiO_2.

Electrochemical Performance of ALD Modified LSCF-GDC

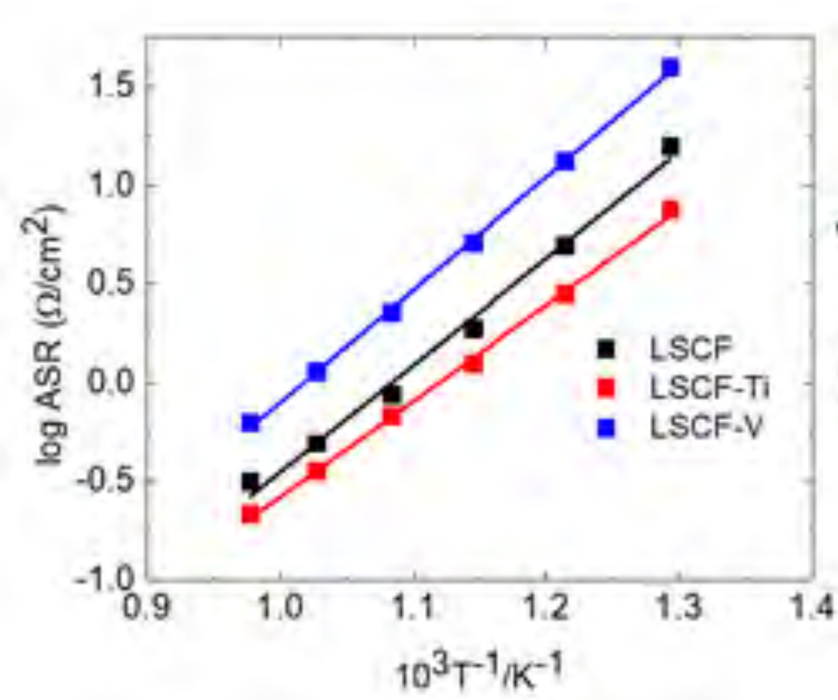
Effect of ALD Oxidizer and N_2 Annealing on Electrochemical Performance



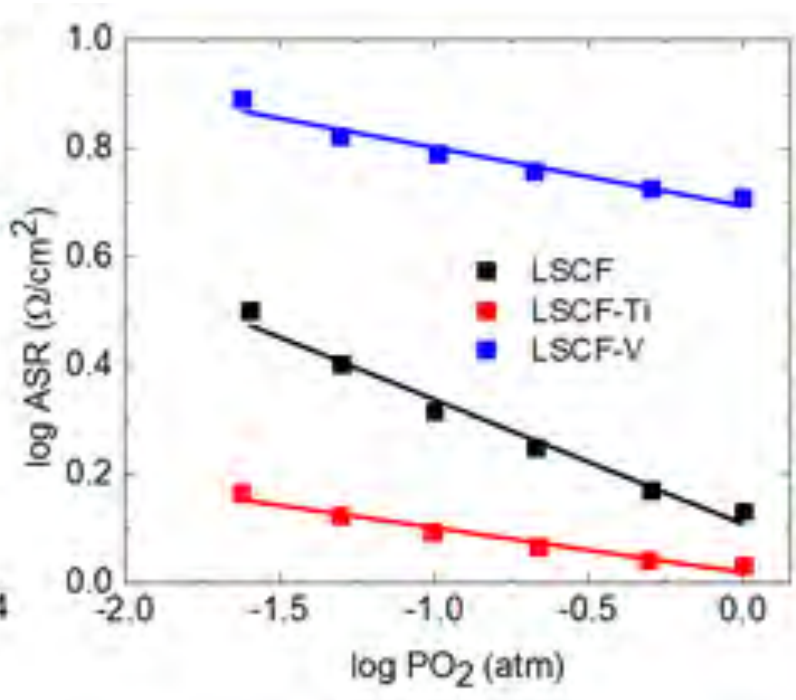
- It was hypothesized that tuning the non-stoichiometry of the ALD films could enhance kinetics, so the effect of different oxidizers (and pulse times) were tested.
- Annealing in pure N_2 for 1 hour at 400°C was also used to tune non-stoichiometry.
- Annealing significantly lowered total ASR below 650°C.

ALD Modified LSCF

Arrhenius Plot

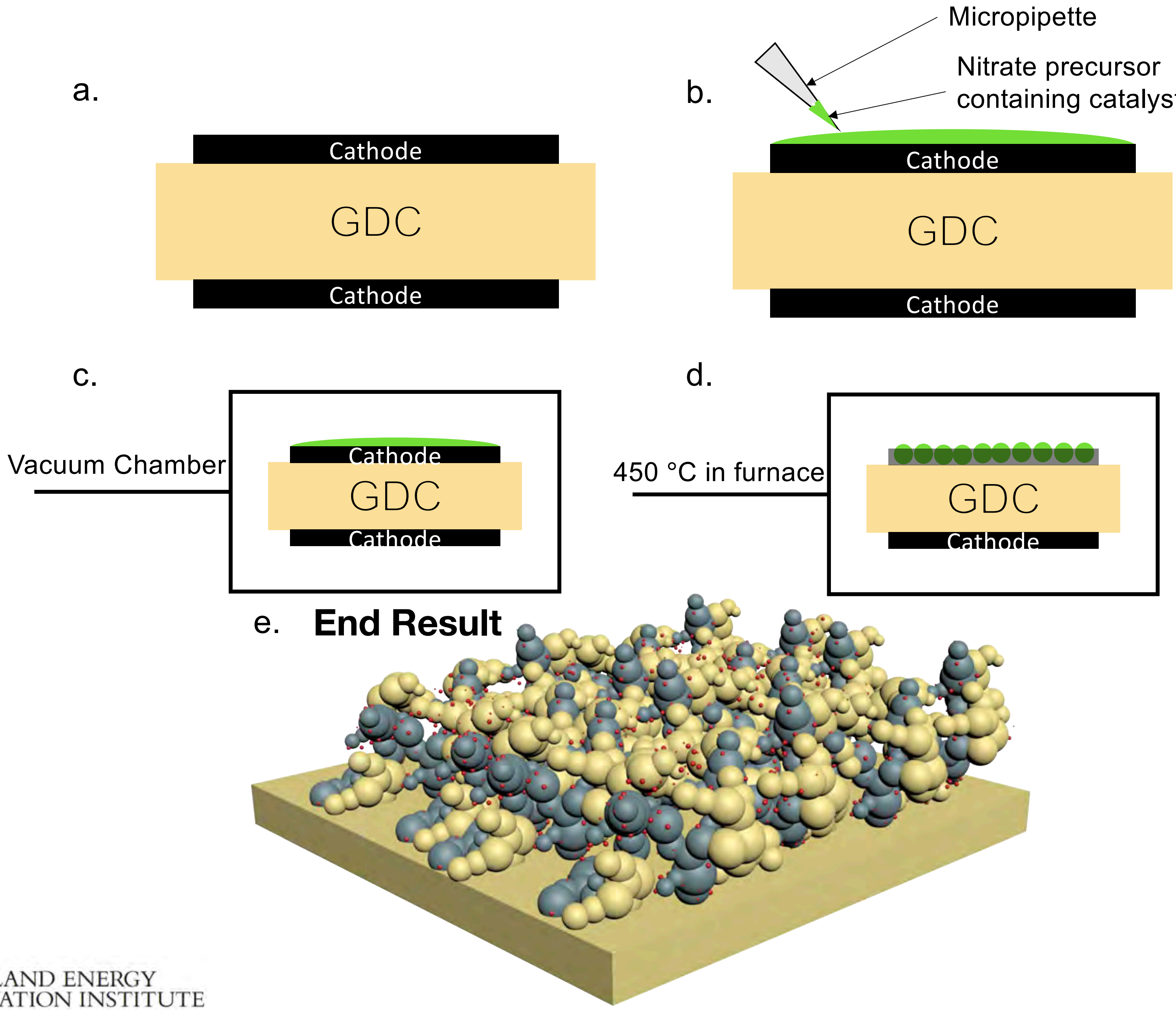


Double Log Plot



- TiO_x modified cell shows a lower ASR in all tested temperature region.
- In contrast, VO_x modified cell shows an opposite trend with an increase in ASR.
- For pO_2 dependence, unmodified cell has a slope of 0.22. TiO_x modified cell has a lower ASR across all pO_2 range with a decrease in the slope.

Solution Infiltration Procedure



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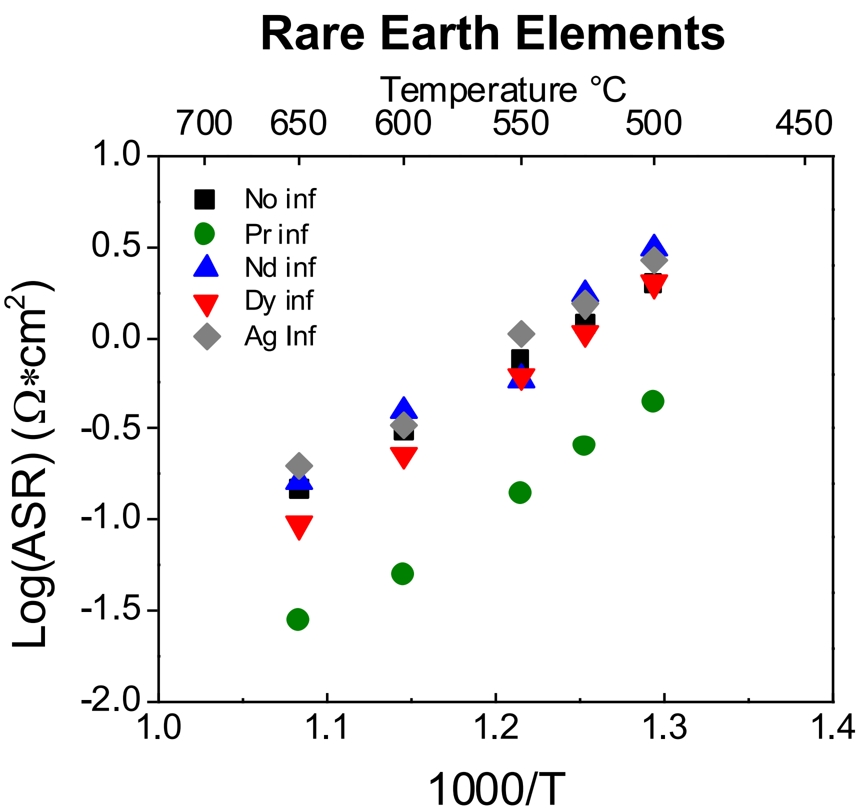
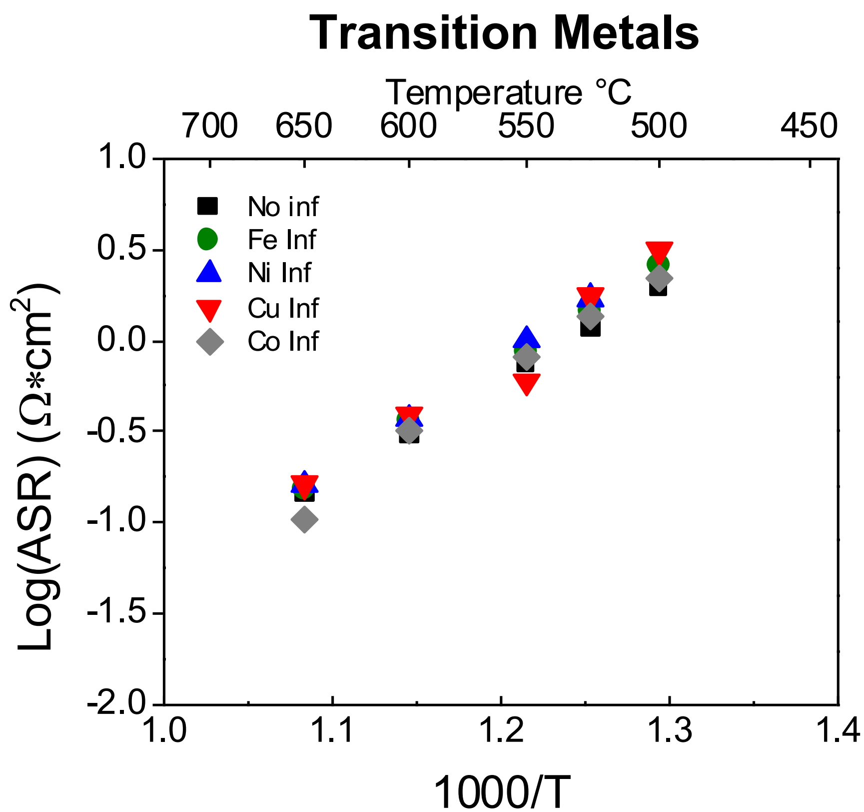
Electrochemical Performance of Surface Modified SSC

Screening over multiple elements





Pr modified SSC shows promising electrochemical performance

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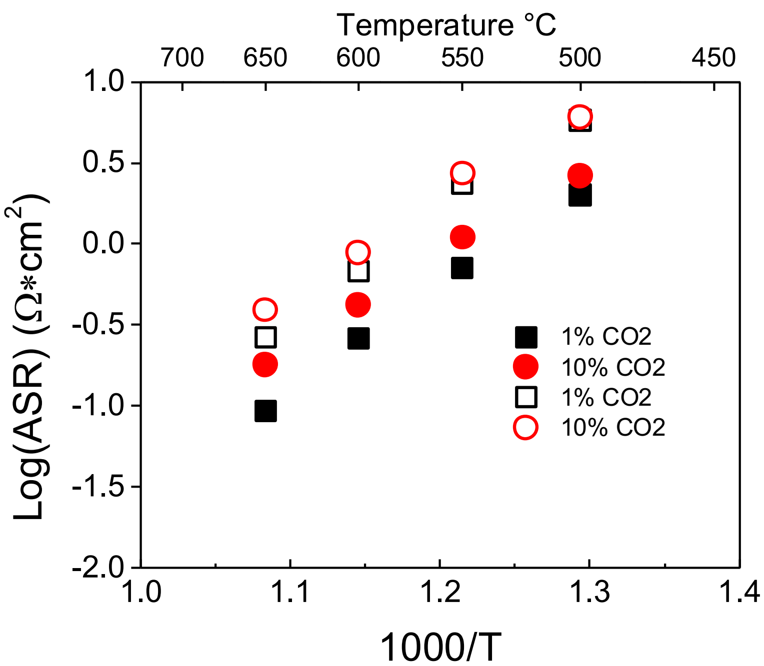
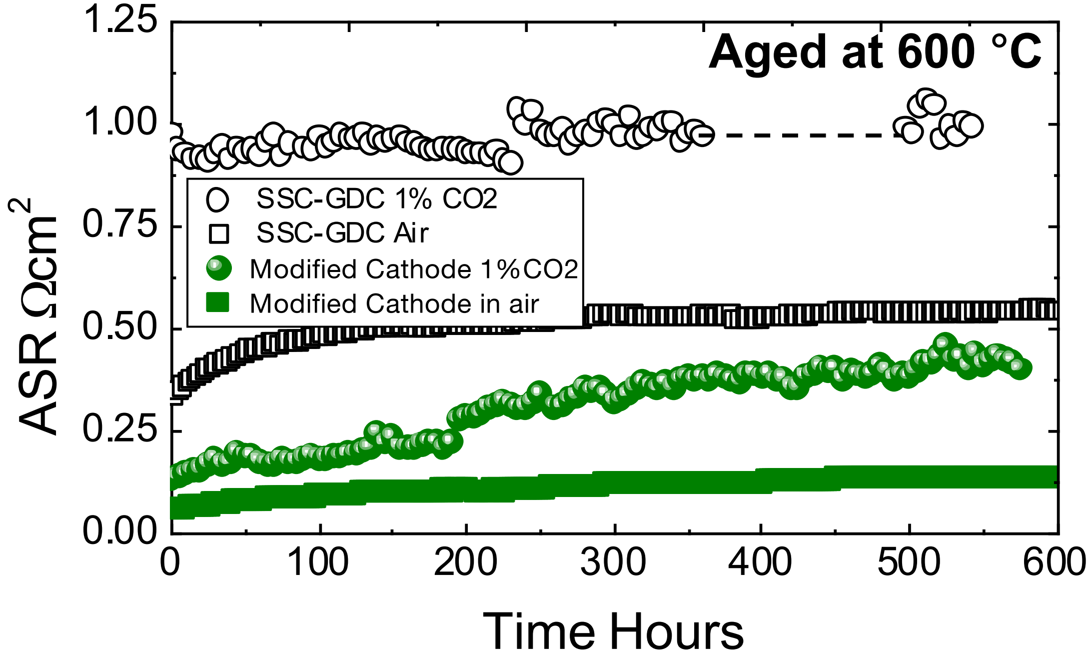
Impact of CO_2 on Cathode Performance

Cathode ASR as a function of CO_2



***Open Symbols: SSC-GDC**
Closed Symbol: Surface Modified SSC-GDC

Long-Term Stability in Different Gas Environments



- CO_2 has much less impact on modified cathodes
- Modified cathodes show high stability in 1% CO_2

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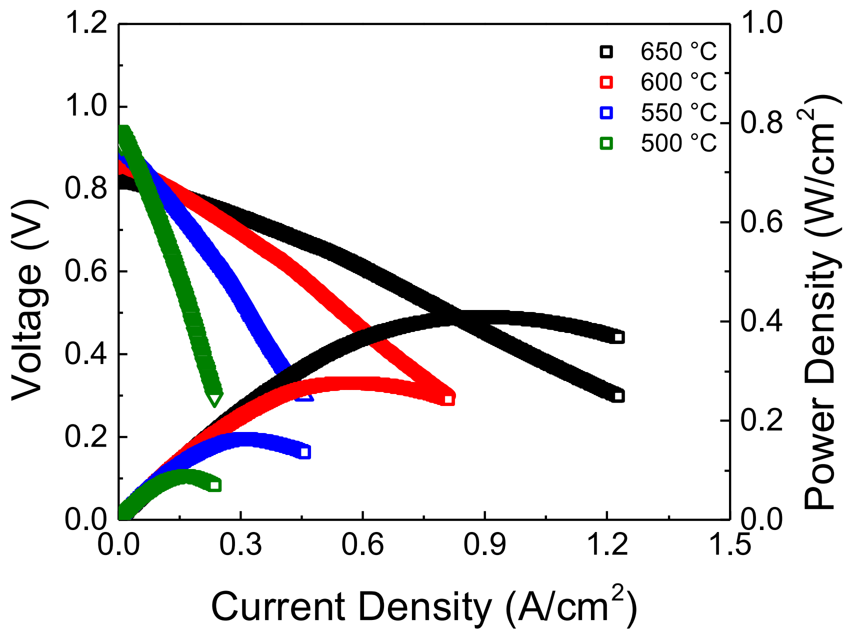
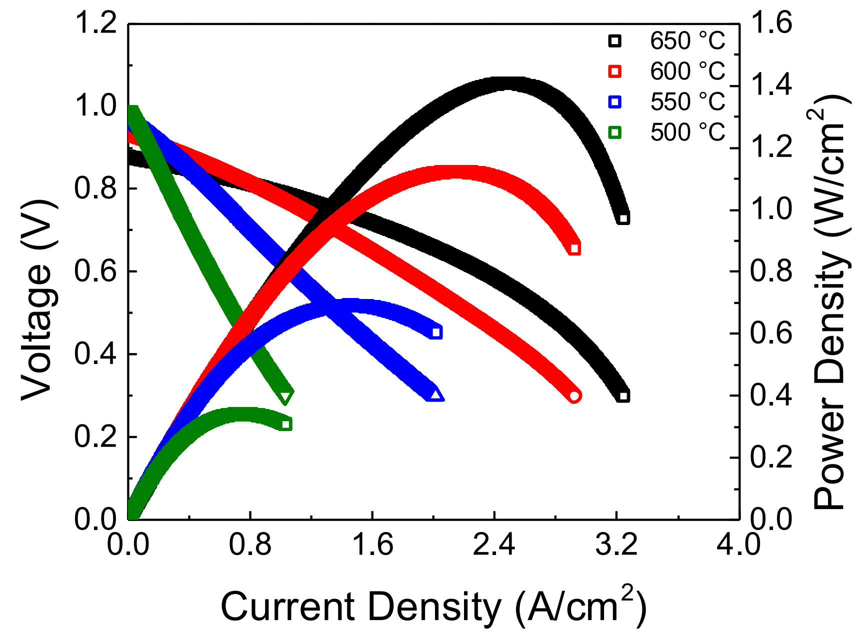
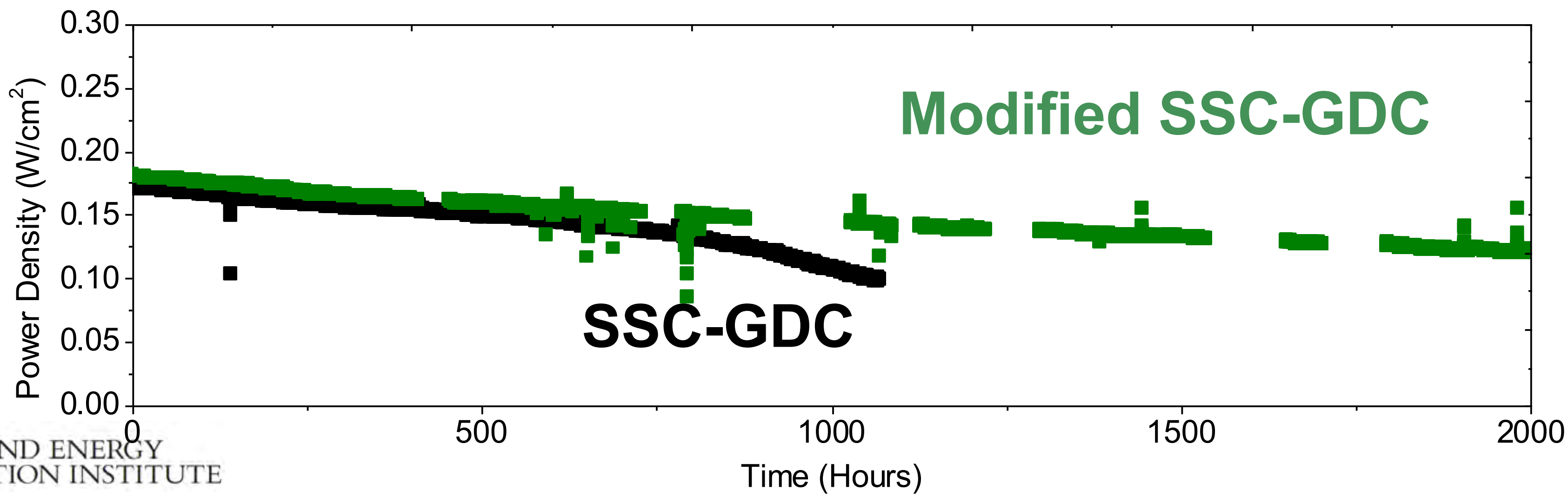
Surface Modified SOFC Performance

Baseline Cell: SSC-GDC/GDC/Ni-GDC



Cathode Modified Cell





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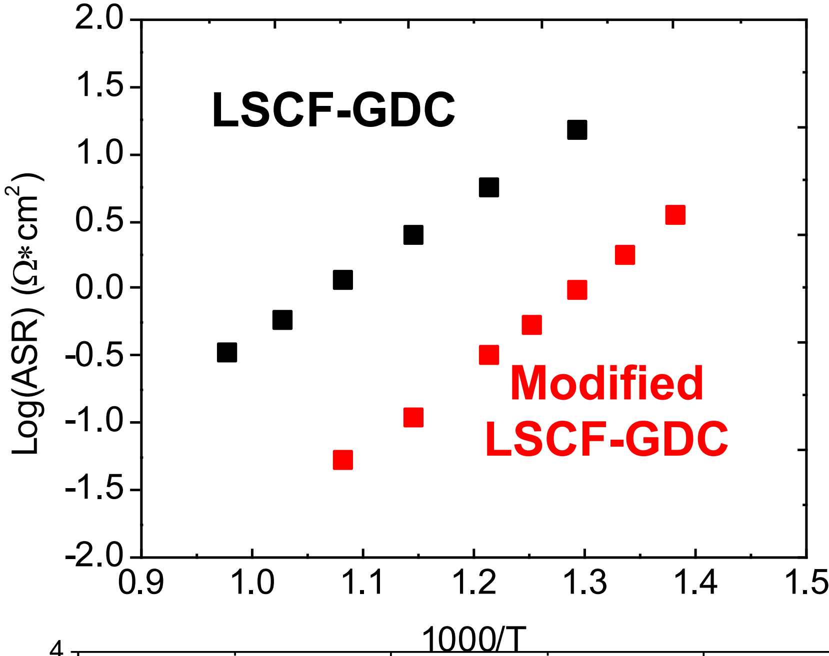
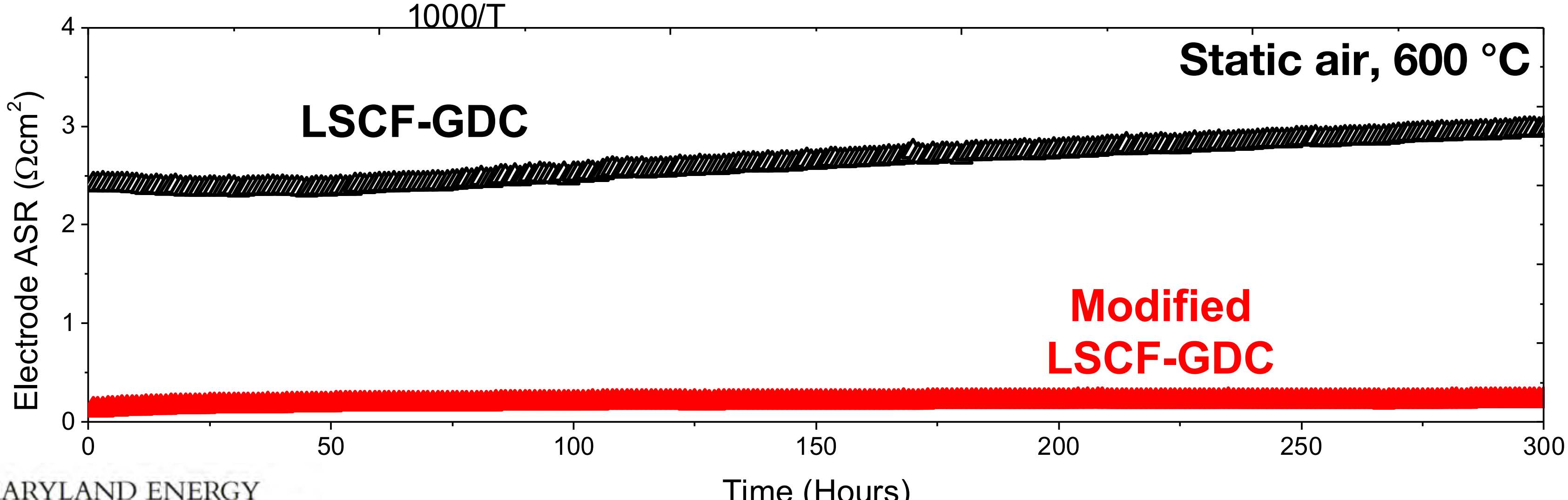
Performance & Stability of Modified LSCF

The surface modification technique can apply widely to different cathodes



Determined via Symmetric Cell Configuration

1. Area specific resistance (ASR) decreases an order of magnitude after modification
2. Modified cathode shows improved stability



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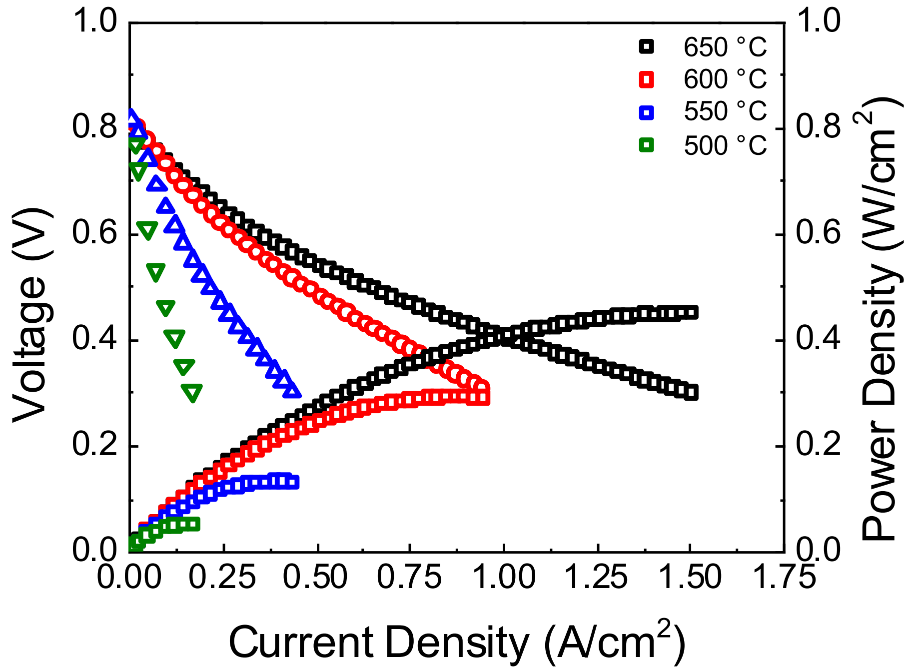
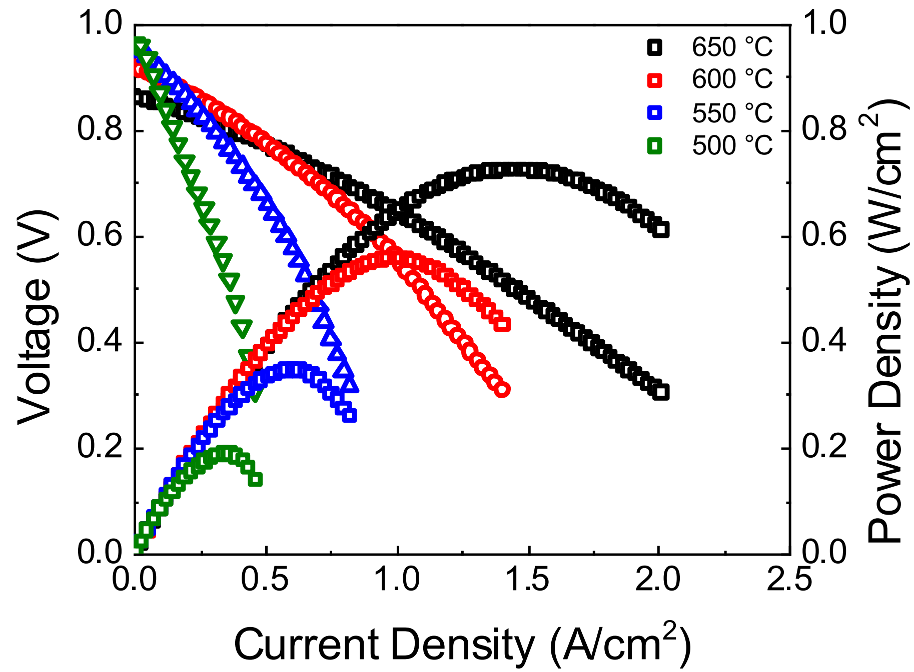
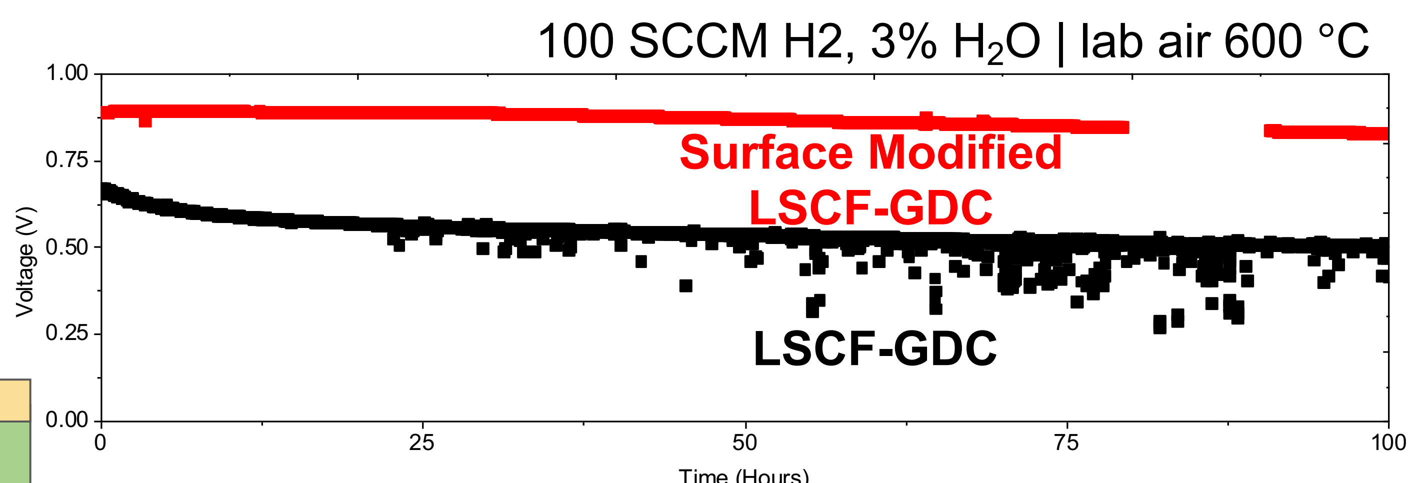
Surface Modified SOFC Performance/Stability

Baseline Cell: LSCF-GDC/GDC/Ni-GDC

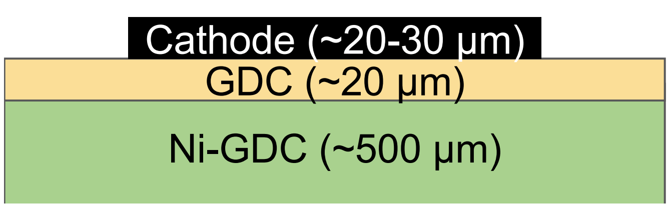


Cathode Modified Cell





Cell Configuration



Anode Surface Modification

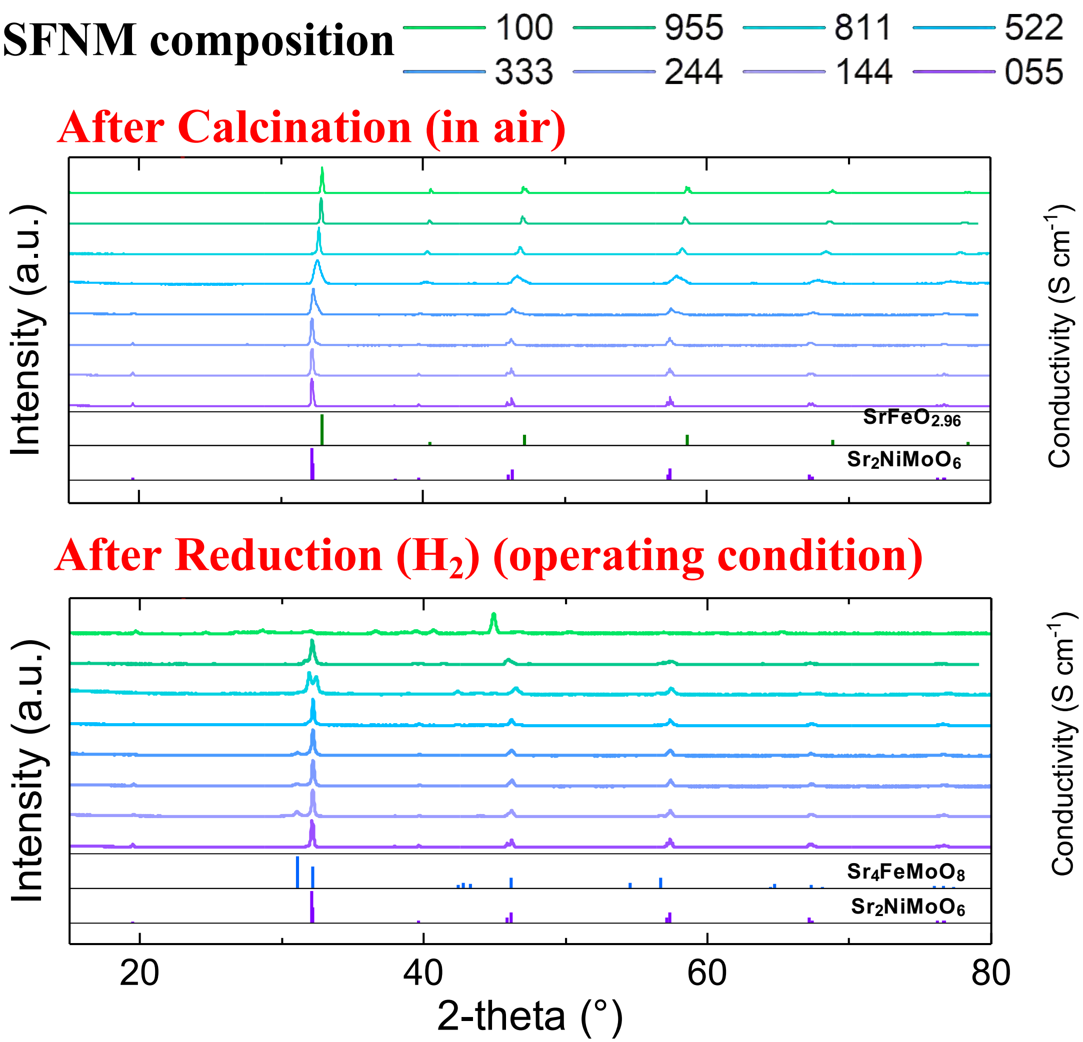
1. Development of Ceramic Anodes
   -increase intrinsic surface activity by particle exsolution

2. ALD modified Ceramic Anodes

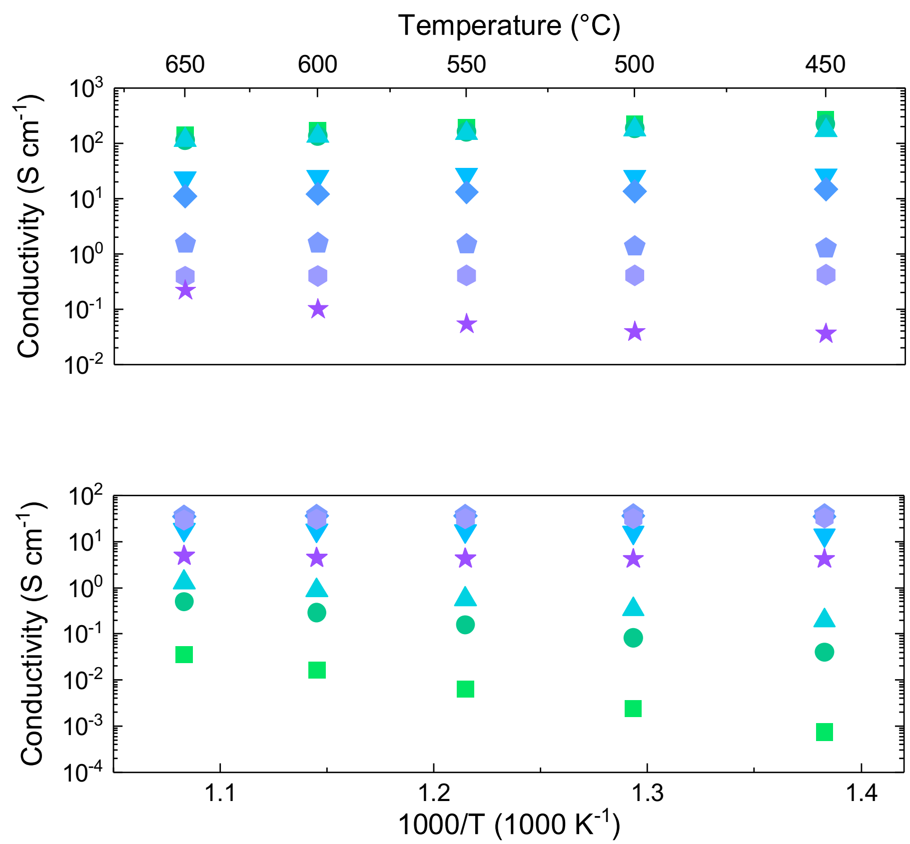
3. Solution Infiltration Modified Ceramic Anodes

4. Performance/Durability Enhancement of Surface Modified Anodes

$Sr(Fe,Ni,Mo)O_{3-\delta}$ Phase Characterization



$Sr(Fe,Ni,Mo)O_{3-\delta}$ Conductivity



- Increased doping stabilizes phase from perovskite to double perovskite.
- Highly doped SFNM is stabilized in reducing conditions with minor Ruddlesden-Popper secondary phase formation
- Heavily doped compositions retain their phase while also increase in charge carrier concentration. $\sigma > 35$ S/cm from 450-650°C

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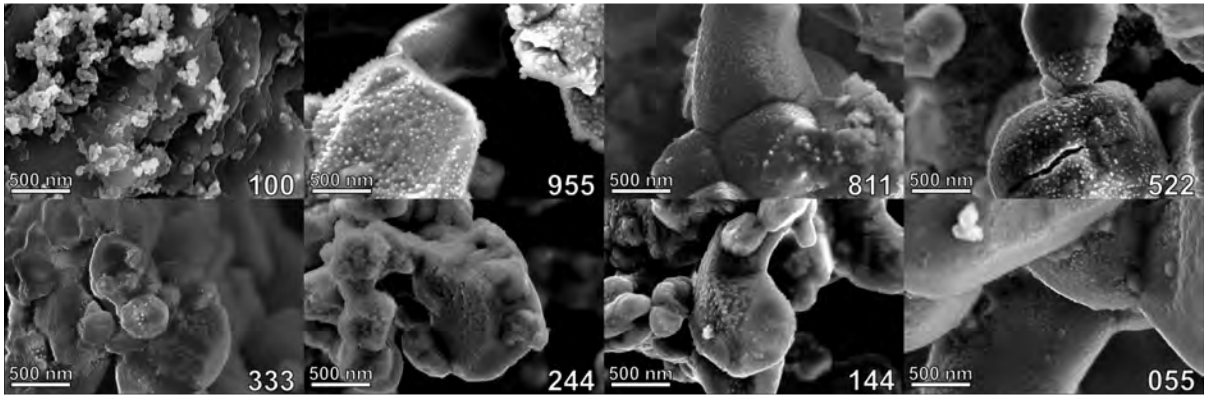
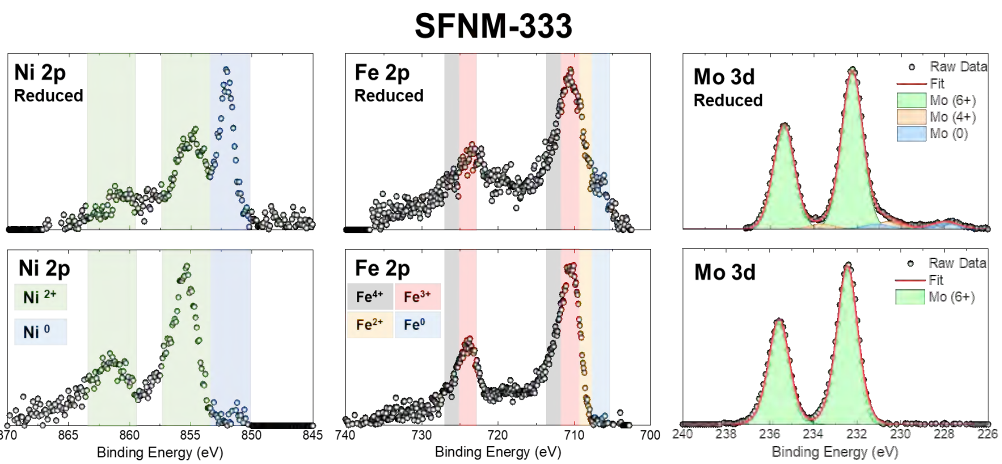
Exsolution Morphology & Composition

Surface Morphology



- Reduced at 600 °C for 24 hrs in H_2
- Exsolved particle size and spatial density are controlled by parent material composition

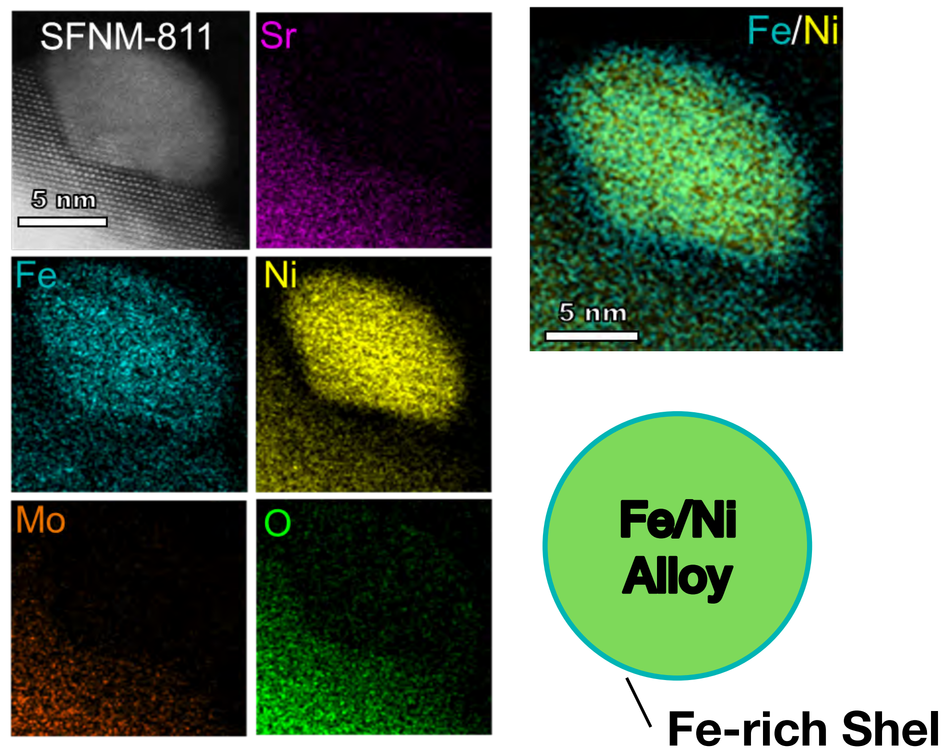
Surface Chemistry Analysis - XPS



XPS: Exsolved particles contain metallic Ni and Fe (slight Mo, depending on the SFNM composition)

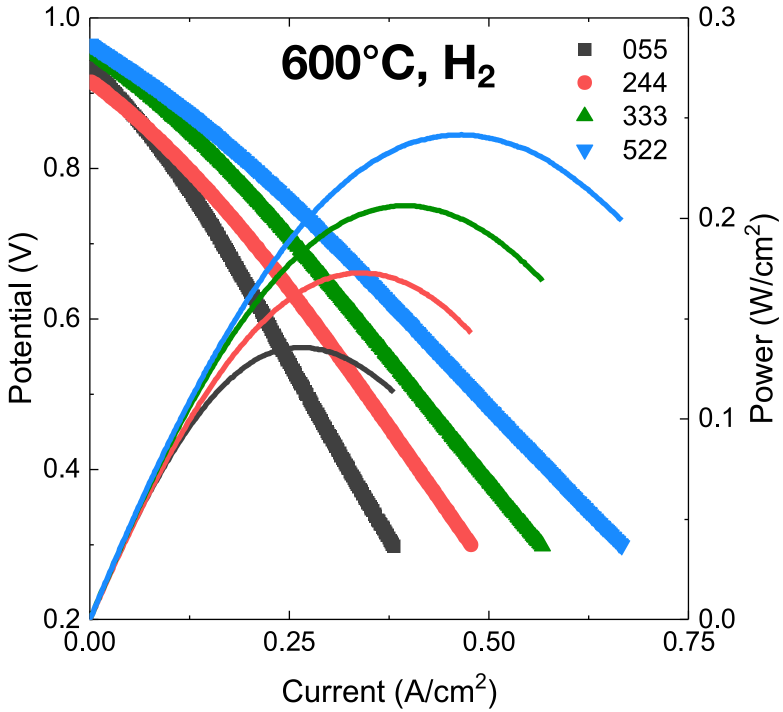
TEM: Exsolved particles have Fe-rich shell.

- TEM

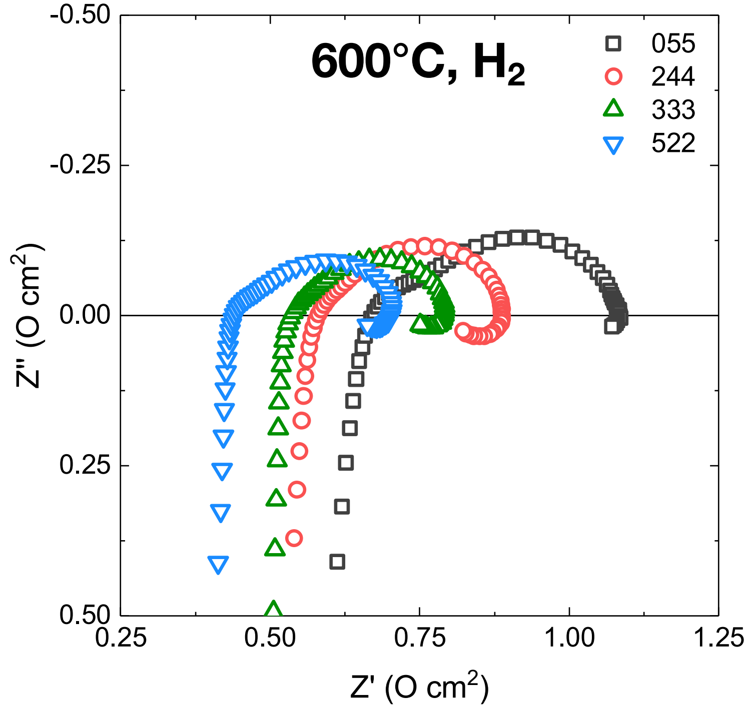


SFNM Composition Effects on Cell Performance

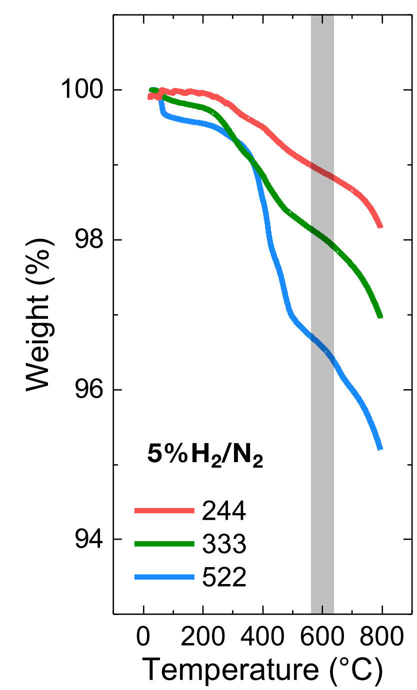
Current-Voltage Behavior



EIS at OCV

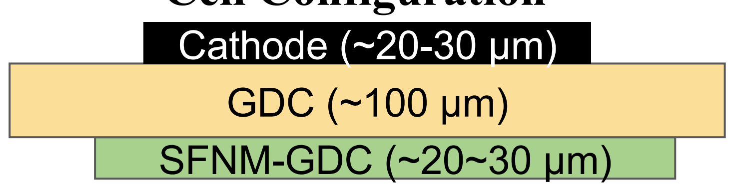


TGA



- Determined using GDC electrolyte supported cells
- Performance strongly depends on parent perovskite and exsolved particle properties

Cell Configuration



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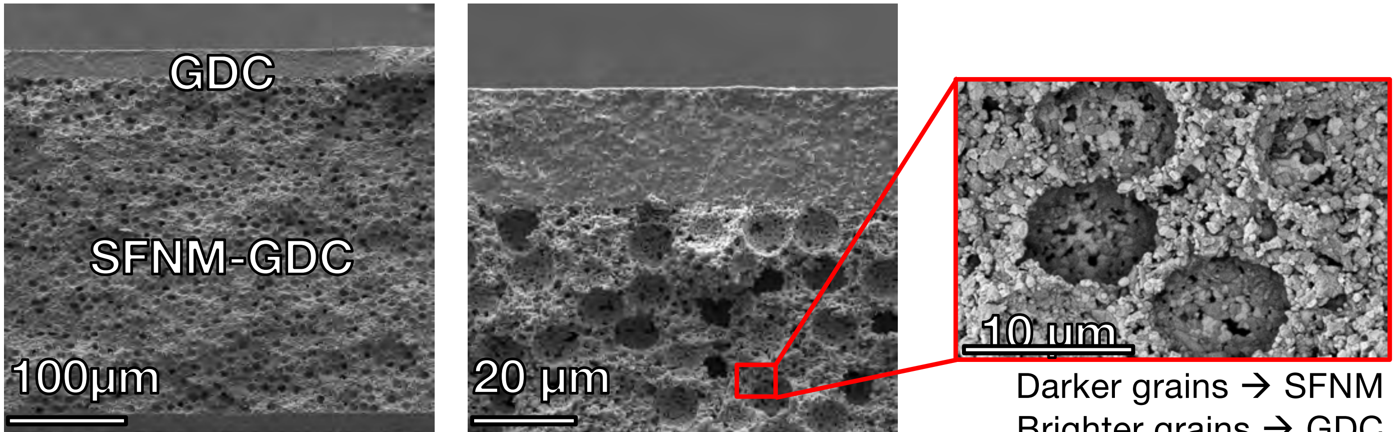
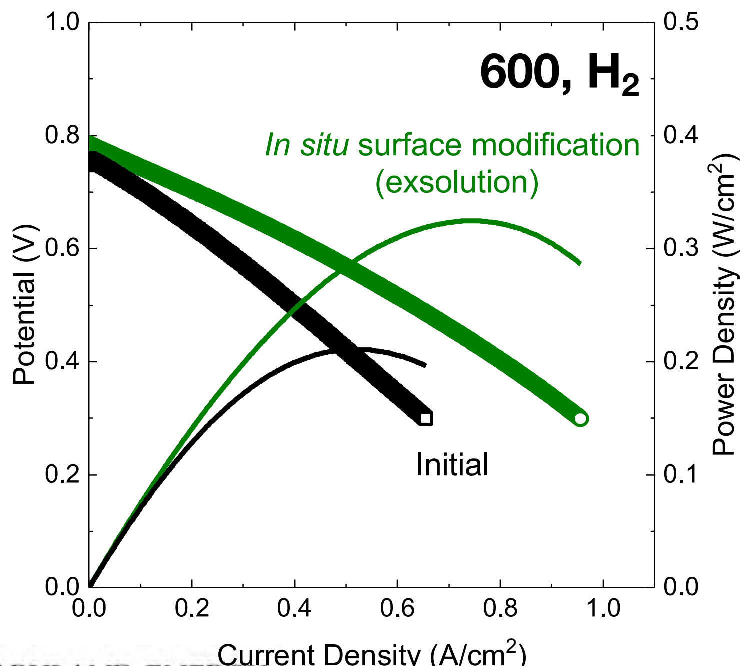
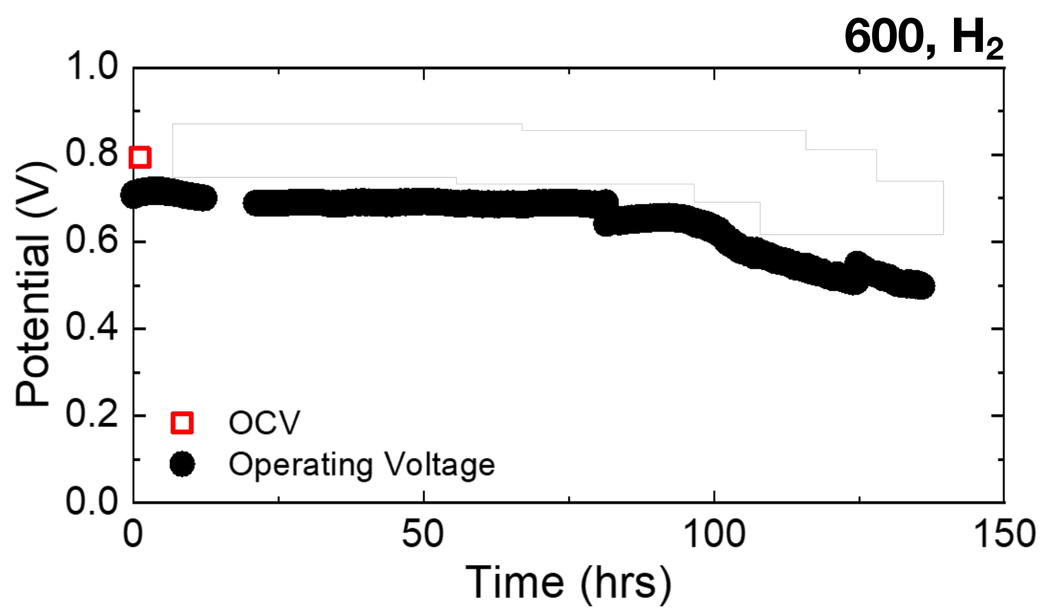
Development of SFNM Ceramic Anode Supported Cells

Cell structure: good anode-electrolyte interface



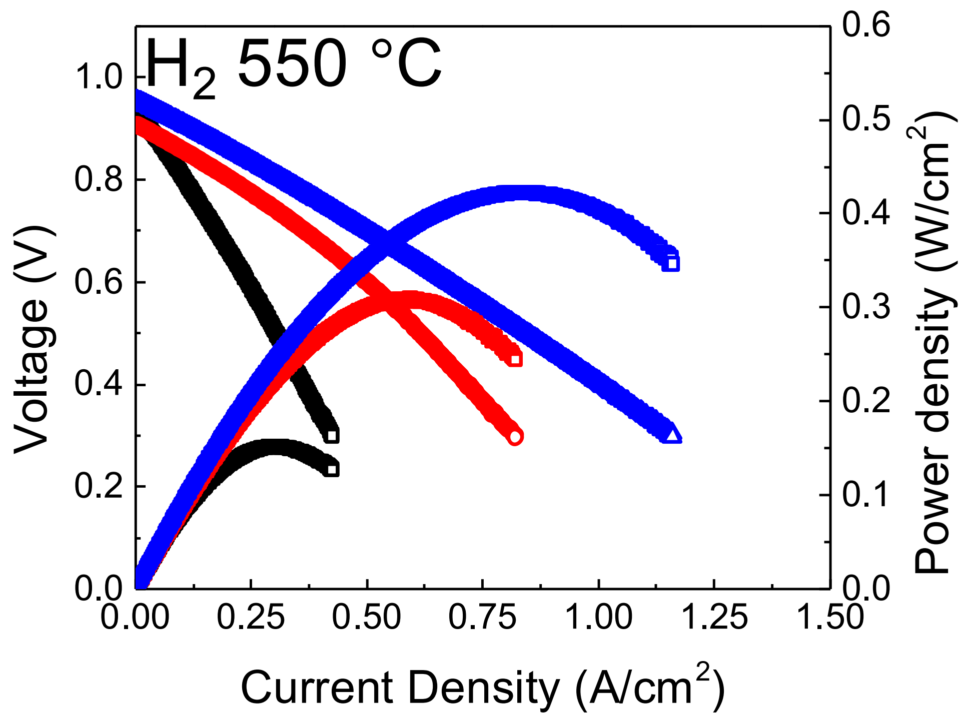
Darker grains → SFNM
Brighter grains → GDC

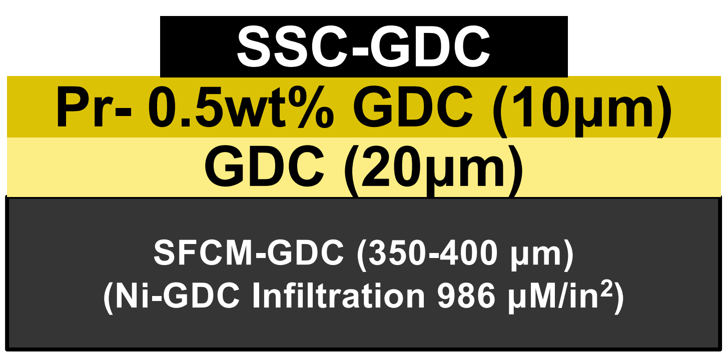




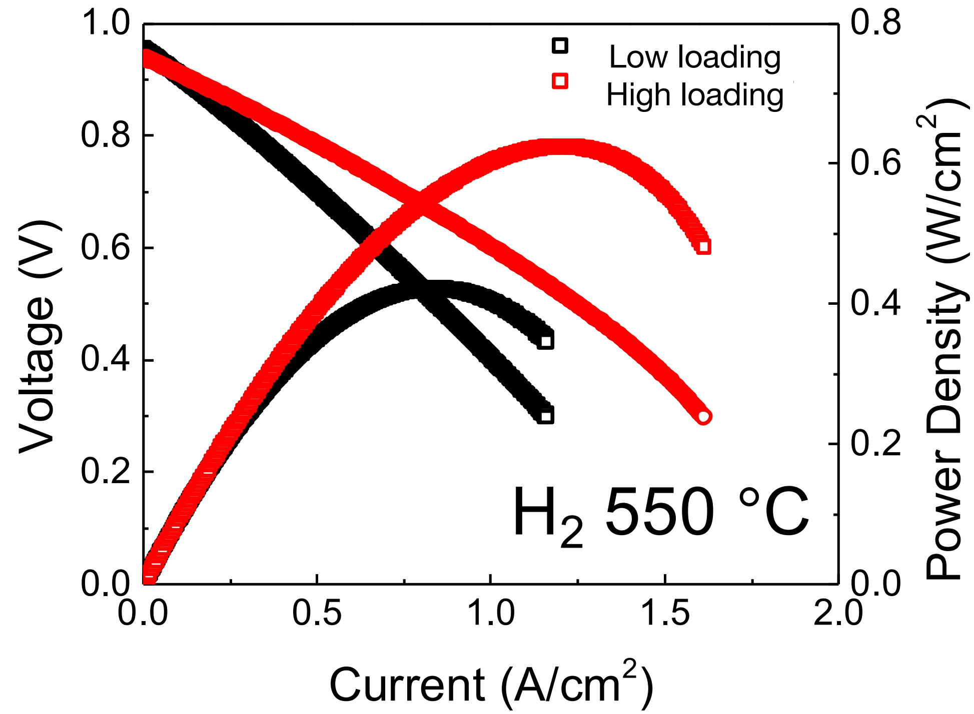
Ni-GDC Co-infiltrated SFCM Anode

Pretreatment Temperature Effect



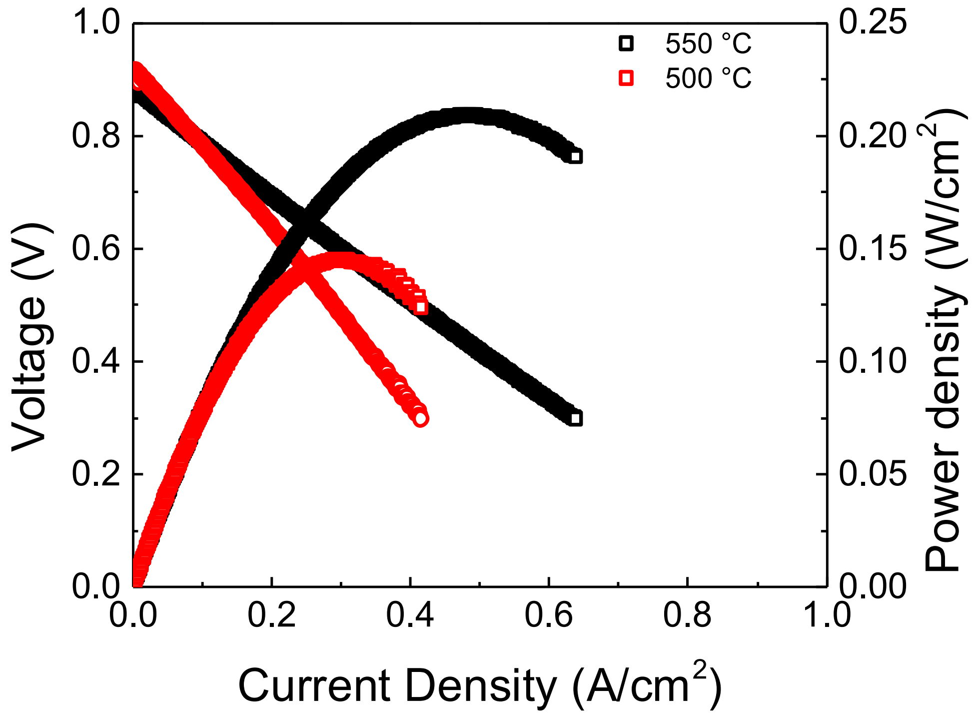


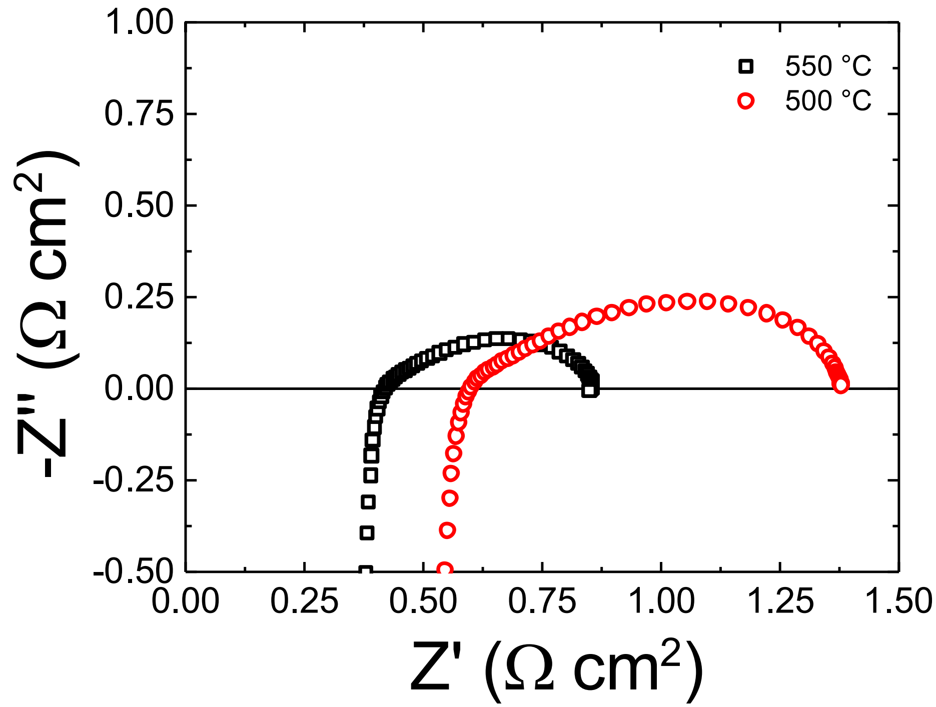
Loading Effect

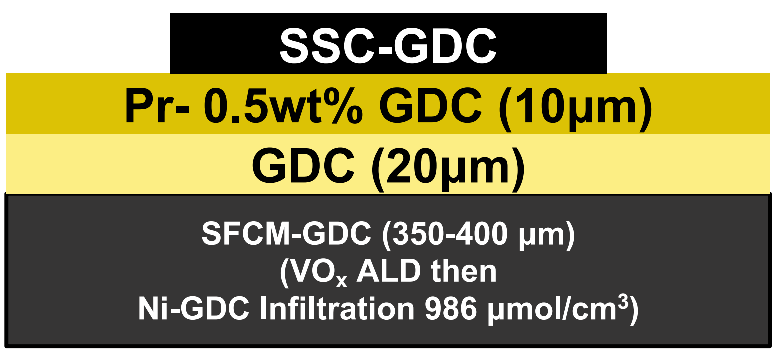


- Optimization of solution infiltration into SFCM anode
- Both loading and reduction temperature affect the performance
- Shows a peak power density over 0.6 W/cm^2 at 550 °C

VO_x ALD on SFCM-GDC Ceramic Anode

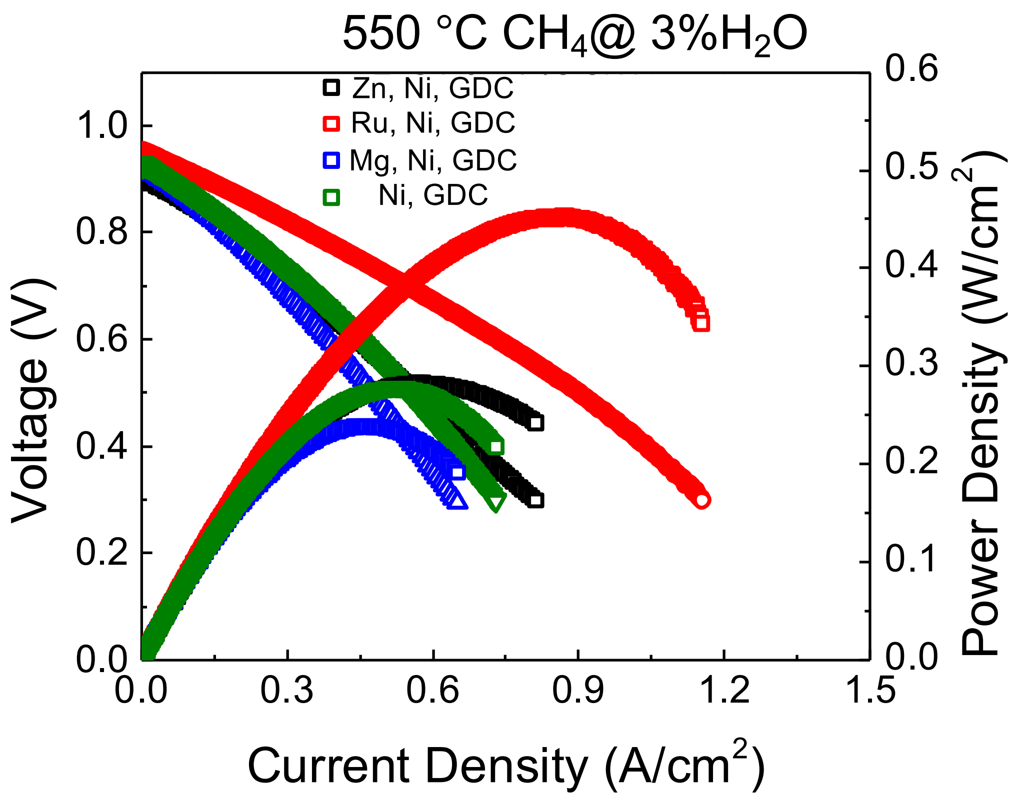






- Vanadium ALD modified SFNM ceramic anode with Ni/GDC co-infiltration
- Shows peak power density of 0.21 W/cm^2 at 550 °C

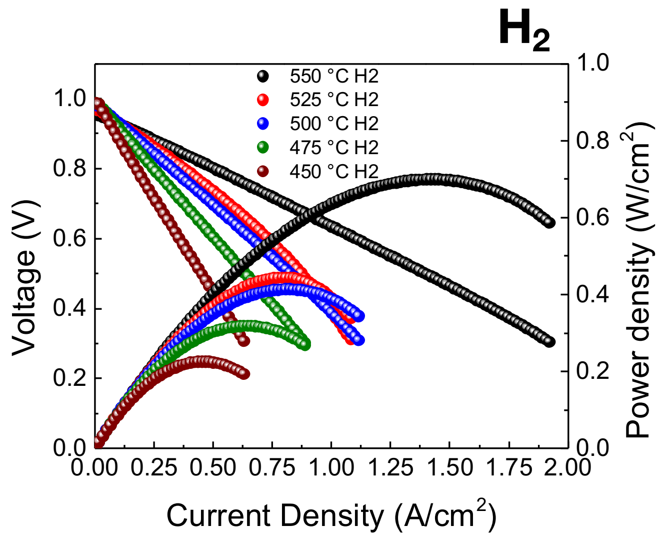
SFCM Performance in Methane

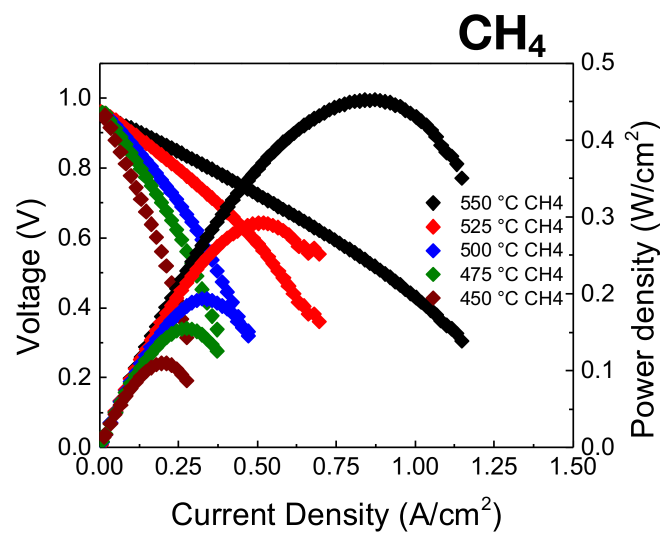


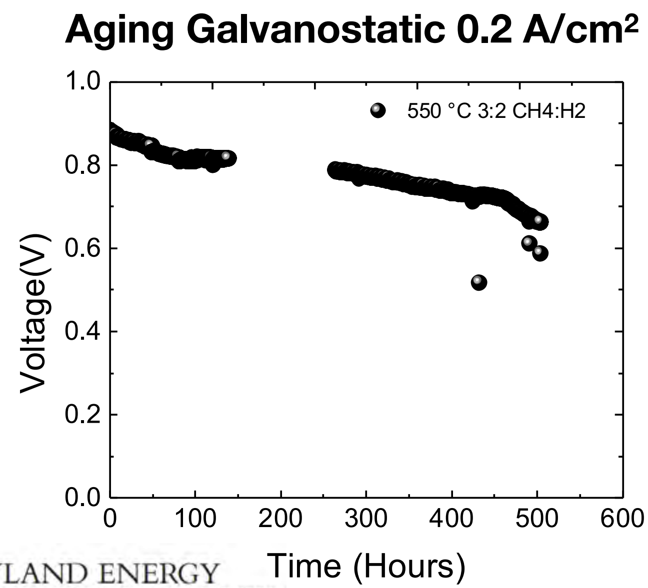
- Screened anode infiltrates
- Shows peak power density over 0.4 W/cm^2 at 600 °C in methane

SFCM Performance in Methane

Ni-Ru-GDC co-modified SFCM







Modified Ceramic Anode shows:

- Peak power density over **0.7** W/cm^2 at **550** °C in **H_2**
- Peak power density over **0.45** W/cm^2 at **550** °C in **CH_4**
- Continuous operation over 500 hours in CH_4/H_2 at **550** °C

Conclusions

Control Surface Segregation

- **Temperature**: different segregation mechanisms are observed at different temperature regimes
- **Time:** revealed the surface segregation process- (1) nucleation at grain boundaries, (2) surface migration, (3) particle growth
- ***p*O_2** : Defect chemistry of LSCF can either promote or suppress SrO segregation.
- ***p*CO_2** : Promotes the nucleation step, and suppress the particle growth
- **A-site Stoichiometry**: Suppress SrO segregation but no impact on preventing CO_2 induced phase segregation
- **Perovskite Composition**: Significantly affected segregated cations and mechanism

ALD Modified Cathodes

- Different elements show different effects on the cathode electrochemical performance
- Ti improved LSCF cathode ASR but V coated cell does not show any improvement
- Annealing conditions of ALD coatings affect electrochemical performance
- Demonstrated the ALD impact on both cathode and anode modification

Conclusions

Solution Infiltrated Cathodes

- The non-ohmic area specific resistance can be reduced by ~1 order of magnitude.
- The increase in surface electrocatalyst loading could result in the blocking effect.
- Modified cathodes show enhanced performance and durability (over 2000 hrs in full cells).
- Also increases CO_2 tolerance.

Self Assembled Exsolved Nanoparticles on Ceramic Anodes

- The parent material SFNM composition directly controls the exsolved particle size/density/composition.
- A core/shell structure of exsolved particles can be achieved by tuning material composition.
- Shows promising performance < 600 °C

Solution Infiltrated Anodes

- Demonstrated multiple factors can affect the properties of infiltrated ceramic anodes.
- Peak power density over 0.7 W/cm^2 at 550 °C in H_2
- Peak power density over 0.45 W/cm^2 at 550 °C in methane
- Stability increased over 500 hours

Future Work

- Integrate the optimized cathode and anode to full cells

  - We demonstrated promising full cell results and plan to optimize the modification process.

- Post-testing characterization on surface modified SOFCs

  - We will perform post-modern chemical, structural characterization to provide feedback on the surface modified electrodes.

Publications & Presentations

"Performance and Durability Enhancement for Low-Temperature Solid Oxide Fuel Cells via Surface Chemistry Modification," I.A. Robinson, Y.L. Huang, S. Horlick, A.M. Hussain, A. Pesaran, and E.D. Wachsman, submitted (2020).

"Understanding Strontium Segregation on $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$," E. Ostrovskiy, Y.L. Huang, E.D. Wachsman, in preparation, (2020).

"Mitigating Electronic Conduction in Ceria-based Electrolytes via External Structure Design," I.A. Robinson, Y.L. Huang, S. Horlick, J. Obenland, N. Robinson, J. Gritton, A.M. Hussain, and E.D. Wachsman in preparation, (2020).

"Understanding and Controlling Exsolution kinetics on $SrFe(Ni,Mo)O_3$," S.A Horlick, Y.L. Huang, I.A. Robinson, and E.D. Wachsman in preparation, (2020).