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

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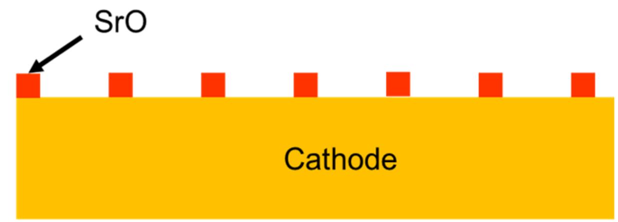
May 1, 2019

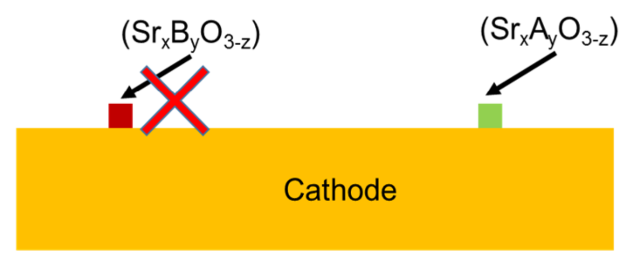
Project Objectives

- Control cathode and anode surface stoichiometry
- Correlate catalytic activity through surface defect chemistry
- Quantify degradation rates/performance and reveal the underlying mechanisms on tuned stoichiometric electrodes
- Utilize thermodynamics to minimize phase segregation (e.g., $SrO/SrCO_3$) in cathodes and advanced ceramic anodes
- Develop cost-effective and scalable techniques to modify the electrode surface stoichiometry for enhanced performance and long-term stability

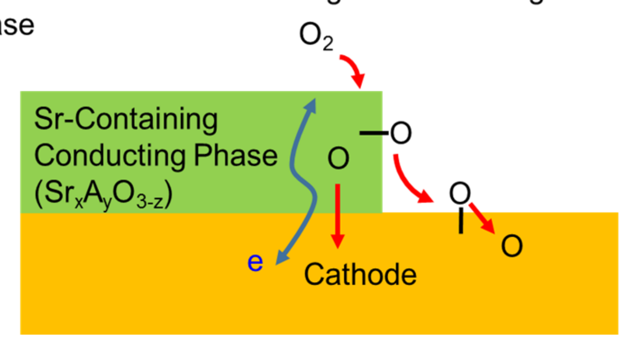
(a) Self-assembled or controlled SrO segregation



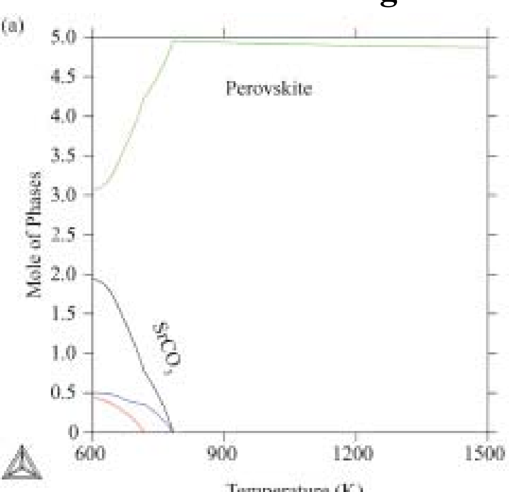
(b) Introduce transition metal dopants to achieve either insulating or conducting phases



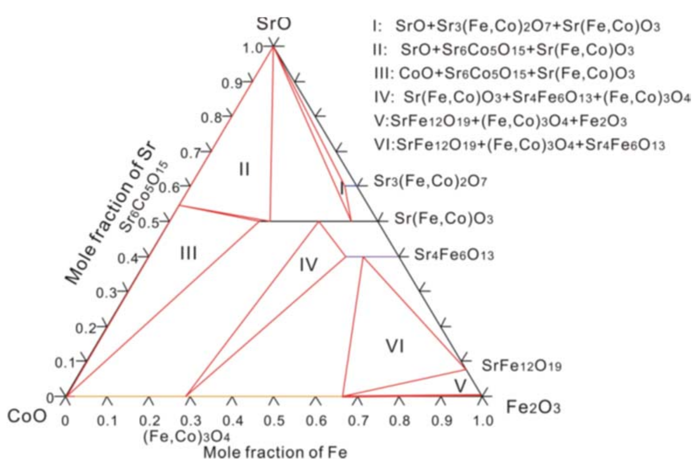
(c) The ORR is enhanced through Sr-containing phase



SrO-LSCF Phase Diagram



Sr-Co-Fe-O Phase Diagram



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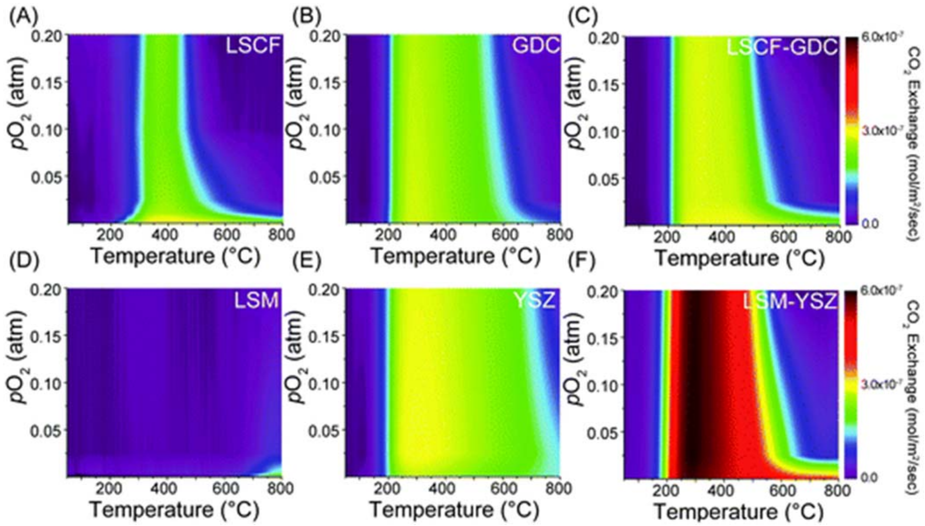
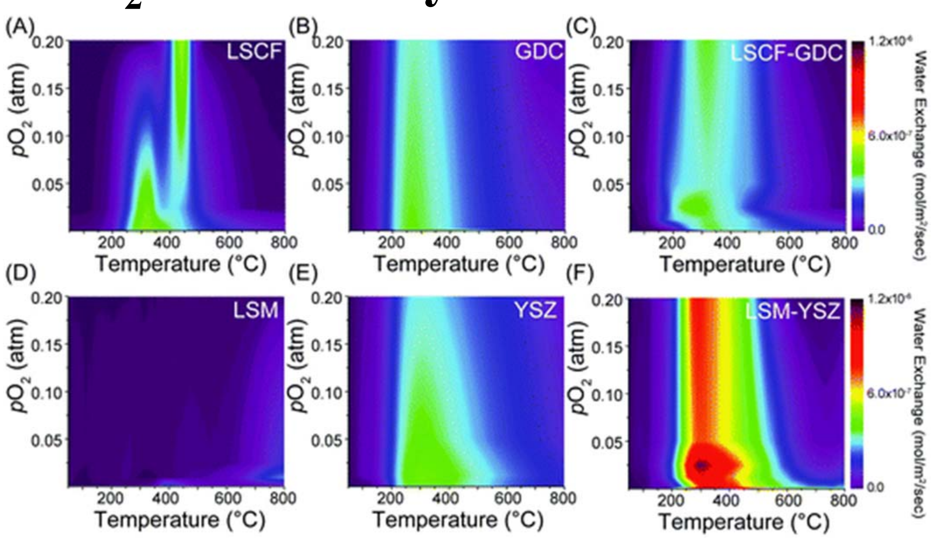
Zhang, W.-W.; Chen, M.; Povoden-Karadeniz, E.; Hendriksen, P. V. *Solid State Ionics* 2016, 292, 88-97.
Darvish, S.; Gopalan, S.; Zhong, Y. *Journal of Power Sources* 2016, 336, 351-359.

Surface Reactivity and Surface Cation Segregation

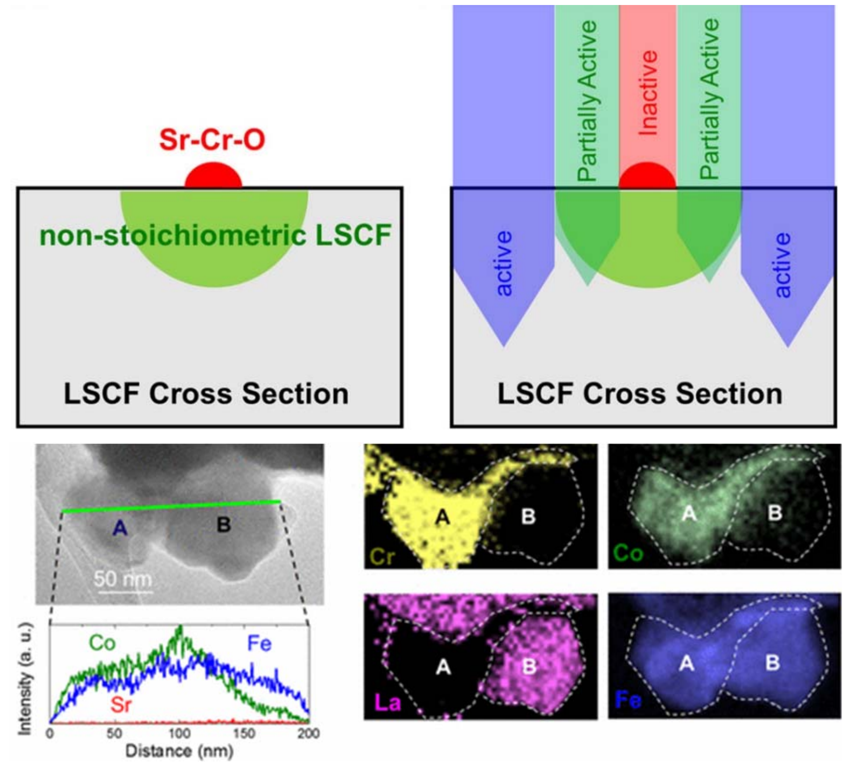
CO_2 Reactivity



H_2O Reactivity



Y.-L. Huang, C Pellegrinelli, A Geller, SC Liou, A Jarry, L Wang, Y Yu, H. Bluhm, E. J. Crumlin, K. J Gaskell, B. W. Eichhorn, E. D Wachsman, *Energy & Environmental Science*, **10**, 919-923 (2017)



Y.-L. Huang, A. M. Hussain, C. Pellegrinelli, C. Xiong and E. D. Wachsman, *ACS Applied Materials & Interfaces*, **9**, 16660-16668 (2017).

- CO_2 and H_2O reactivity on cathodes indicate surface carbonate & hydroxide formation impacts O_2 exchange
- Oxygen transport can be divided into three surface pathways:
  1. Electrochemically inactive pathway (Sr–Cr–O secondary phase)
  2. Partially active pathway (effective region)
  3. Normal active pathway.

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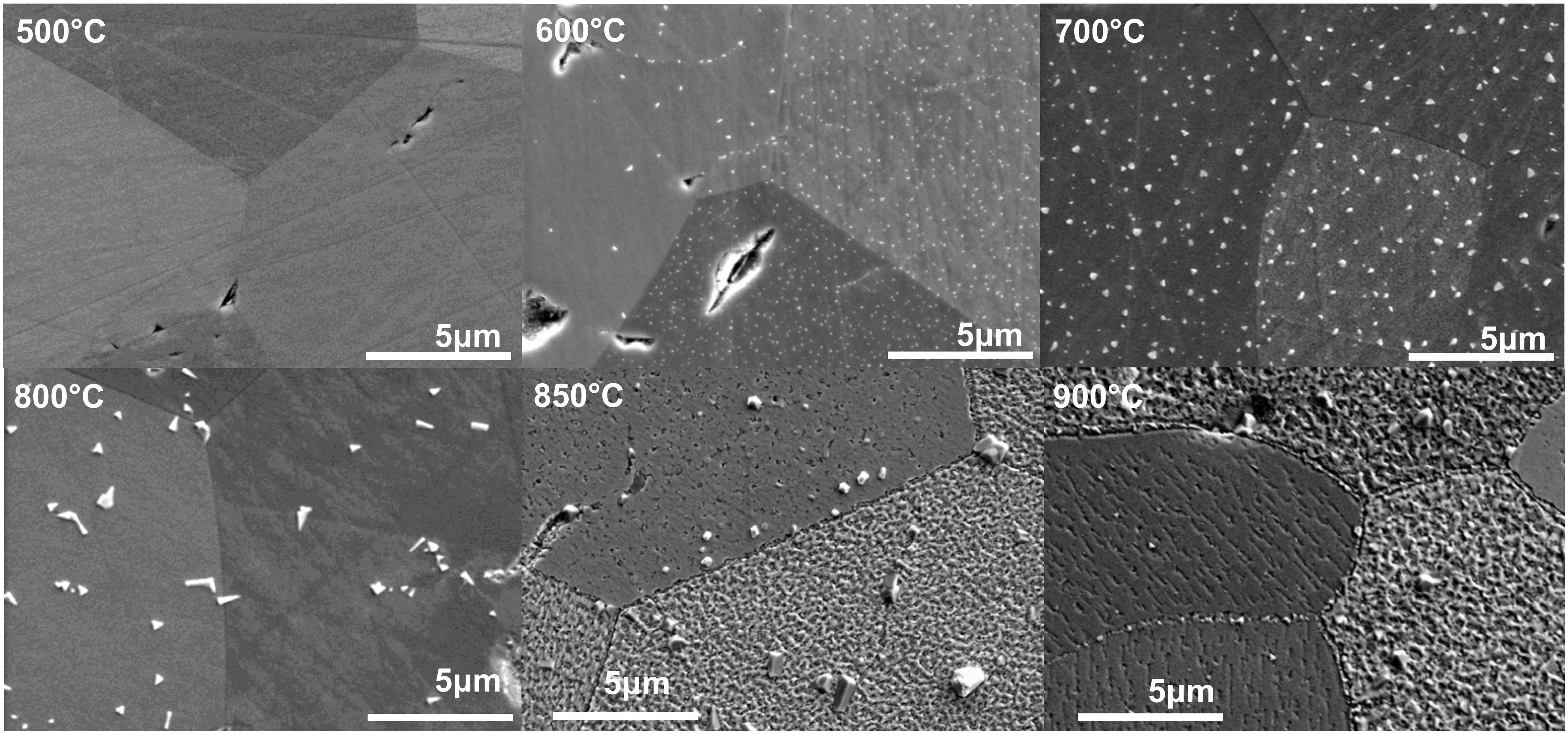
Temperature Effect on LSCF Surface Segregation

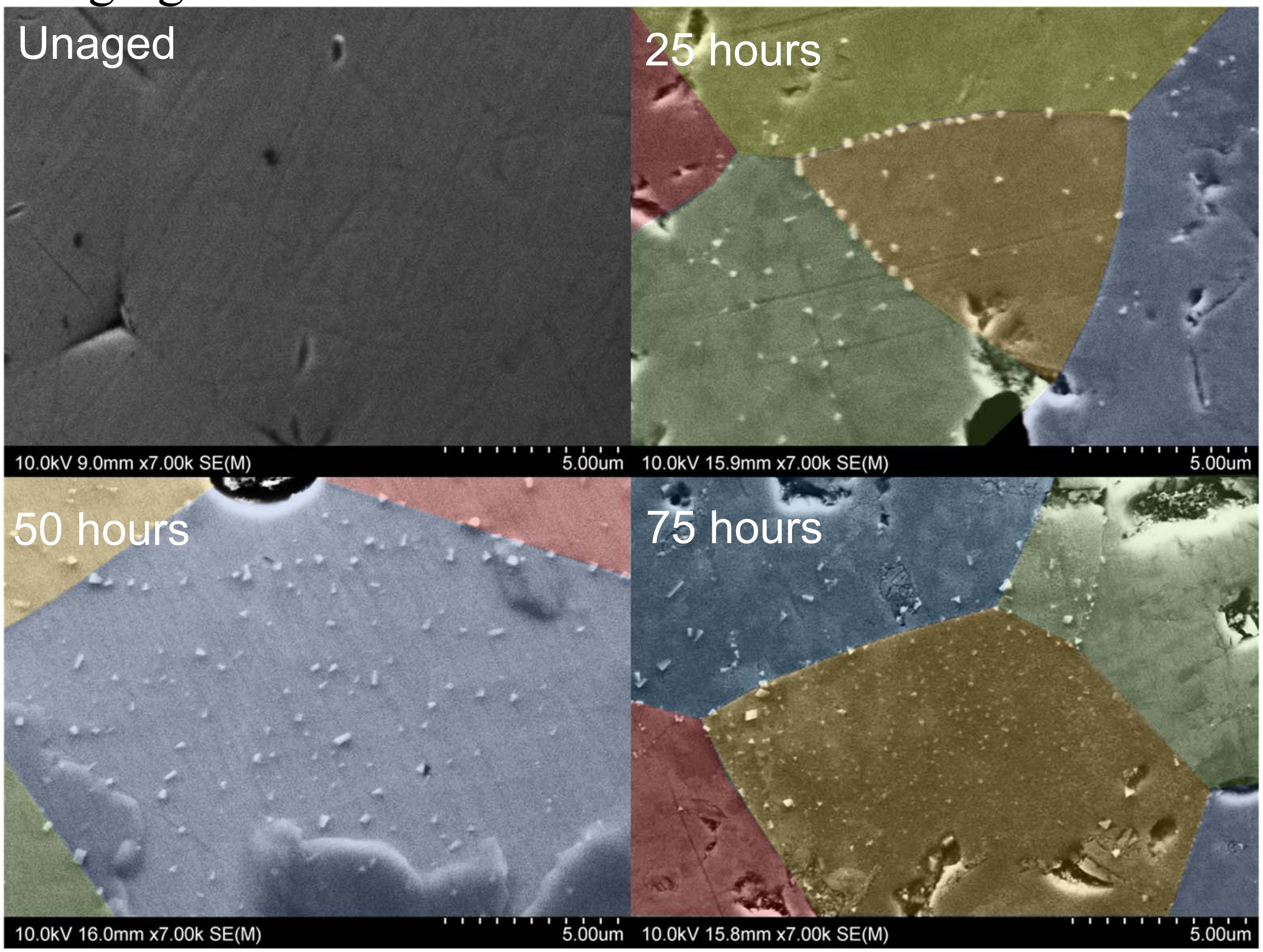
Aging of Dense LSCF Surface in Synthetic Air for 25 hrs



- Increase in temperature promotes surface SrO precipitation (size, numbers)
- Different mechanism observed at >850 °C, porous surface and grain orientation dependence.

Time Effect on LSCF Surface Segregation

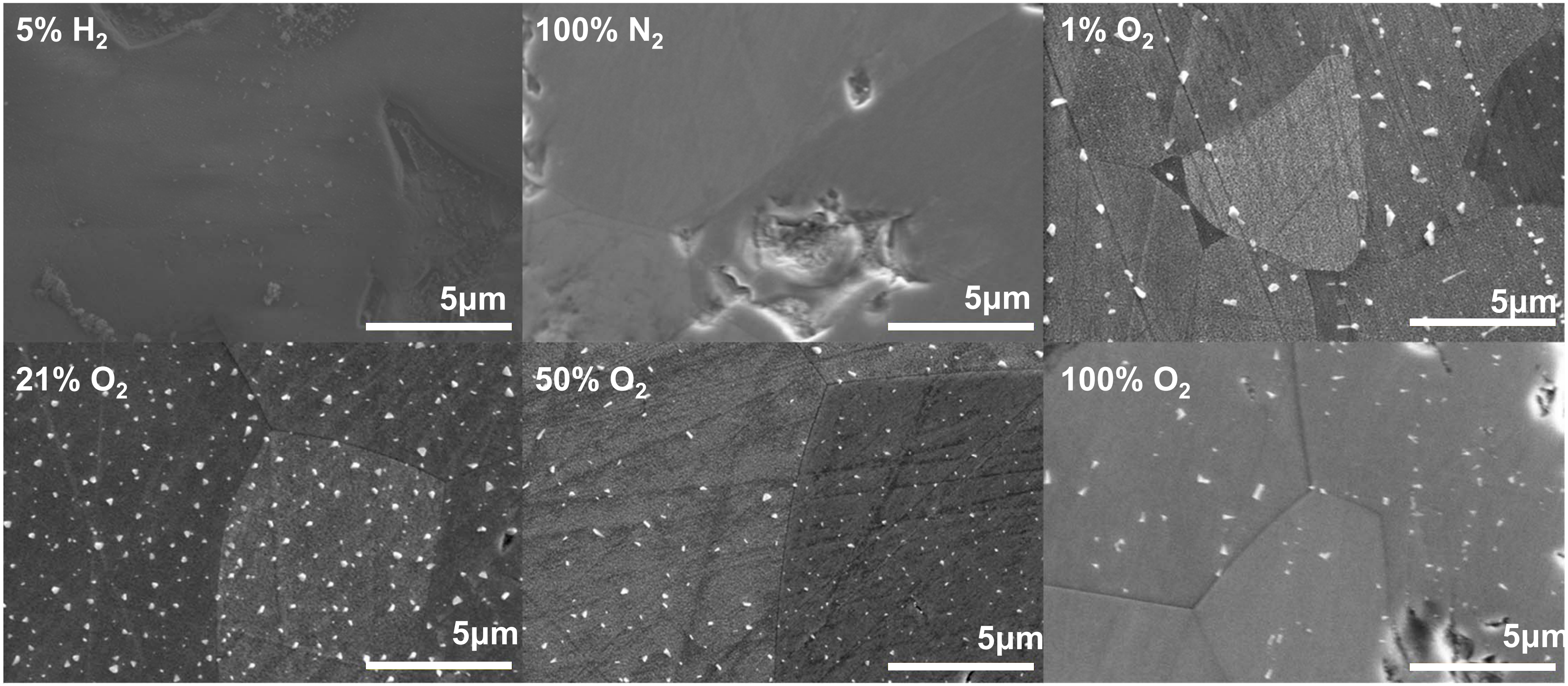
Aging of Dense LSCF Surface at **800 °C** in Static Air



- Different grains color highlighted
- Segregation Process: SrO nucleates at grain boundaries and then migrates to grain center.

pO_2 Effect on LSCF Surface Segregation

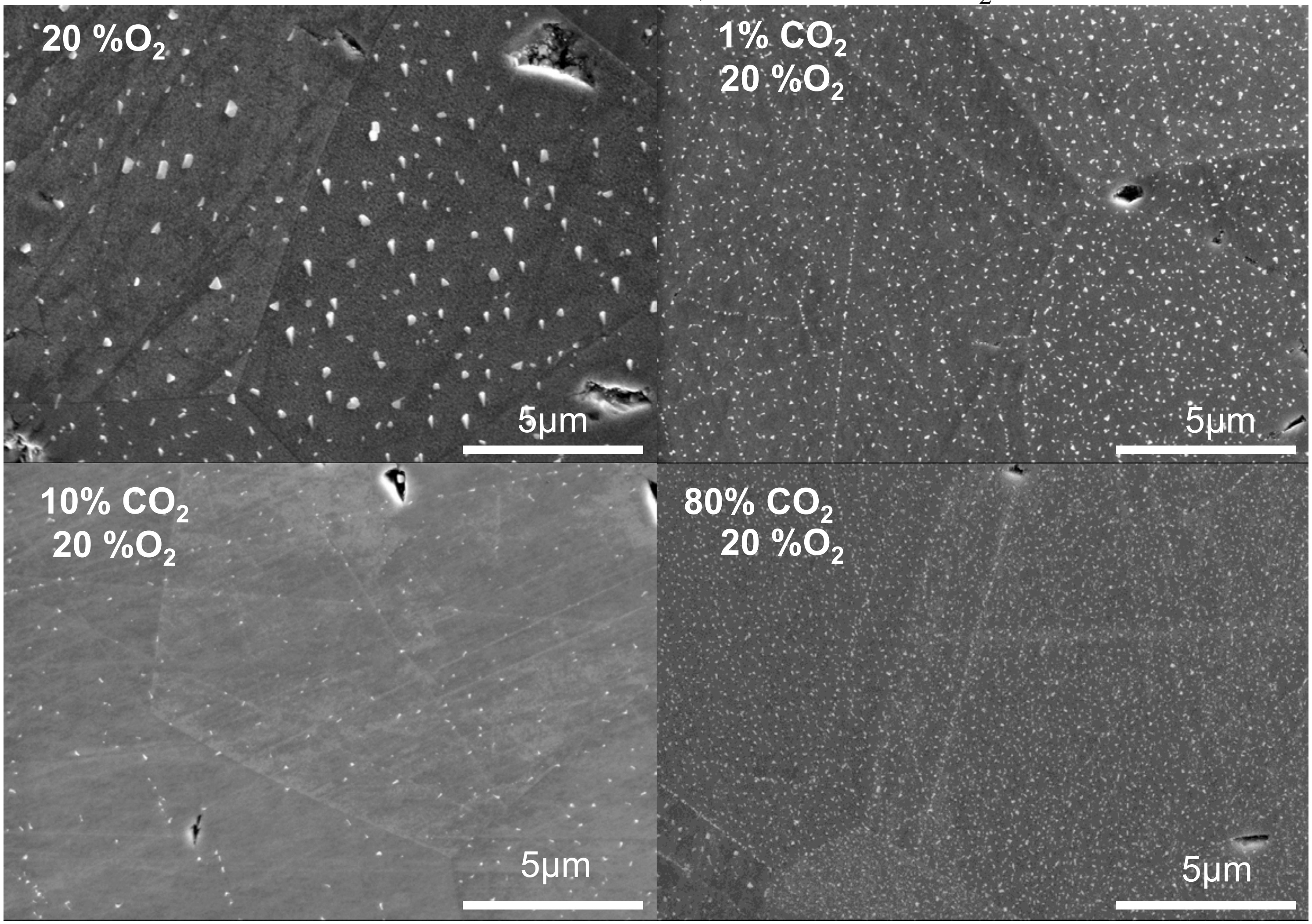
Aging of Dense LSCF Surface at **700 °C** for 25 hrs



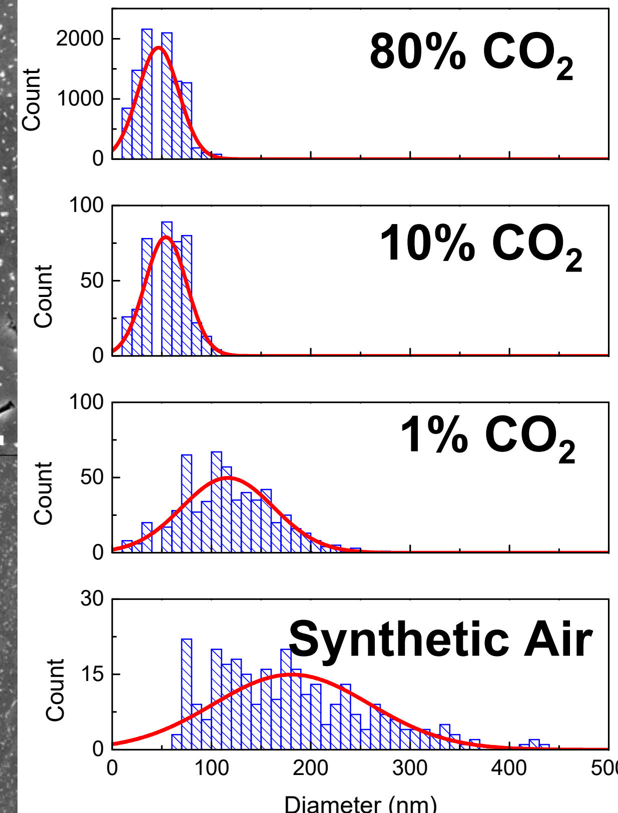
- Increase in *p*O_2 first promotes SrO segregation up to ~21%
- However, further increase in *p*O_2 supresses SrO segregation
- Likely correlate to defect chemistry of LSCF

pCO_2 Effect on LSCF Surface Segregation

700 ° C for 25 hrs, balanced with N_2

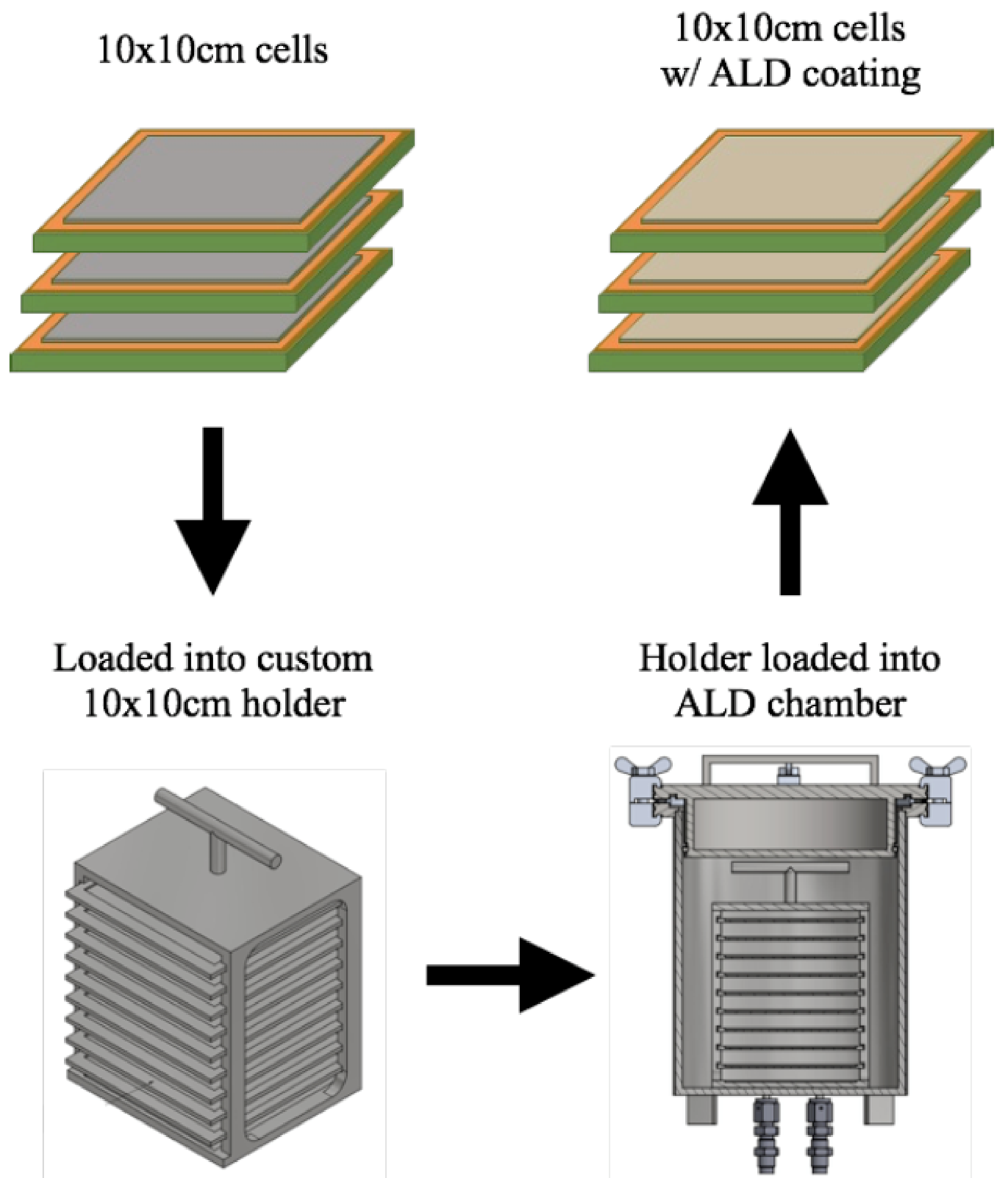


Particle Size Distribution



- Increase in *p*CO_2 decreases precipitate particle size and increases particle number.
- Promotes nucleation and suppress particle migration/growth.

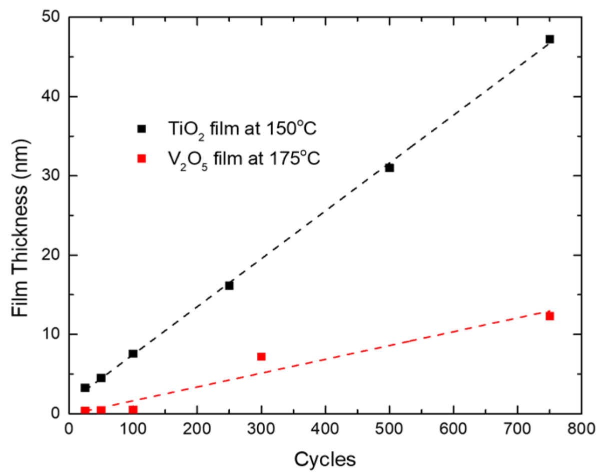
ALD of MO_x Electrocatalysts



Custom ALD system capable of multiple 10 cm x 10 cm cells

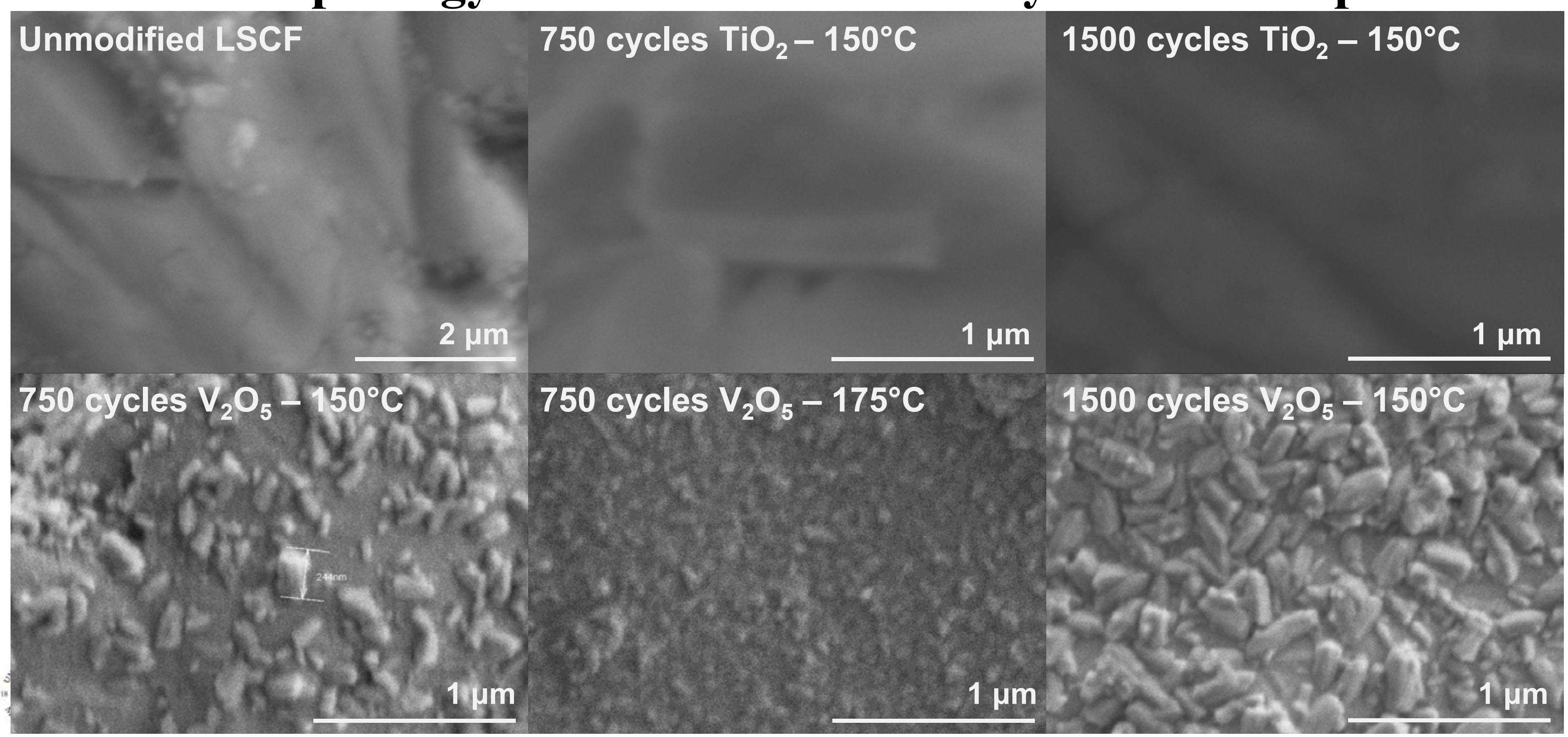
TiO_x and VO_x ALD Surface Modification of LSCF

Growth Rate Calibration



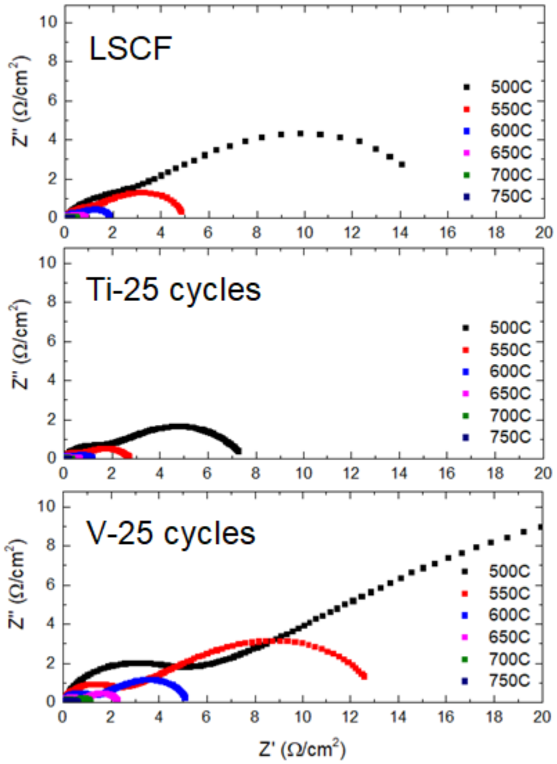
- ALD deposited TiO_x and VO_x to form $SrTiO_x$ and $SrVO_x$
- Growth Rate per ALD cycle shows clear linear trend for Ti but not V
- ALD deposition on sintered LSCF surface shows uniform deposition of Ti but not V

Surface Morphology as a function of ALD cycles and temperatures

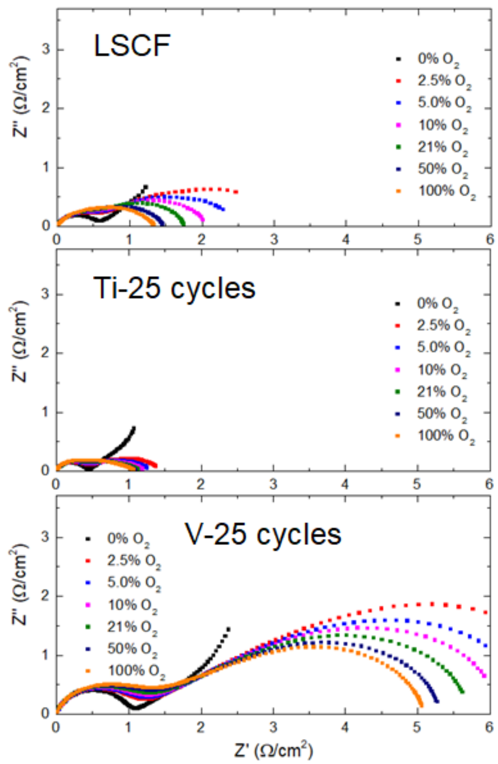


Electrochemical Performance of ALD Modified LSCF-GDC

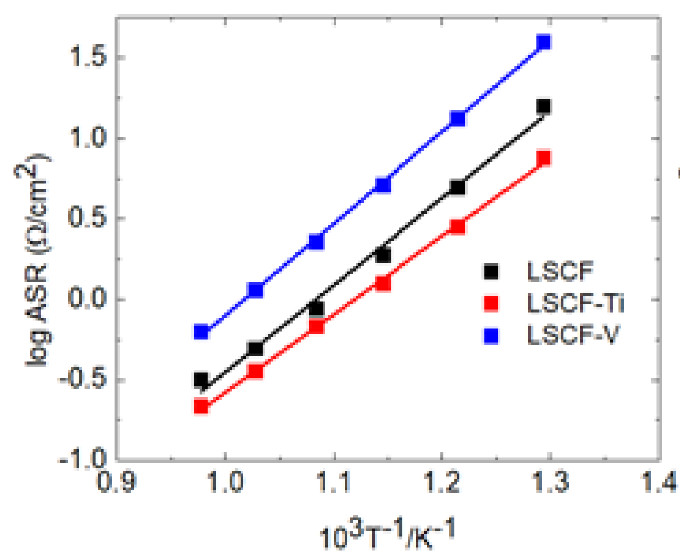
Temperature Dependence

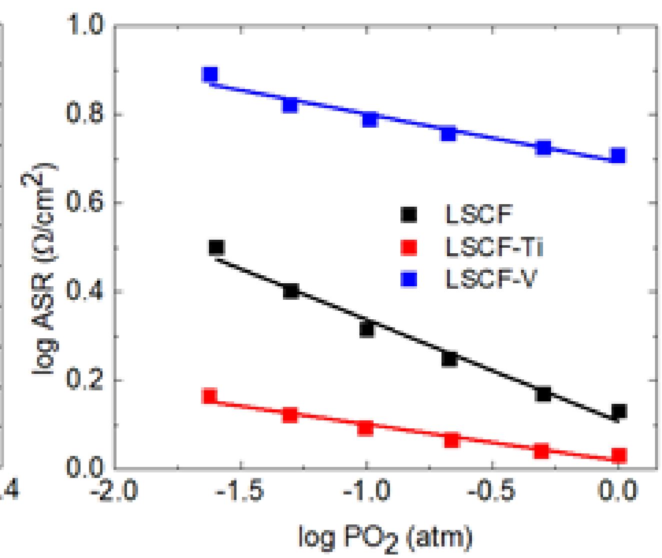


***p*O$_2$ Dependence**

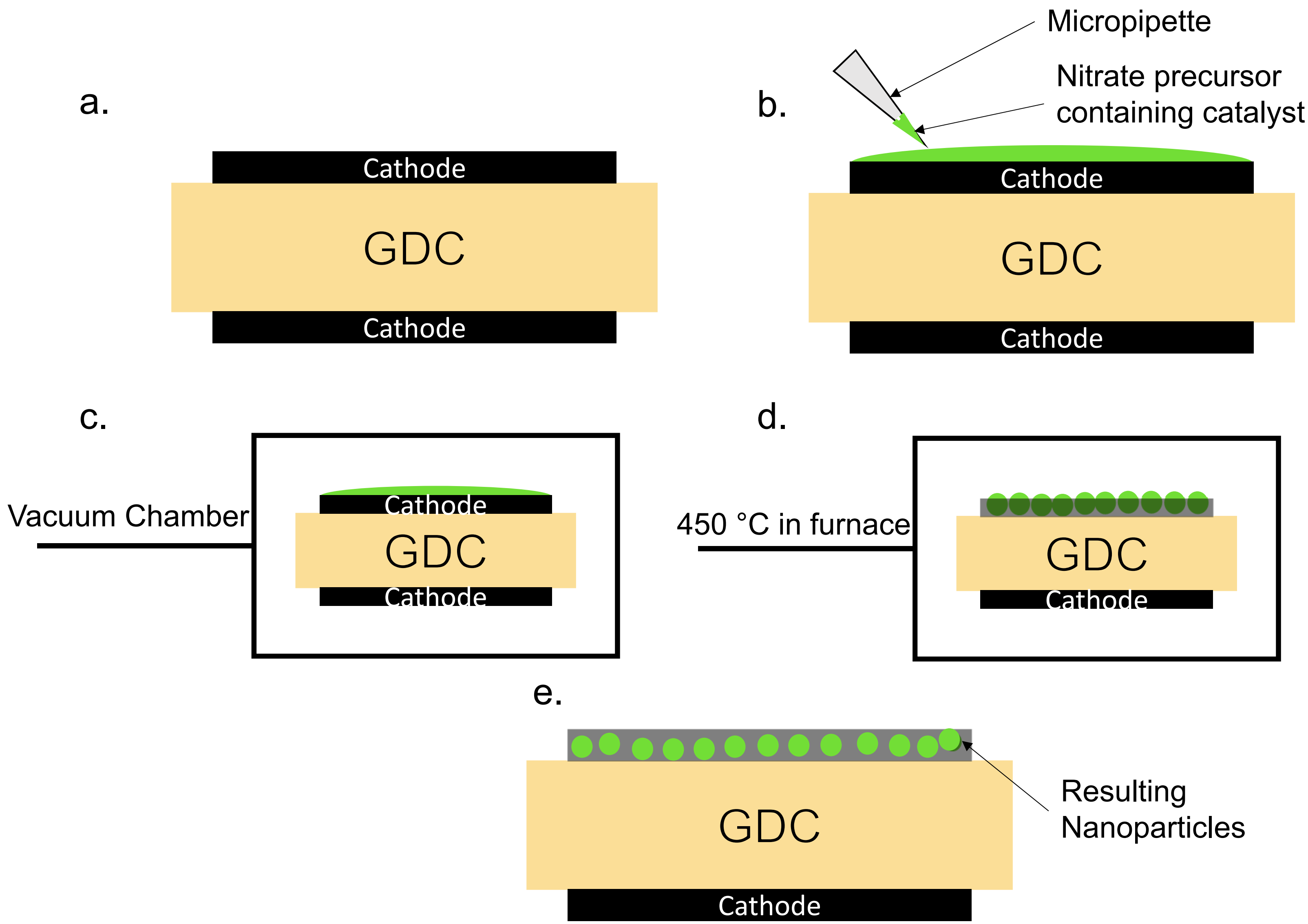


- ALD of Ti significantly lowered LSCF cathode impedance for all temperatures and *p*O$_2$ investigated while V increased it

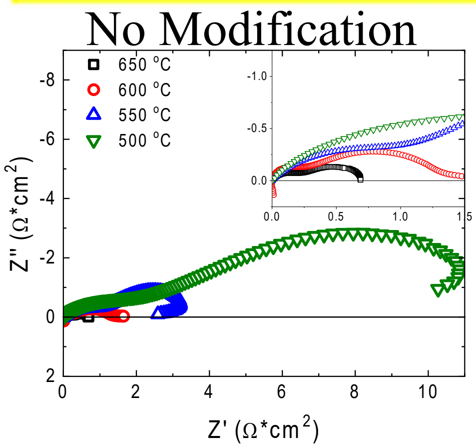


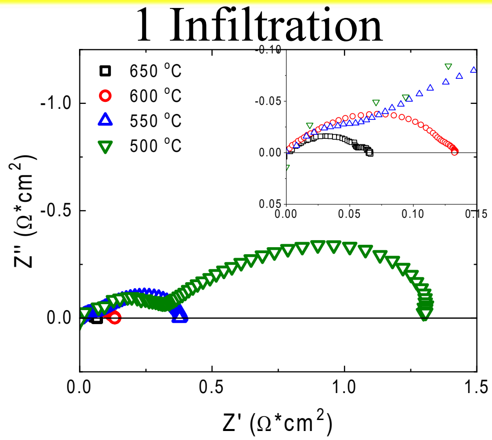


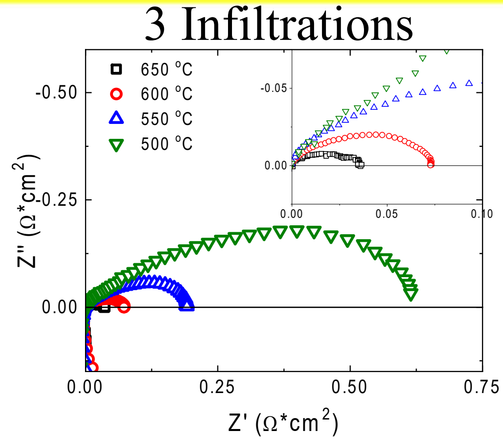
Solution Infiltration of MO_x Electrocatalysts

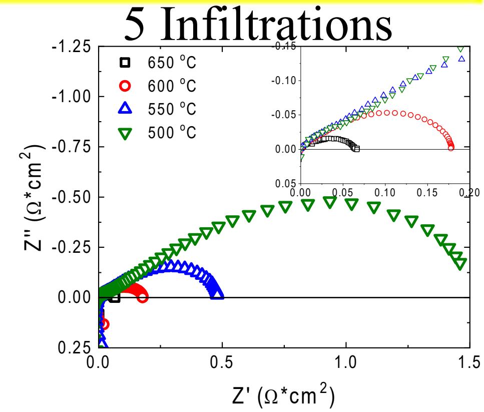


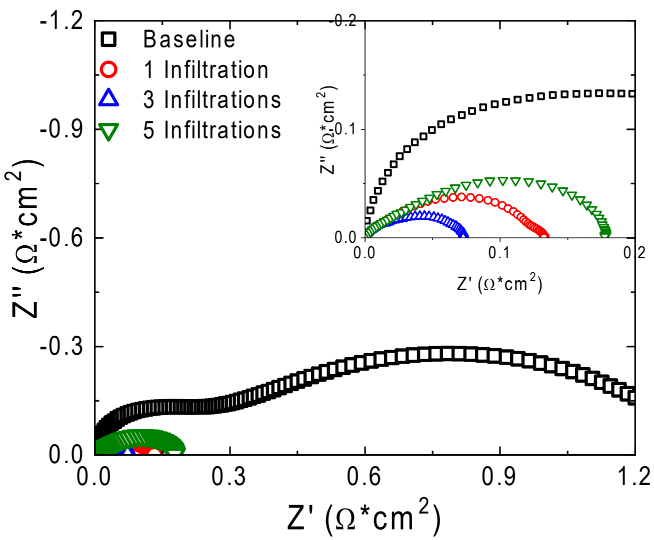
Solution Infiltration of MO_x Electrocatalysts

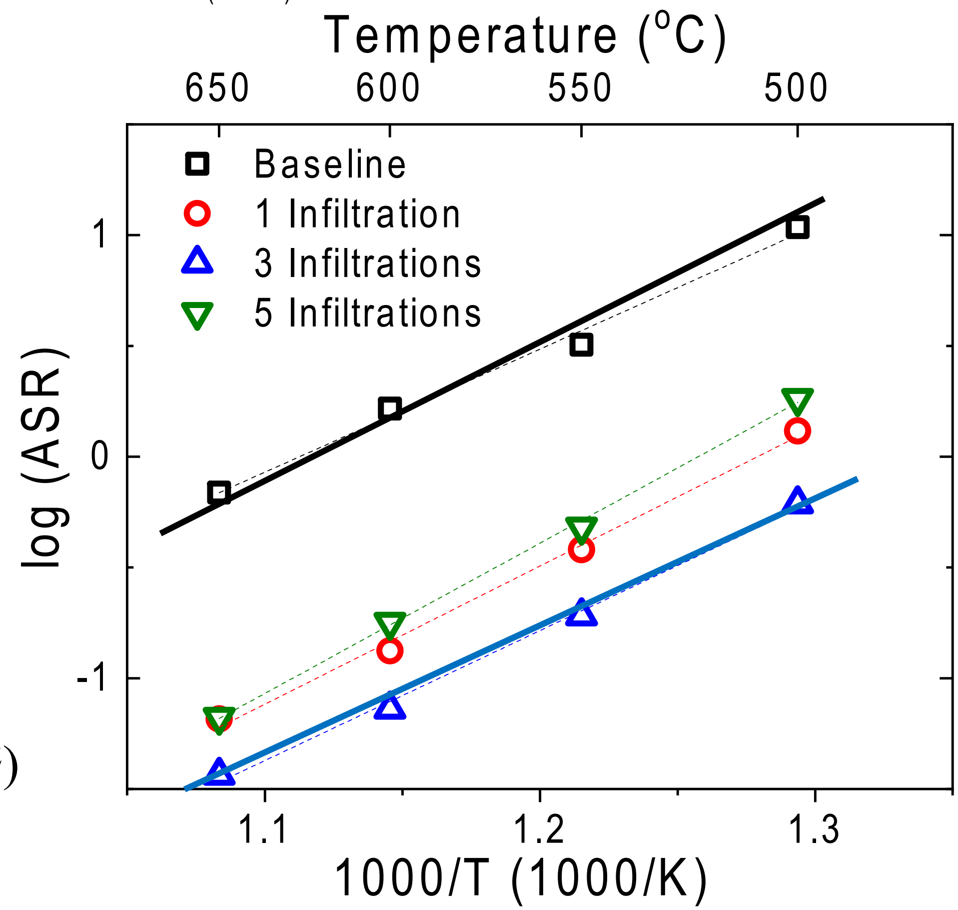










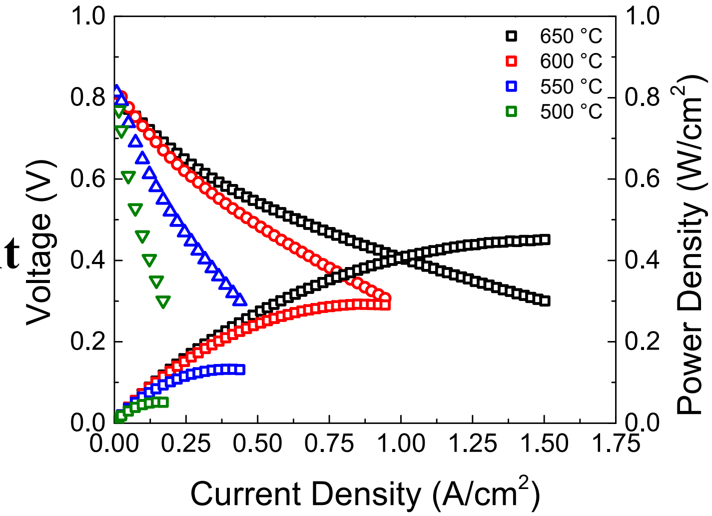


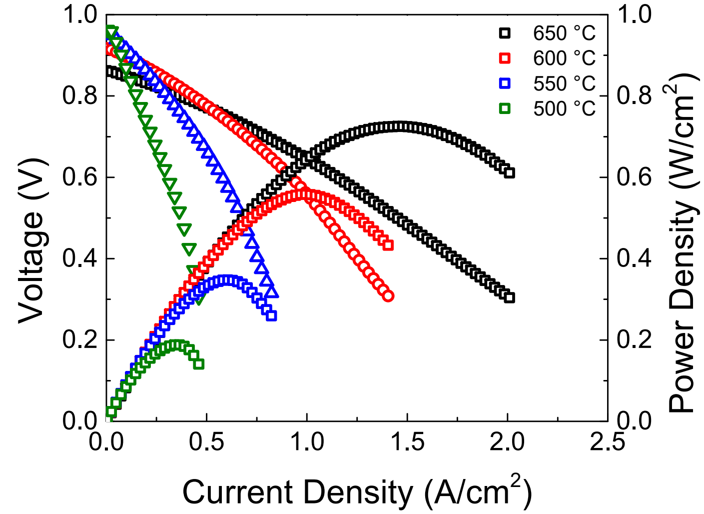
- Modification reduced ASR by order of magnitude
- 3 Infiltrations showed best improvement ASR @ 600 °C of 0.073 Ω cm^2 (unmodified cell 1.64 Ω cm^2)
- Higher loading eventually blocks active sites.

MO_x Surface Modified SOFC Performance

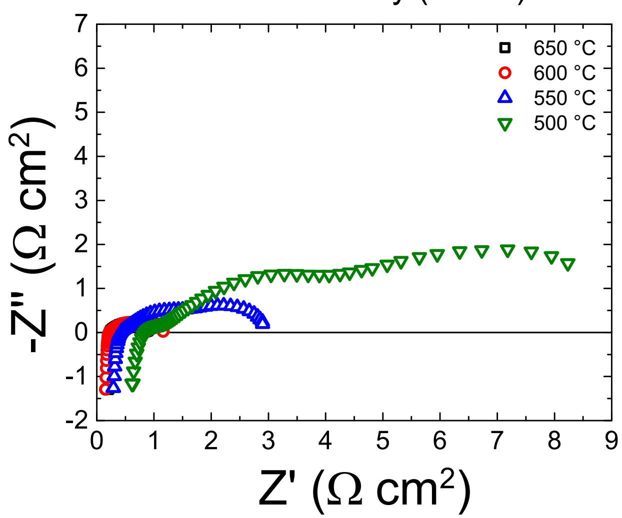
Baseline Cell: LSCF-GDC/GDC/Ni-GDC | **Cathode Modified Cell**

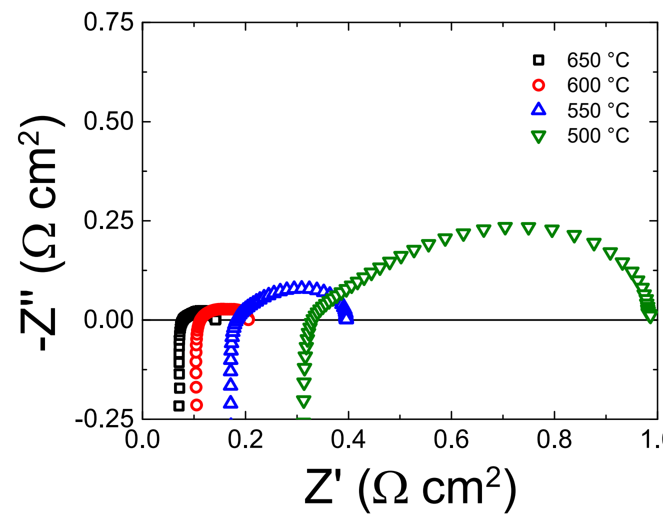
I-V Measurement

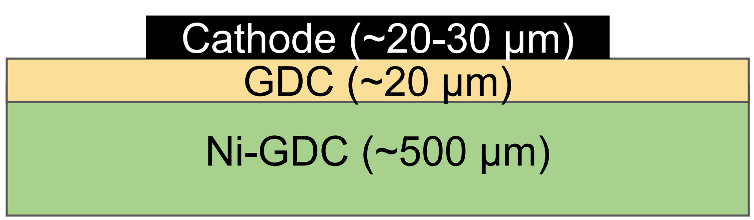




Cell Impedance







- Higher OCP
- Lower Activation Polarization
- Higher Energy Density

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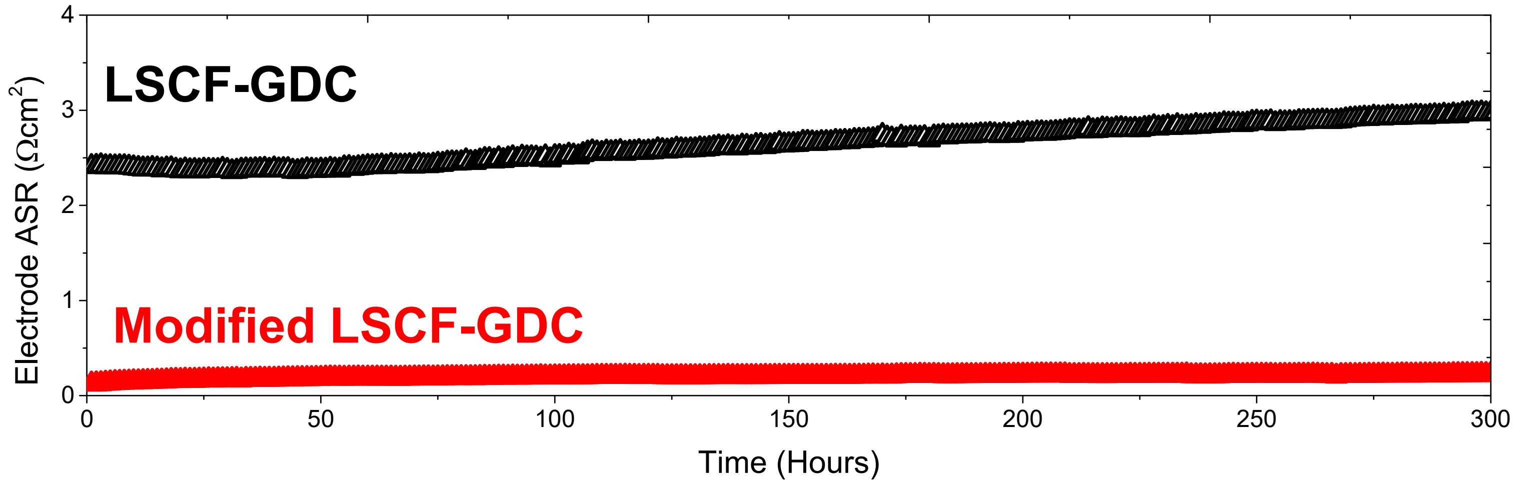
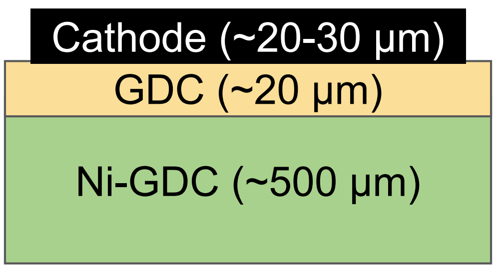
Stability of MO_x Surface Modified Cathode

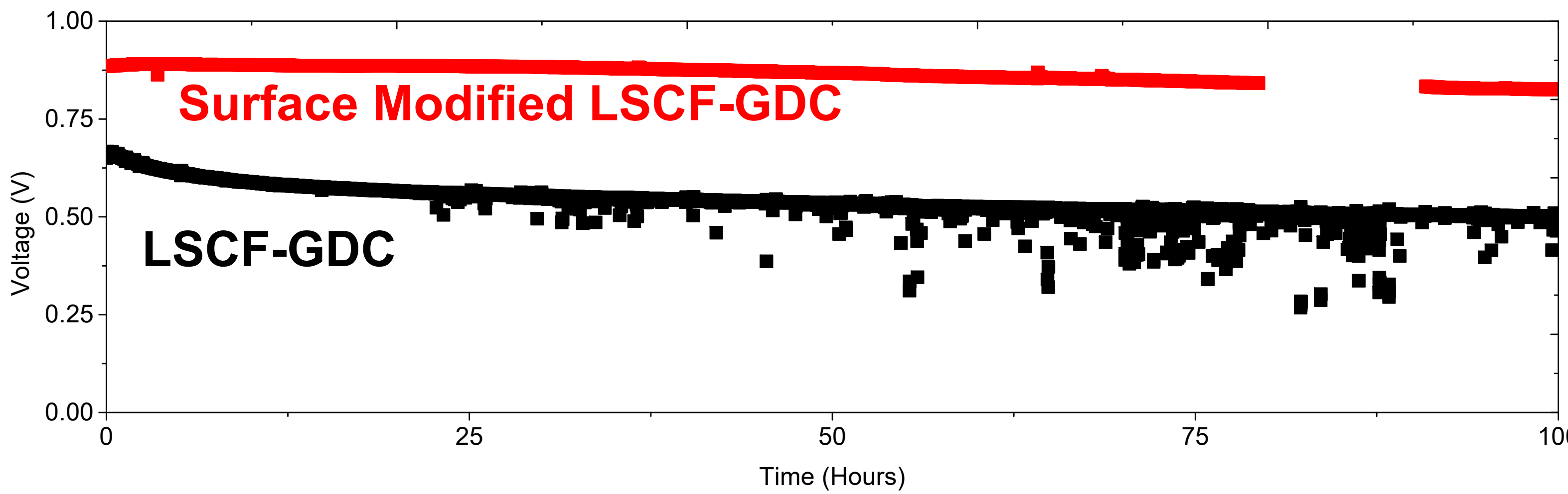
EIS 600°C air



- Orders of magnitude lower and more stable ASR
- Still running

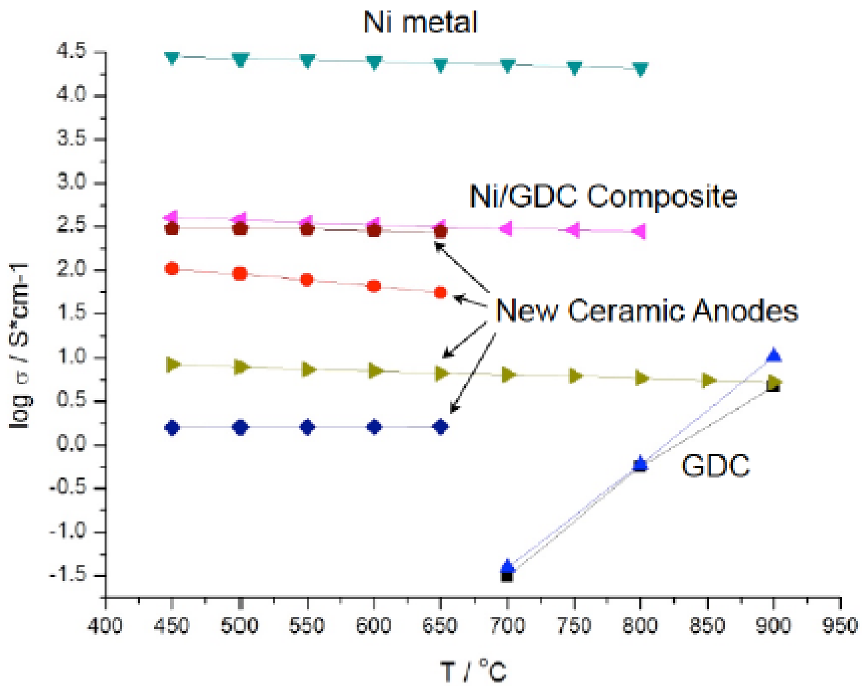


200 mA/cm^2 600°C
H_2-3%H_2O/air



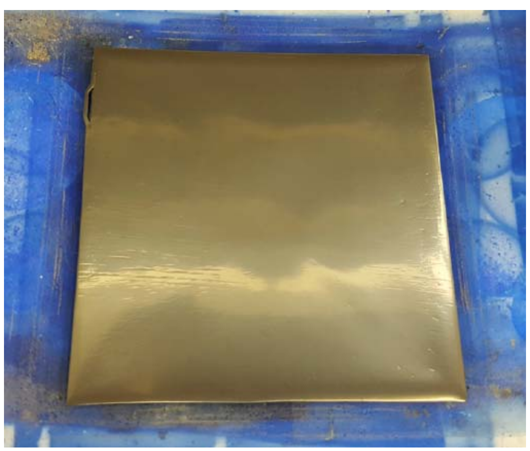
- Higher and more stable voltage at constant current
- Still running

Extend to Redox Tolerant Ceramic Anodes

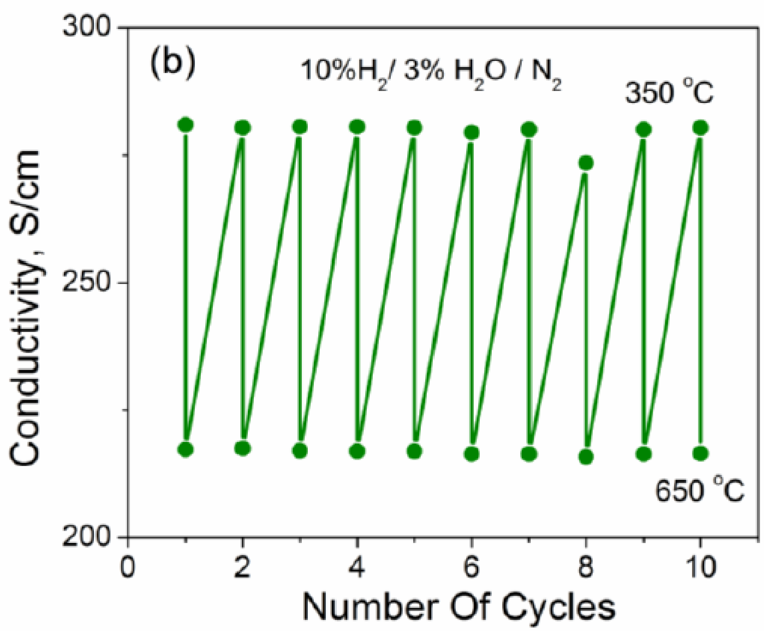


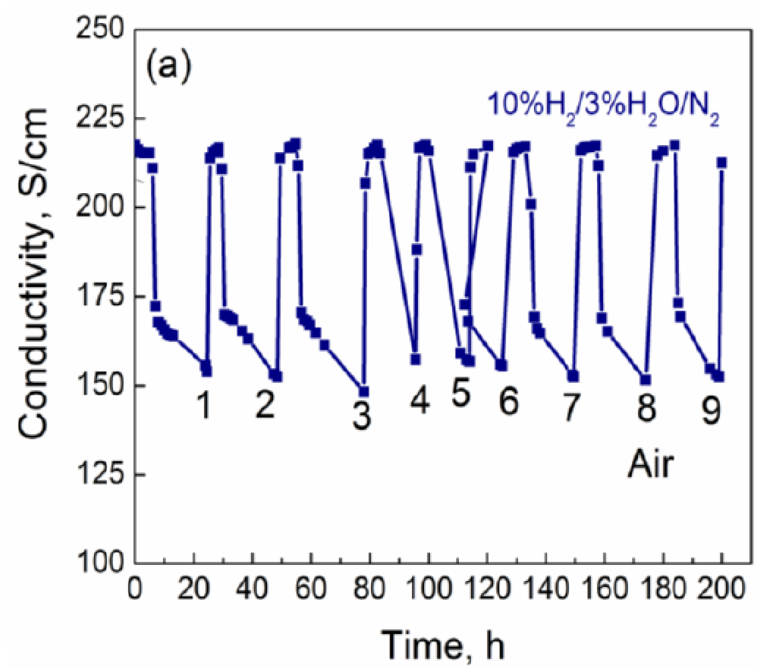
New ceramic anodes developed in our lab:

- Comparable conductivity to Ni/GDC
- Enable thermal and fuel to air cycling
- Will be using above approaches to mitigate Sr segregation issues



5 cm x 5 cm Cell





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Acknowledgments

Dr. Yi-Lin Huang
Ian Robinson
Eugene Ostrovskiy
Sam Horlick
Zixiao Liu

US Department of Energy, National Energy Technology Laboratory
Contract No. DEFE0031662

Seth Lawson