Degradation & Performance Studies of ALD-Stabilized Nano-Composite SOFC Cathodes

DE-FE0031250 – FOA 1735

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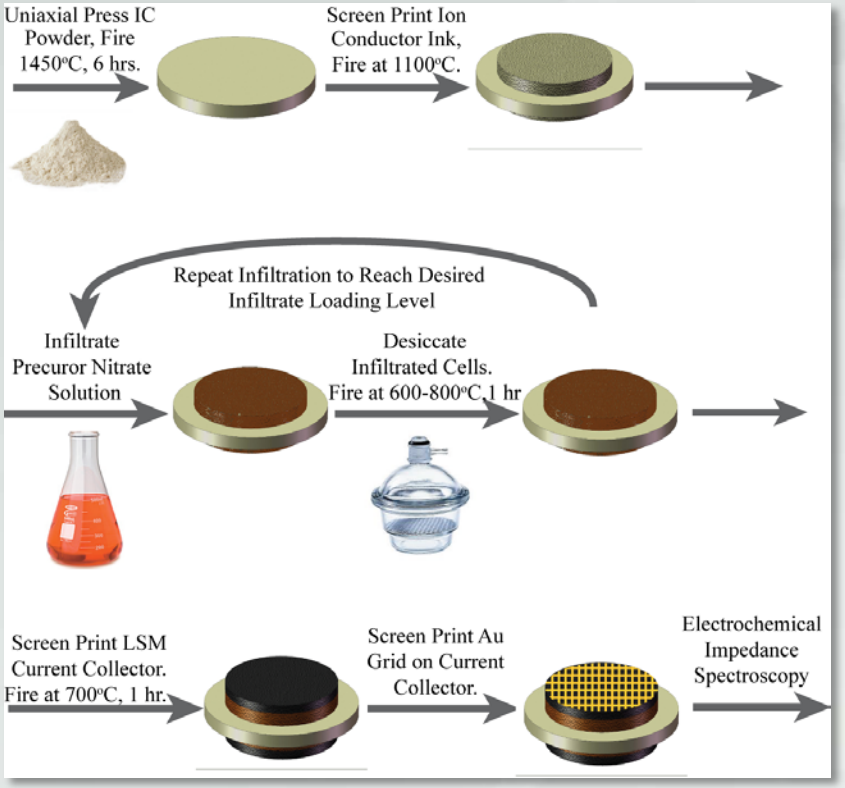
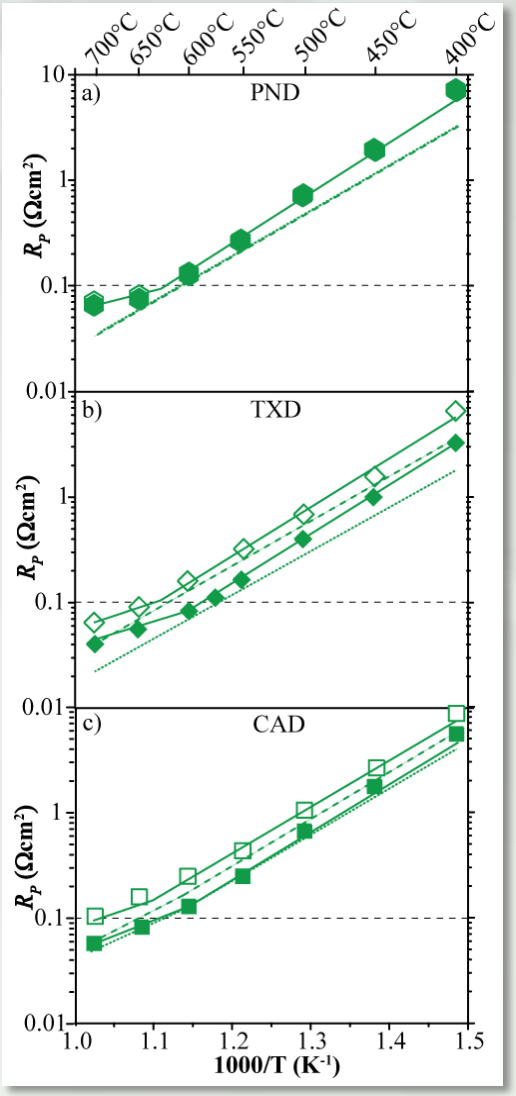
November 30, 2017

Previous work by the Nicholas Group has shown that the desiccation of LSCF infiltrate solution leads to improved performance of 0.1Ωcm² at ~575ºC





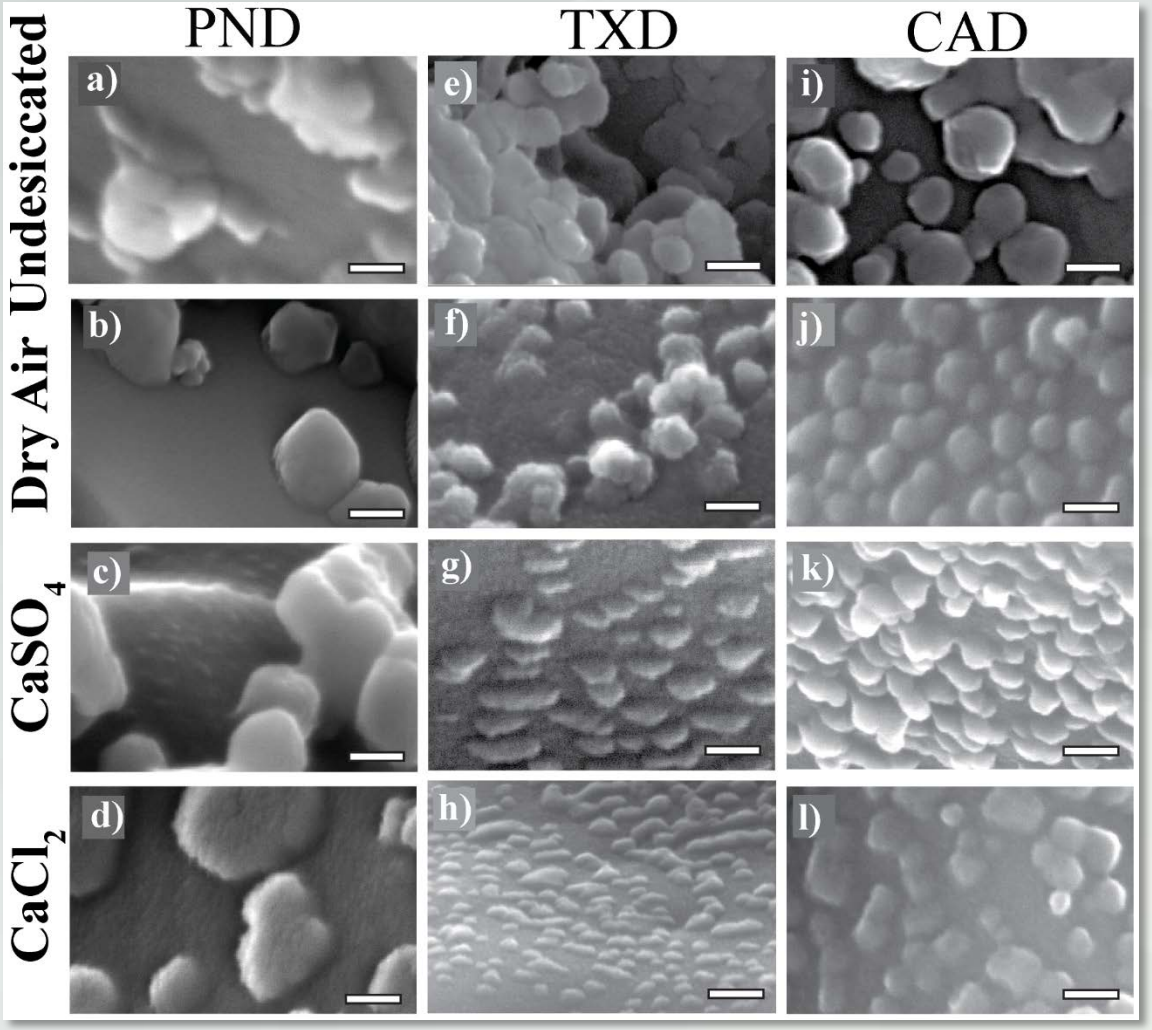
PND= Pure Nitrate Derived

TXD= Triton X-100 Derived

CAD=Citric Acid Derived

Inclined dashed lines are SIMPLE model predictions made with the observed particle size predictions

Precursor Solution Desiccation Reduces Average $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-x}$ (LSCF) Infiltrate Particle Size



PND=Pure Nitrate Derived

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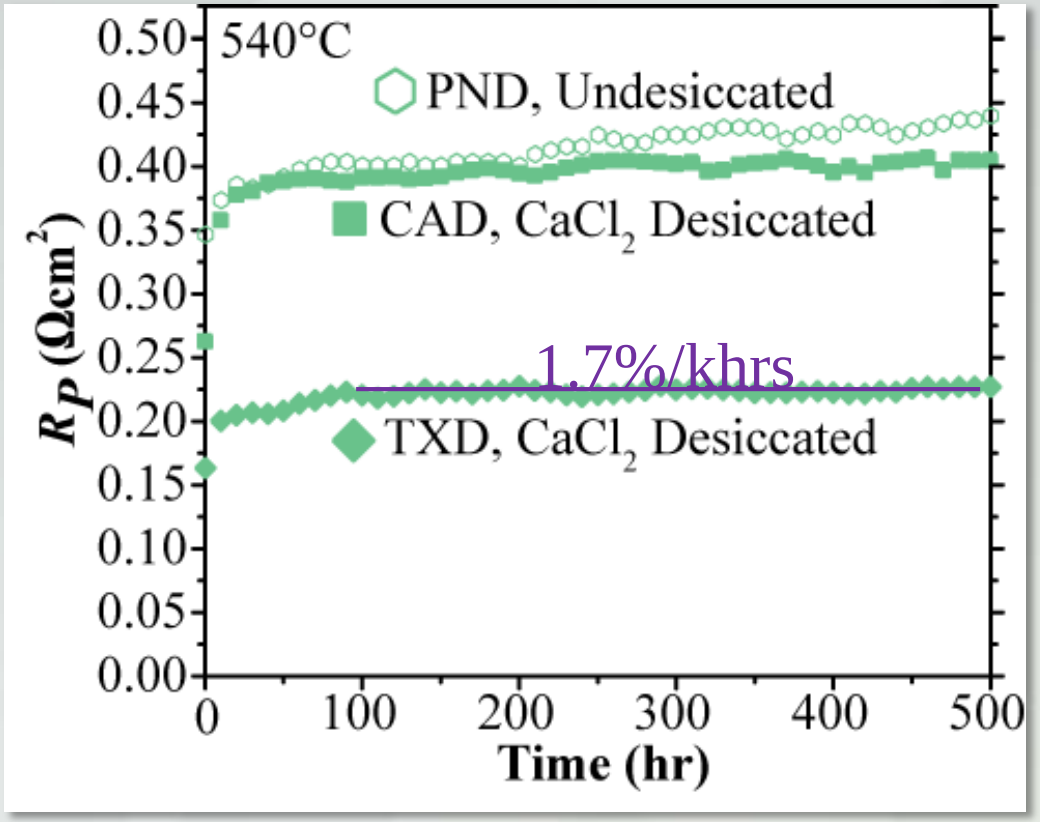
All scale bars are 50 nm wide

Burye and Nicholas, J Power Sources, 301, 287-298 (2016)

Unfortunately, uncoated nano-composite cathode stability is a major concern



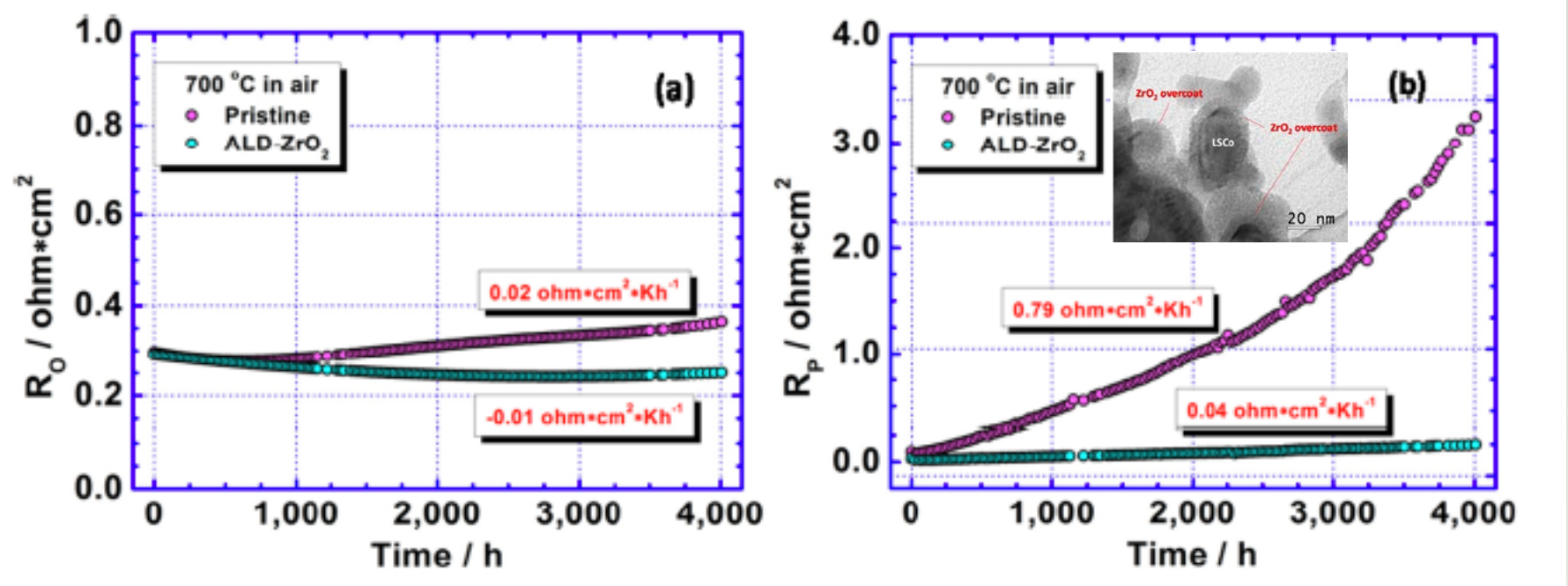
DOE target degradation rate: 0.2%/khrs

Commercial cells degradation rate: 0.5%-1%/khrs

Burye and Nicholas, J Power Sources, 301, 287-298 (2016)

http://www.netl.doe.gov/File%20Library/Events/2014/2014%20SECA%20workshop/Shailesh-Vora.pdf

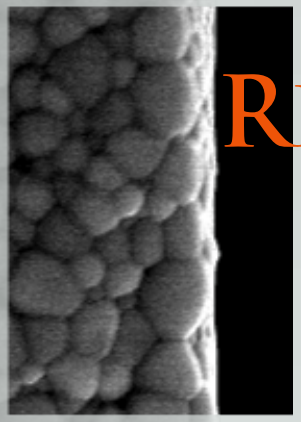
Previous Work by the Huang Group has Shown that Electrodes with ALD-ZrO_2Coated LSC nanoparticles have improved stability and good performance

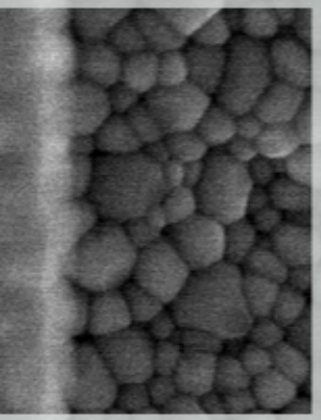


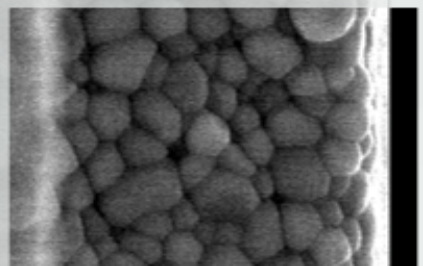
LSC on LSGM ($La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-\delta}$) scaffold (firing nitrates with TX-100 at 800°C for 1h)

- The assumed stabilization mechanism is the prevention of LSC nanoparticle coarsening Sr segregation

Gong, Yunhui, et al. *Nano letters* 13.9 (2013).





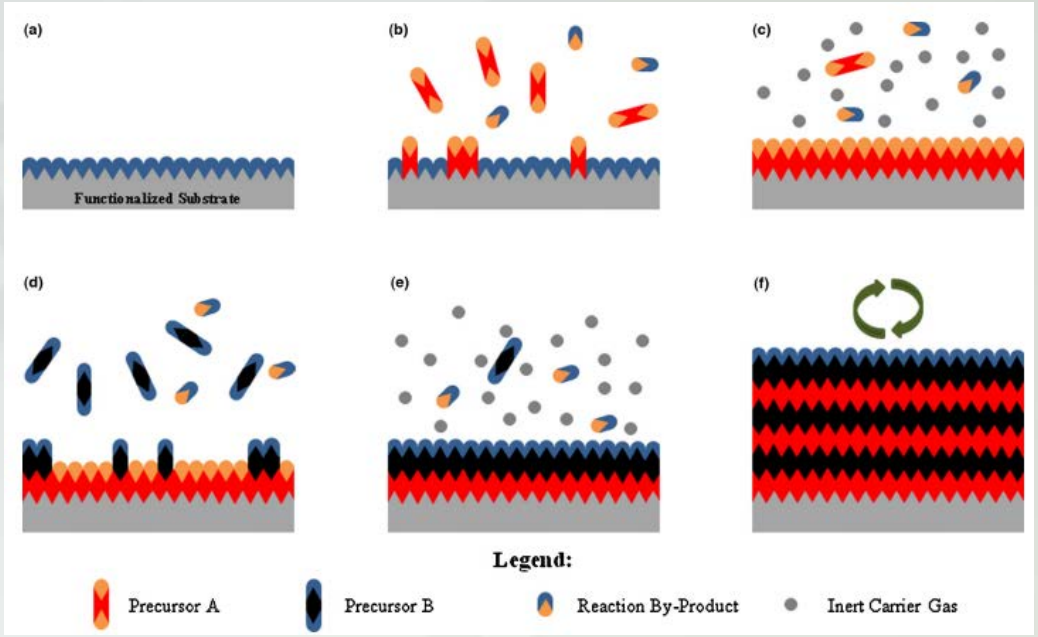


Research Objectives

- **Optimize the ALD overcoat microstructure to maximize the performance and stability of infiltrate size-tailored LSCF-GDC cathodes**
- Deconvolute the degradation mechanisms active in size-tailored, ALD-stabilized LSCF-GDC cathodes
- Evaluate the performance and stability of size-tailored, ALD-stabilized Co_3O_4-GDC cathodes

Atomic layer deposition (ALD) has been used for thin-film deposition for over 50 years.

ALD was invented by Valentin Borisovich Aleskovskii (left) and Stanislav Ivanovich Koltsov (right) in 1960s



Huang Group Nanotech Savannah 200 Atomic Layer Deposition System

Precursor A deposition– Excess precursor and by-products purged by inert gas– Precursor B deposition – Excess precursor and by-products purged

- ALD can form conformal layer structures at modest temperature (<350°C)

Johnson, Richard W., Adam Hultqvist, and Stacey F. Bent. *Materials today* 17.5 (2014).

Malygin, Anatolii A., et al. *Chemical Vapor Deposition* 21.10-11-12 (2015).

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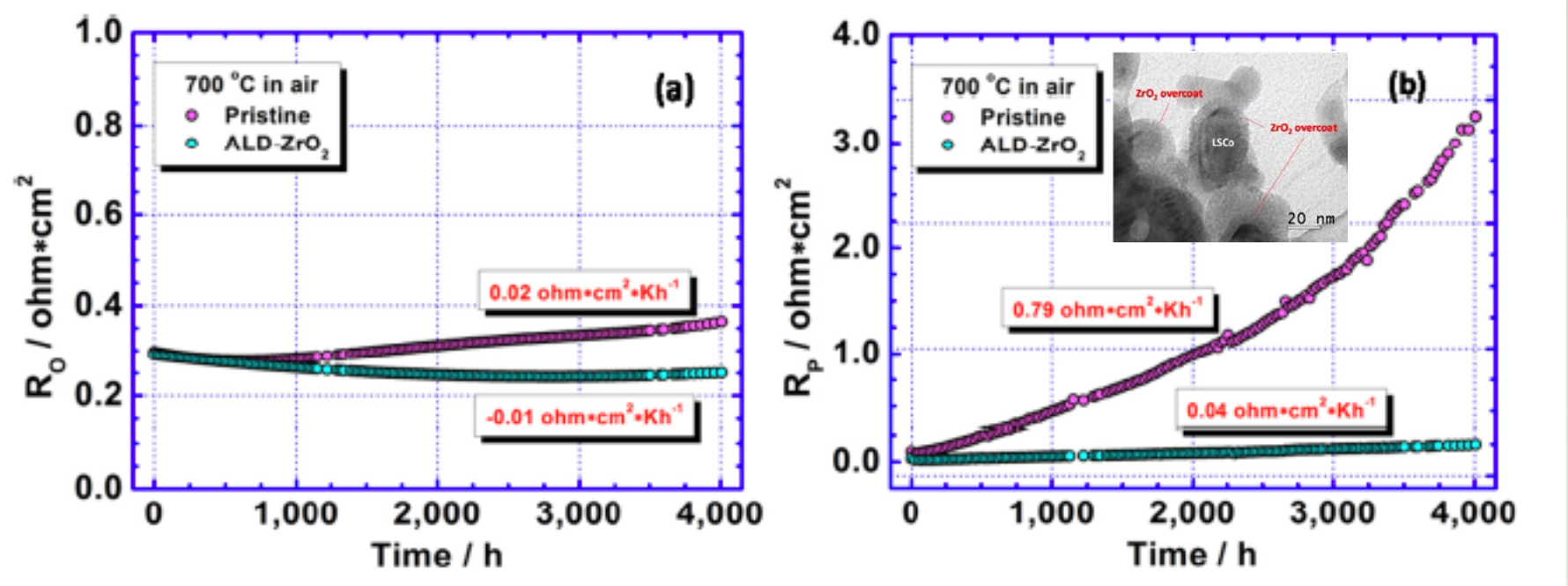

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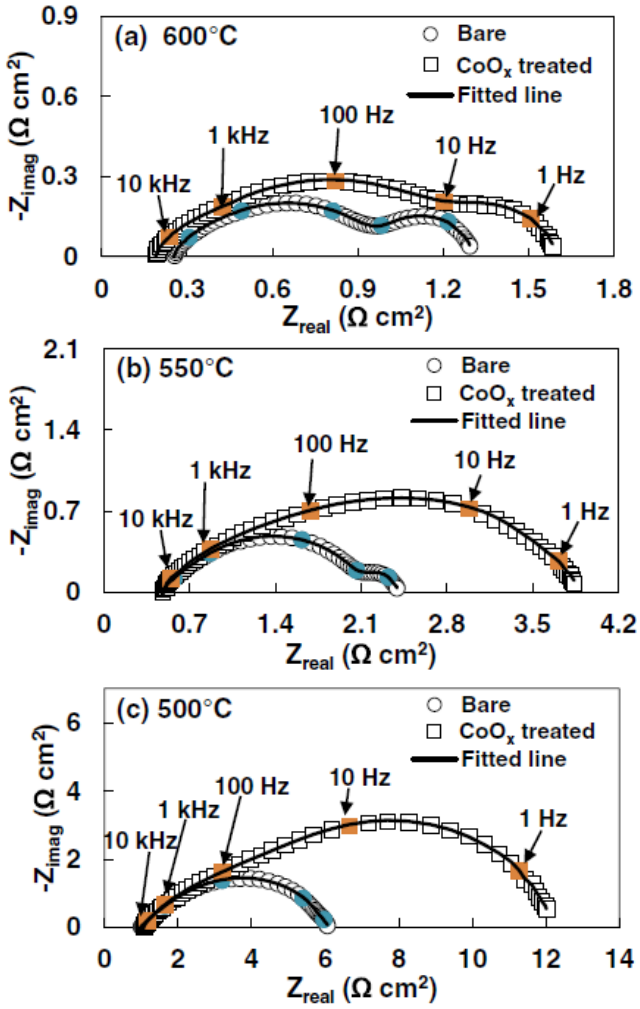
Gong, Yunhui, et al. *Nano letters* 13.9 (2013).

There is literature suggesting ALD coatings may hurt cathode performance



- 1.8nm Co_3O_4 was coated on LSC thin film (PLD, 2.5um)
- Co_3O_4 coated LSC film performed worse than bare cell (Ni-YSZ as cathode and YSZ as electrolyte)
- They claimed Co_3O_4 layer blocked the sites on LSC and affected the O_2 adsorption and/or desorption process..

Choi, Hyung Jong, et al. "Performance degradation of lanthanum strontium cobaltite after surface modification." *Journal of The Electrochemical Society*162.6 (2015): F622-F626.

Phase I SOPO Tasks

- **Task 1.1: Produce ALD-coated, infiltrate-size-tailored LSCF-GDC symmetric cells (Huang and Nicholas)**
- **Task 1.2: Evaluate symmetric cell performance and stability and identify optimal ALD porosity/thickness/deposition conditions (Huang, Validation by Nicholas)**
- Task 1.3: Produce ALD-coated infiltrate size tailored LSCF-GDC SOFCs (Huang, Nicholas, Atrex)
- Task 1.4: Perform long-term fuel cell tests to evaluate electrode performance and stability under SOFC operation (CH_4 at 650C, H2 at 450-650C) (Atrex Energy, Inc.)

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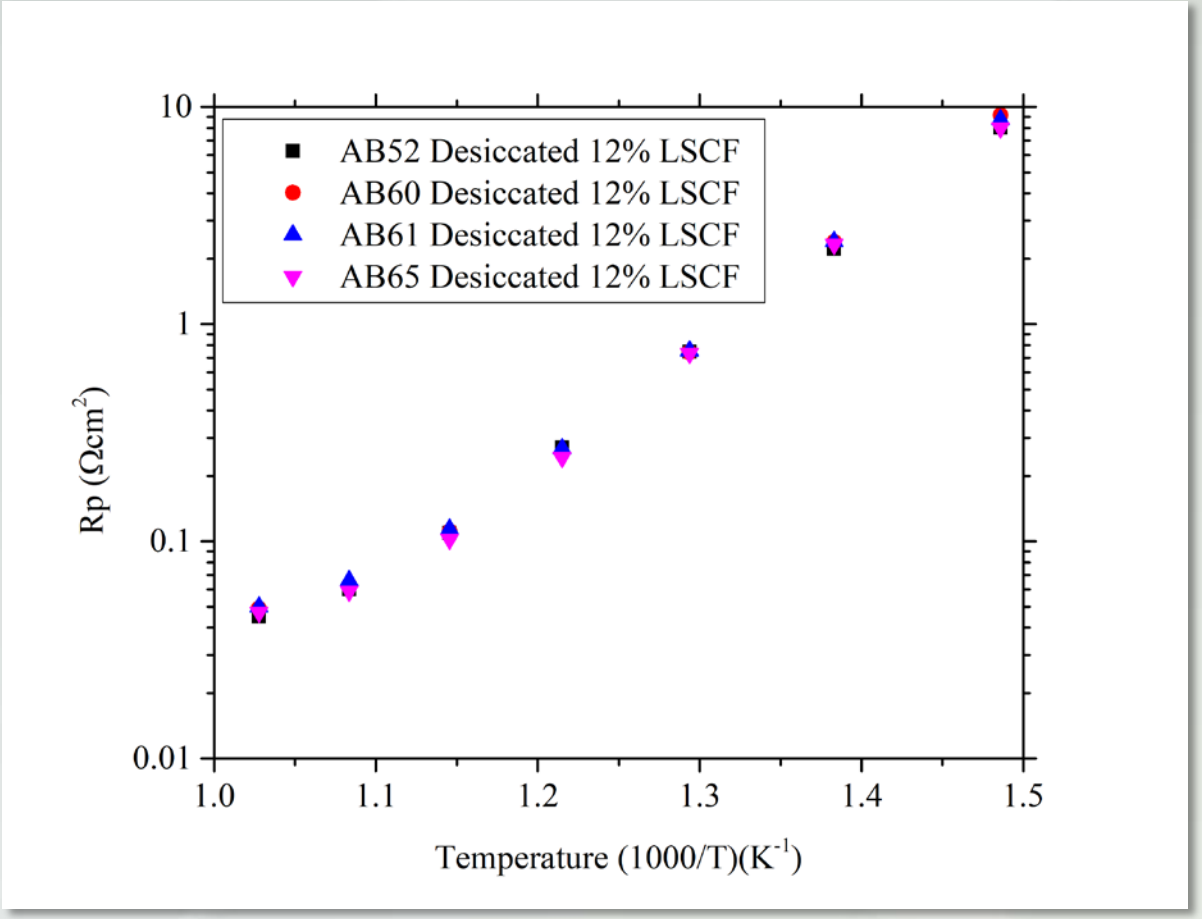
Reproducible ALD-Ready desiccated LSCF-GDC symmetric cells can be produced



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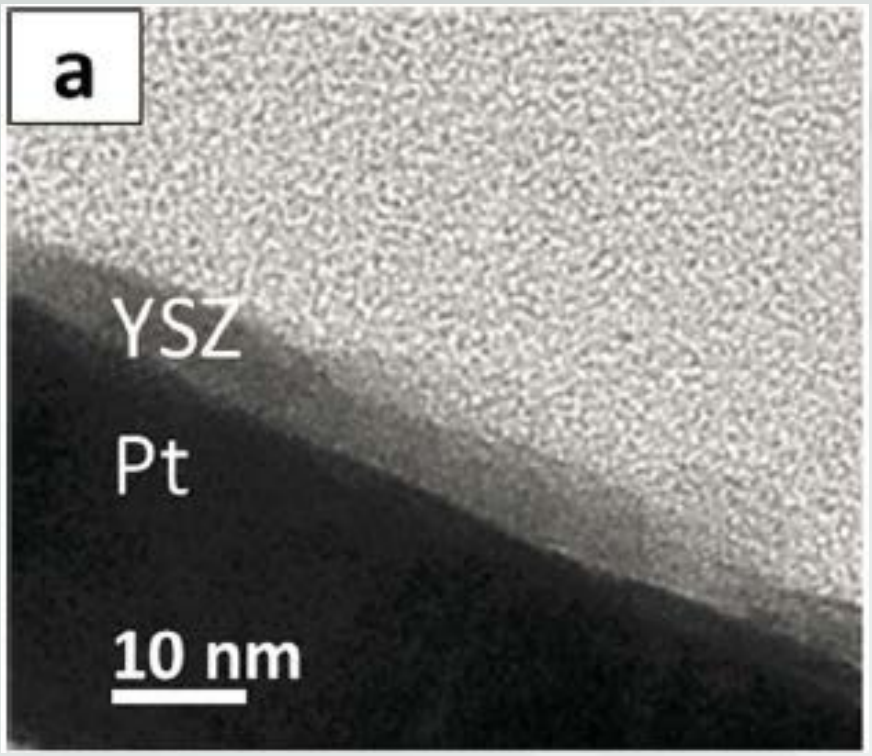
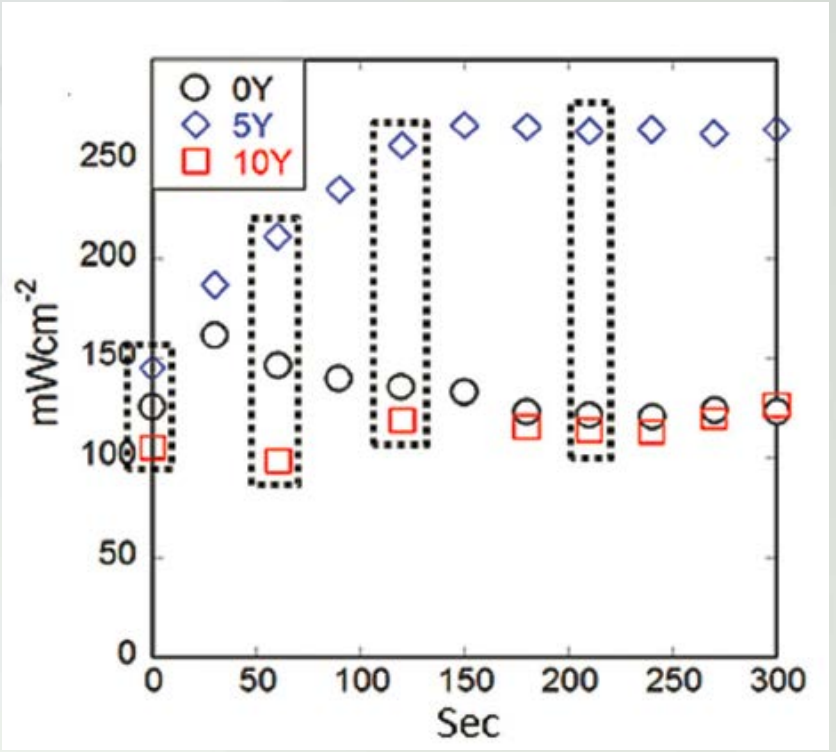
Atrex Energy's Test Capabilities

- Capacity to test 35 tubular cells over 9 cell test stands.
- Independent load control and fuel flow for each cell in every test stand, which typically operated in constant current mode.
- Typical fuel include hydrogen and methane reformate.
- The cell testing laboratory has natural gas, compressed air, hydrogen, pure methane, propane and reducing cover gas plumbed around a central manifold system.

ALD coatings have been reported to change ORR performance



Cross section TEM for YSZ coated Pt

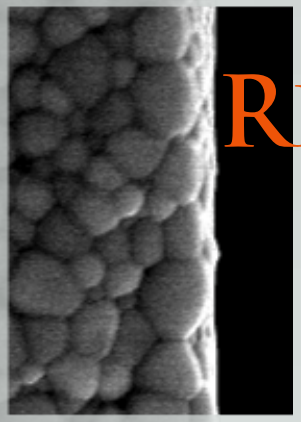


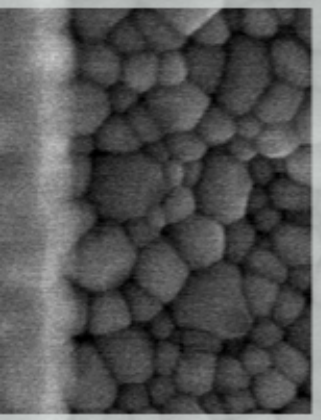
5Y– Thickness of YSZ is 5nm

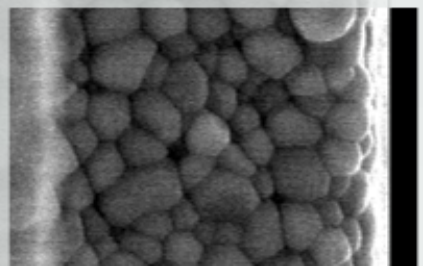
10Y– Thickness of YSZ is 10nm

- YSZ has been coated on Pt and it has changed the ORR performance of Pt cathode.
- It's possible that ZrO_2 ALD Overcoats may alter the ORR performance of SOFC infiltrate particles as well

Chang, Ikwhang, et al. *Advanced Energy Materials* 5.10 (2015).







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Phase II SOPO Tasks

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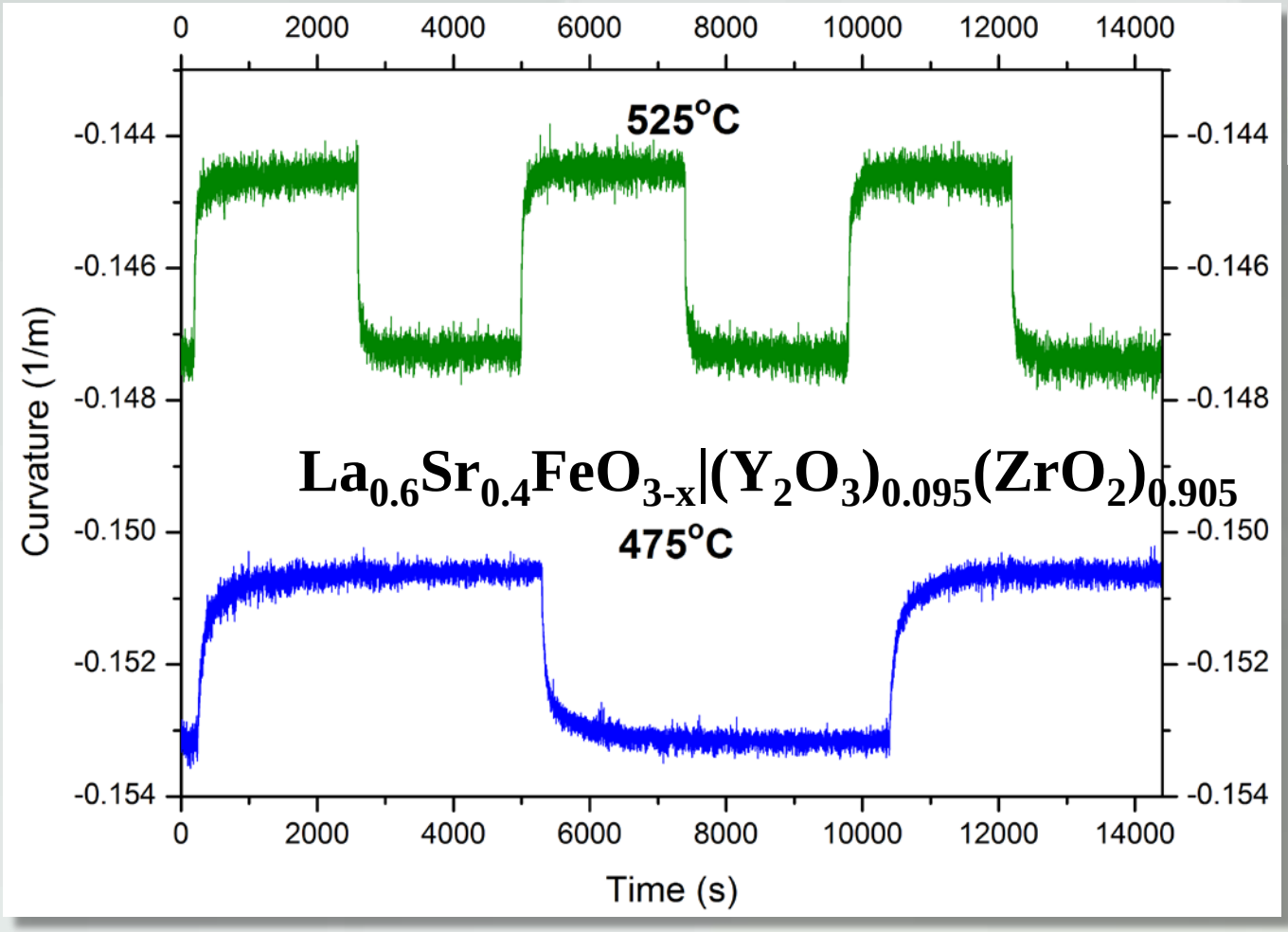
- **Task 2.2: Produce ALD-coated thin film LSCF samples (Nicholas and Huang)**
- **Task 2.3: Perform LSCF Wafer Curvature k_{chem} Measurements vs Aging Time**
- Task 2.4: Use Simple Models to Relate R_P, k_{chem}, and Infiltrate Particle Size Changes (Nicholas)

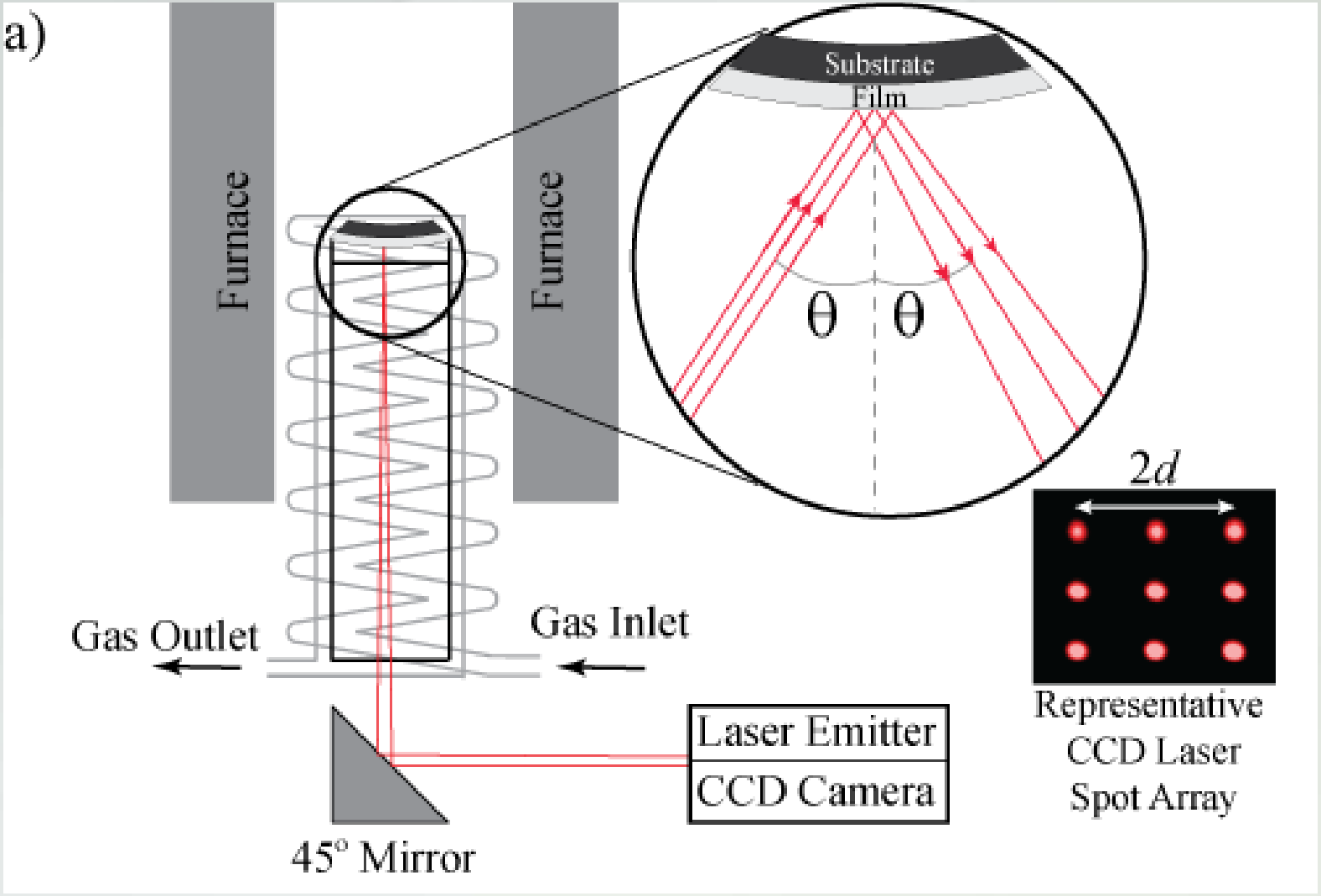
Representative Curvature Data for a Mechano-Chemically Active Material on an Inert Substrate Responding to a Sudden pO2 Switch from 0.2 to 0.02 atm



Yang et al. ECS Transactions. 224th ECS Meeting - San Francisco, CA (2013).

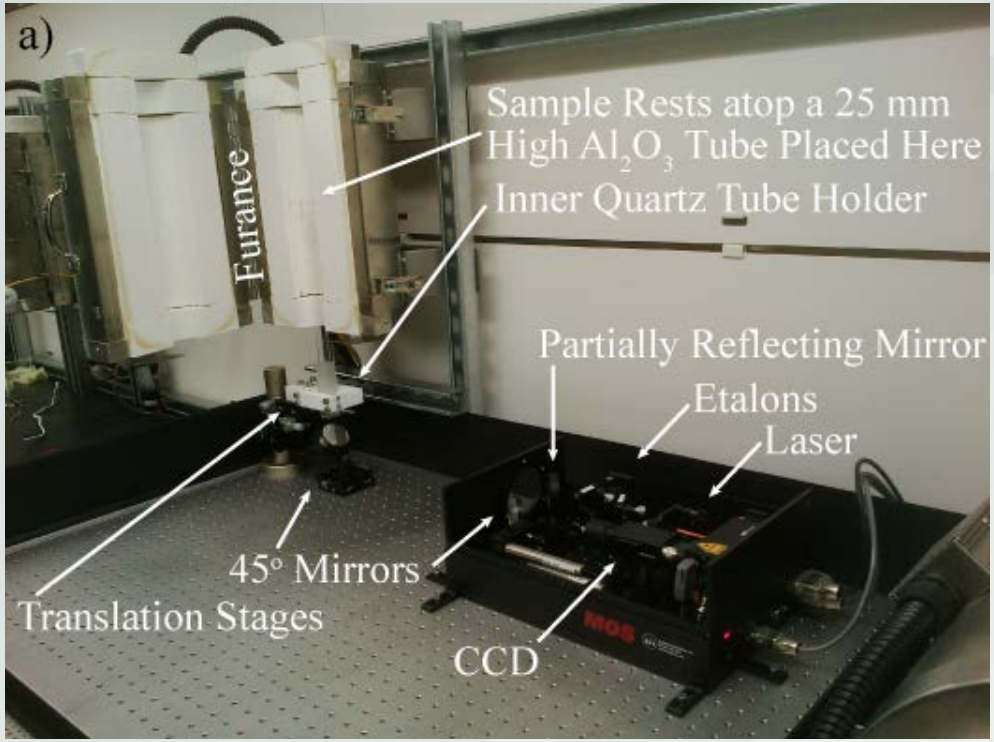
Yang *et al*. Solid State Ionics, 249–250, 123–128 (2013).

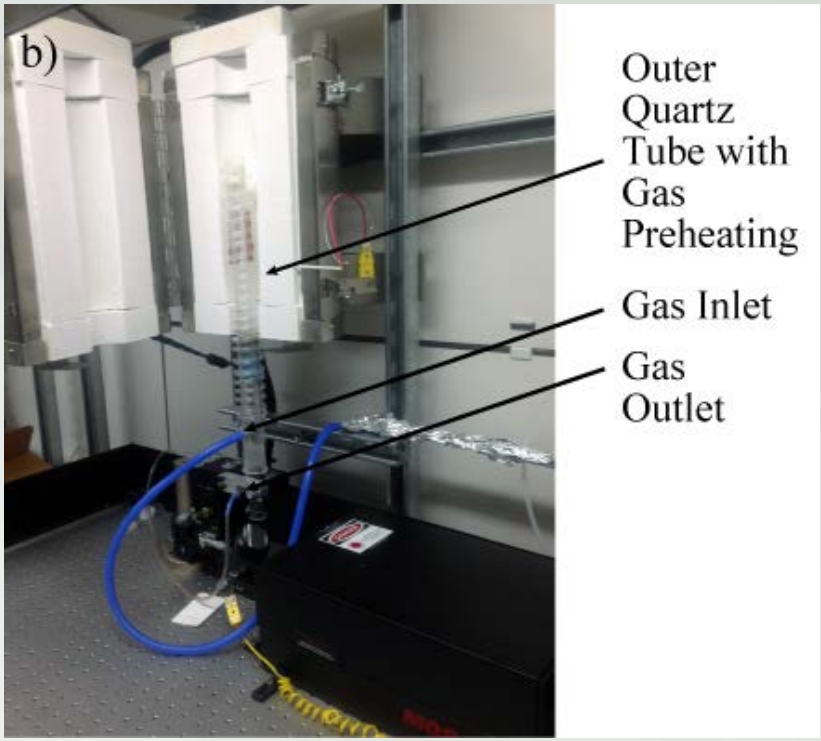
In Situ/In Operando Wafer Curvature Measurements



Nicholas, Extreme Mechanics Letters, (2016) In Press. http://dx.doi.org/10.1016/j.eml.2016.04.006

The Nicholas Group In Situ Wafer Curvature Measurement Setup





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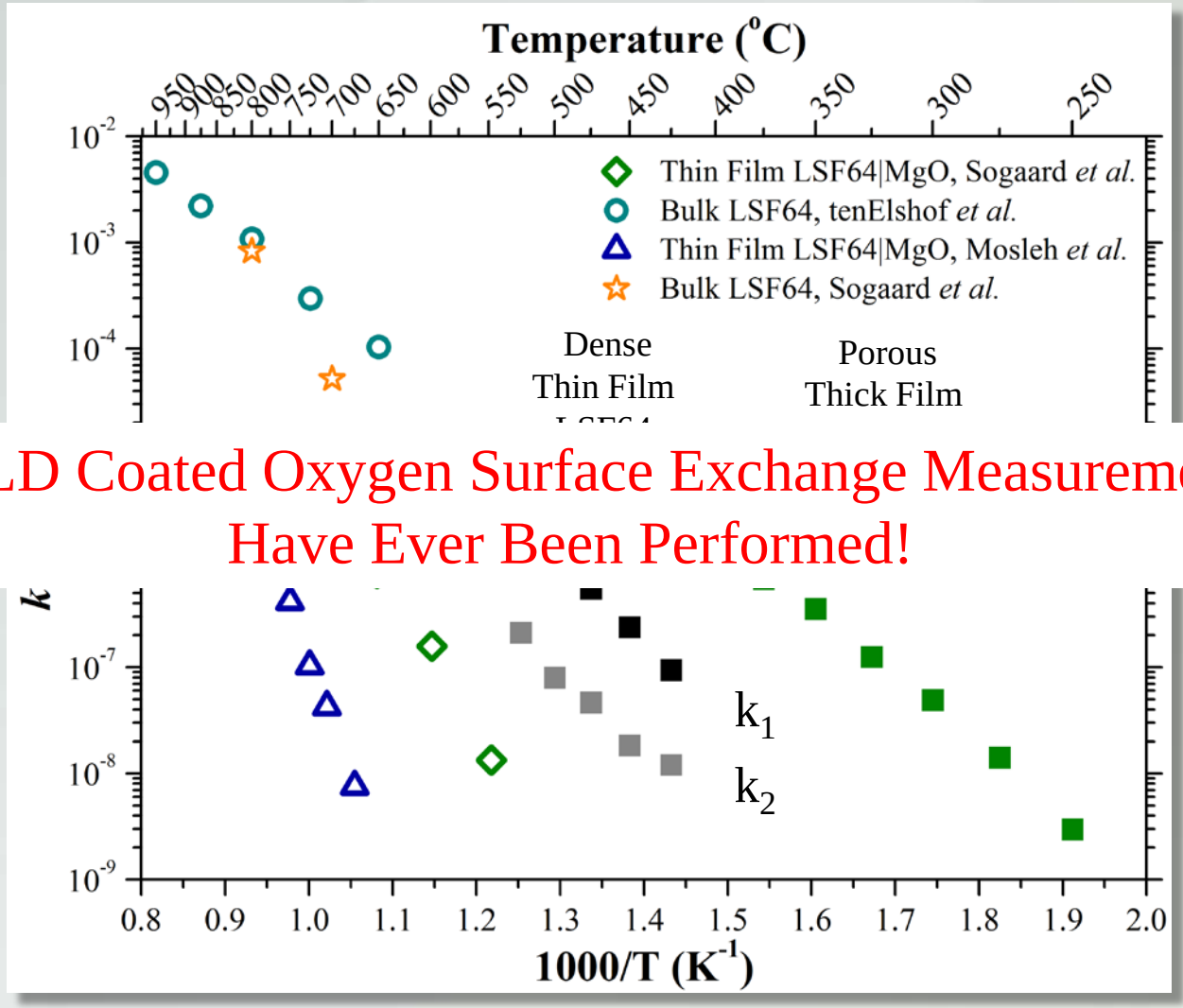
The KR-Measured *k's* Have Activation Energies that Agree with Bulk $La_{0.6}Sr_{0.4}FeO_{3-x}$ Values



No ALD Coated Oxygen Surface Exchange Measurements Have Ever Been Performed!

Sogaard et al. J. Solid State Chem, 180, 1489 (2007); Mosleh et al. J. Electrochem. Soc., 156, B441 (2009); Sogaard et al. J. Electroceramics, 27, 134 (2011); ten Elshof, J. Electrochem. Soc., 144, 1060 (1997); Yang et al. Solid State Ionics 249–250 (2013) 123–128; Yang and Nicholas *J. Electrochem. Soc.*, 161, F3025-F3031 (2014).

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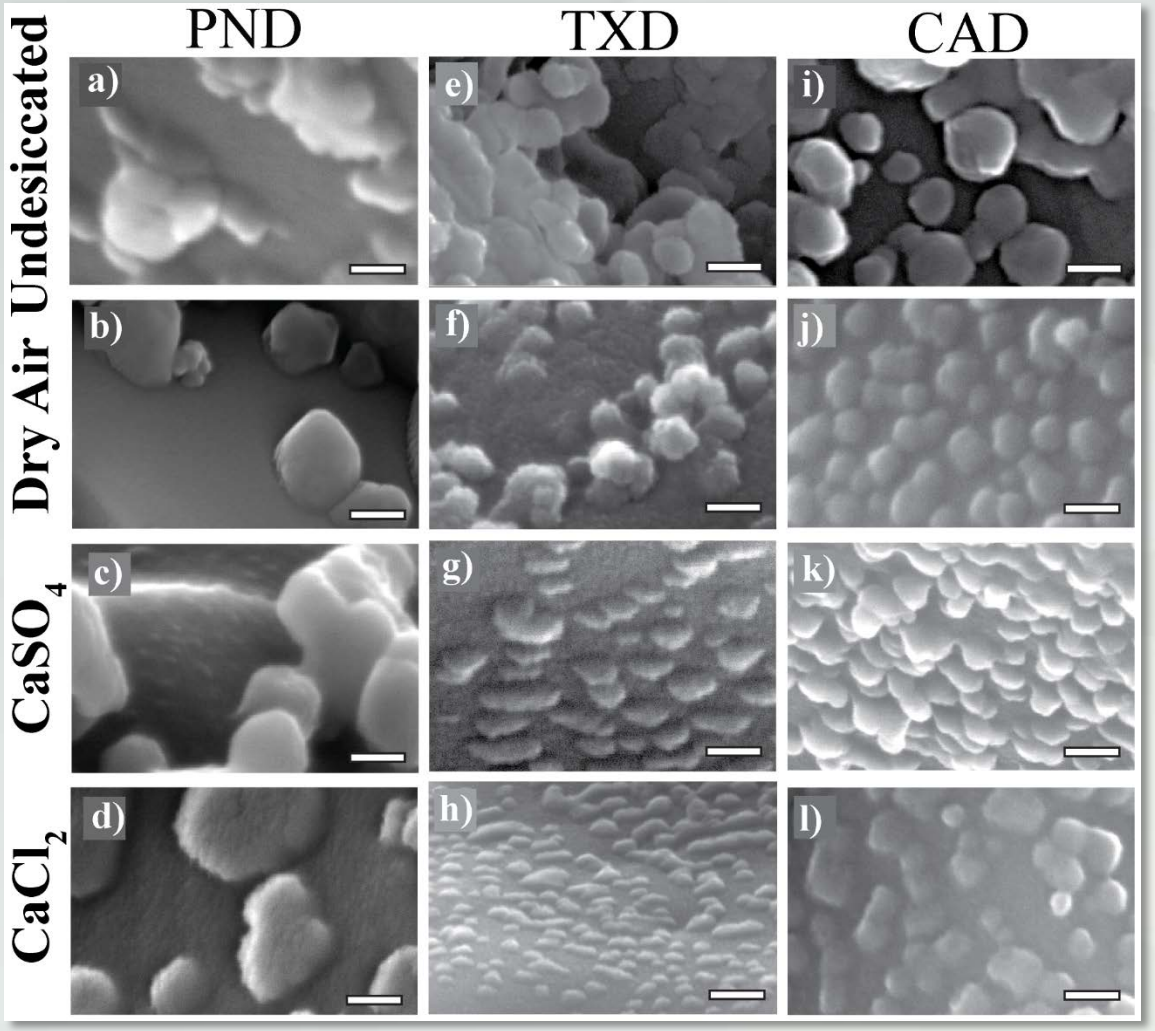
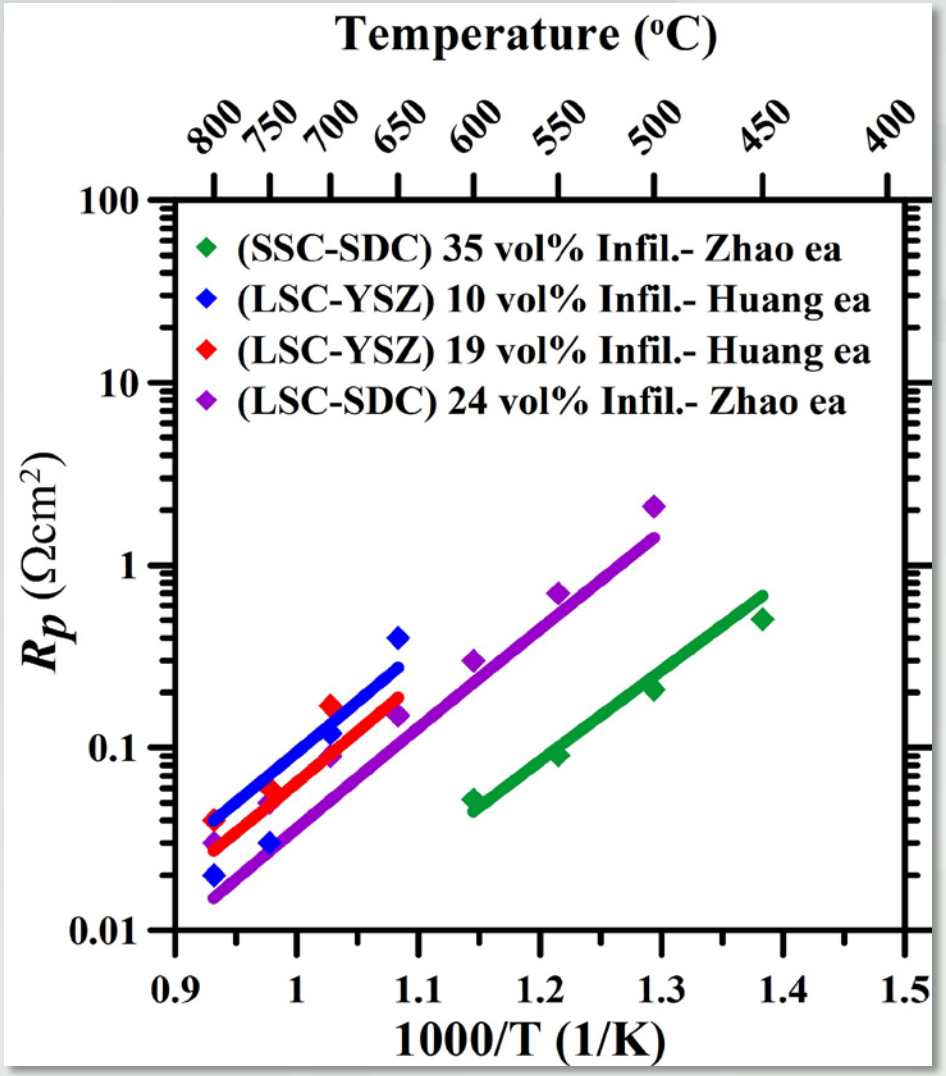
BET and/or SEM infiltrate particle size analysis can be used to track infiltrate coarsening



All scale bars are 50 nm wide

Burye and Nicholas, J Power Sources, 301, 287-298 (2016)

SIMPLE Model Fits to Literature Nano-Composite Cathodes



$SSC=Sm_{0.5}Sr_{0.5}CoO_{3-x}$

$SDC=Sm_{0.2}Ce_{0.8}O_{1.9}$

$LSC=La_{0.6}Sr_{0.4}CoO_{3-x}$

$YSZ=Y_{0.08}Zr_{0.92}O_{1.96}$

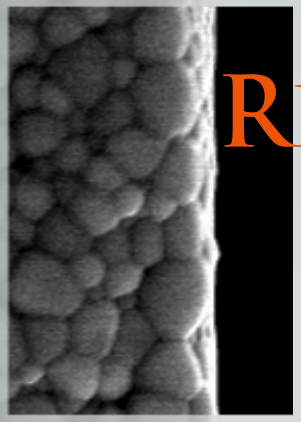
Obtain Custom Rp Predictions for Your Infiltrated Cells Using the SIMPLE Model Calculator at:

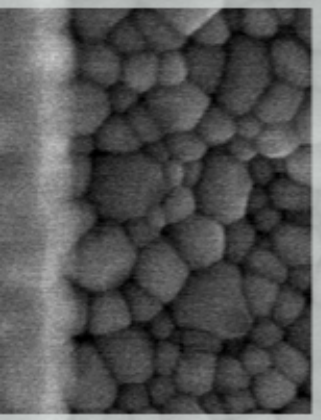
https://www.egr.msu.edu/nicholasgroup/simple.php

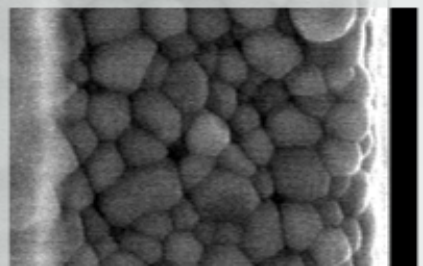
Zhao et al. Journal of Power Sources, v185, p13 (2008).

Zhao et al. Materials Research Bulletin, v43, p370 (2008).

Huang et al. Journal of the Electrochemical Society, v151, pA1592 (2004).







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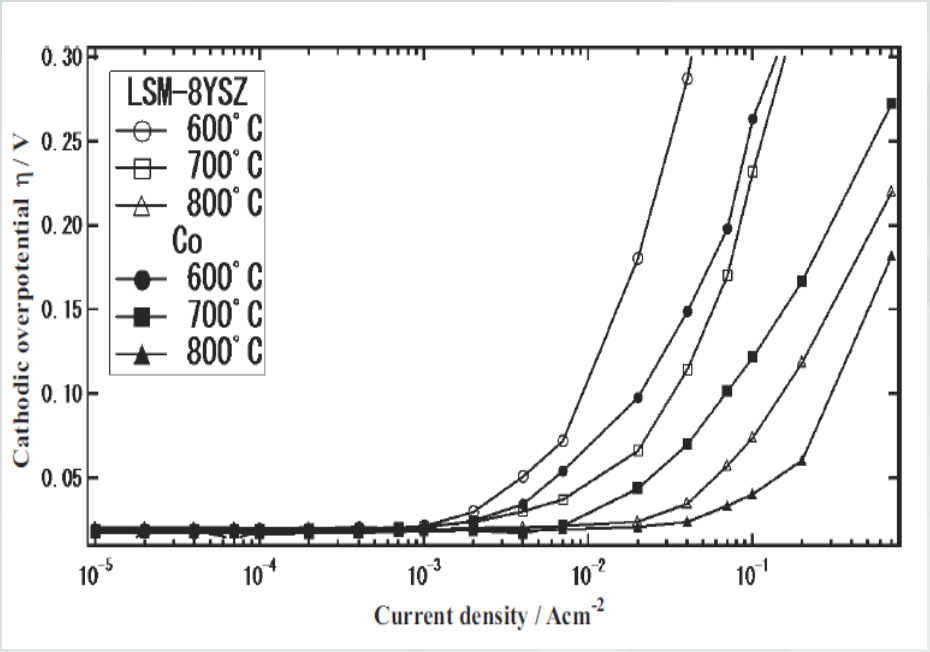
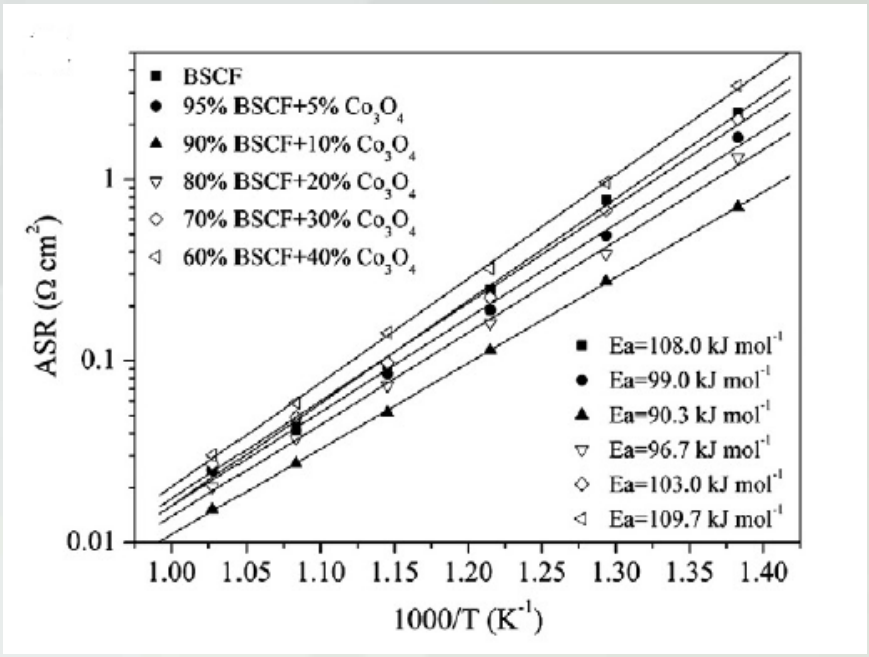
Phase III SOPO Tasks

- **Task 3.1: Produce ALD-coated, infiltrate-size-tailored Co_3O_4-GDC electrodes (Nicholas and Huang)**

- **Task 3.2: Measure the Performance and Stability of ALD-coated infiltrate size tailored Co_3O_4-GDC electrodes (Huang, Validated by Nicholas)**

Co_3O_4 additions are known to improve the performance of many SOFC cathode materials like LSM and BSCF



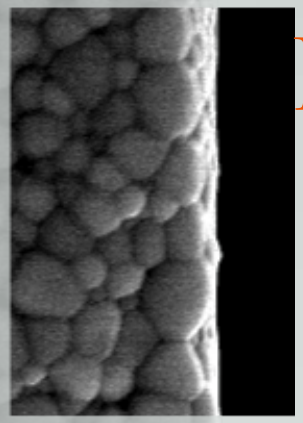


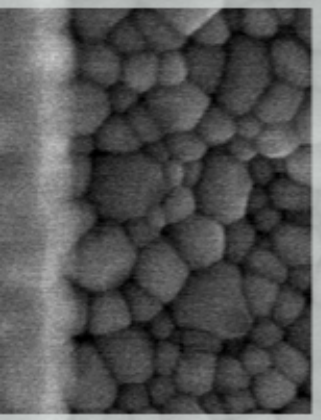
- LSM performance at different temperatures with and without Co_3O_4
- BSCF performance with different loading level of Co_3O_4
- Co_3O_4 can also improve theperformance of GDC, LSC and SSC

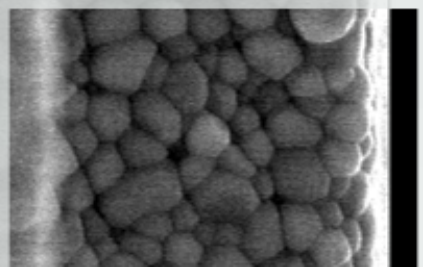
Table 1 Cathode polarization resistances and maximum power densities of fuel cells with different cathode electrocatalysts at 600 °C

	GSC	GSC/Co_3O_4	LSC	LSC/Co_3O_4	SSC	SSC/Co_3O_4
OCV/V	0.89	0.887	0.88	0.882	0.913	0.893
P_{max}/mW cm^{-2}	497	705	463	821	595	1033
R_i/Ω cm^2	0.252	0.171	0.269	0.136	0.233	0.073

Chen, Dengjie, et al. *Electrochemistry Communications* 13.2 (2011)
Imanishi, N. et al. *Fuel Cells* 9.3 (2009).
Haizhou Zhang and Weishen Yang. *Chemical Communications* 41 (2007)







Deliverables

- Performance and stability data on LSCF-GDC and Co_3O_4-GDC cathodes ALD stabilized with various ZrO_2 overcoat microstructures
- The world's first k_{chem} measurement on an ALD-coated oxygen exchange material
- k_{chem} and infiltrate particle size aging data and an analysis of whether the observed trends can explain the measured infiltrated cathode aging behavior
- Documented exchange of PI Nicholas's size-tailored infiltrate processing knowledge and PI Huang's ALD coating knowledge to Atrex Energy