Degradation and Performance Studies of ALD Stabilized SOFC Nano-Composite Cathodes (NCCs)

18 Month Update

Mr. Yubo Zhang,[2] Mr. Yeting Wen,[1]
Dr. Kevin Huang,[1] Dr. Praveen Cheekatamarla
and Dr. Jason D. Nicholas[2]

Funded by the Department of Energy Solid Oxide Fuel Cell Core Technology Program through Agreement Number DE-FE0031672

Program Manager: Joe Stoffa

May 1, 2019

High Performance Circuit Pastes for Solid Oxide Fuel Cell Applications

6 Month Update

Mr. Genzhi Hu,[1] Ms. Aishwarya Bhatlawande,[1] Ms. Jiyun Park,[1] Mr. Robert Termuhlen, [1] Dr. Yue Qi,[1] Dr. Thomas Beiler,[1] Dr. Timothy Hogan,[1] Dr. Hui-Chia Yu,[1] Dr. Praveen Cheekatamarla[2] and Dr. Jason D. Nicholas[1]

Funded by the Department of Energy Solid Oxide Fuel Cell Core Technology Program through Agreement Number DE-FE0031250

Program Manager: Venkat Venkatraman

TALK Outline

ALD-Stabilized Nano-Composite Cathodes

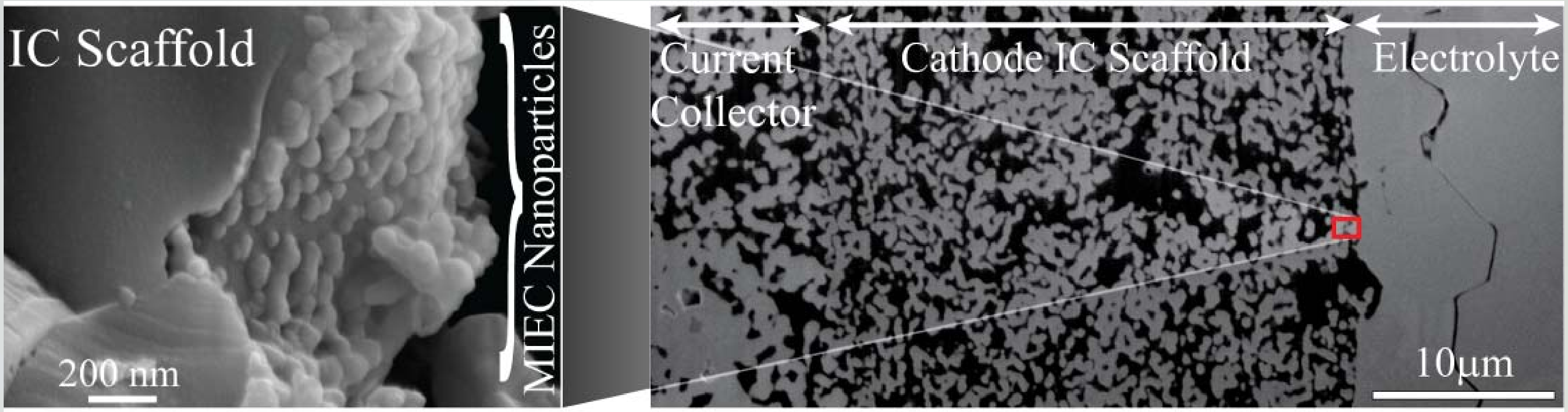
1. **Motivation**
2. Experimental Methods
3. Results and Discussion

Ni-Ag Circuits Pastes

1. Motivation
2. Experimental Methods
3. Results and Discussion

Motivation for MIEC on IC Nano-Composite SOFC Cathodes

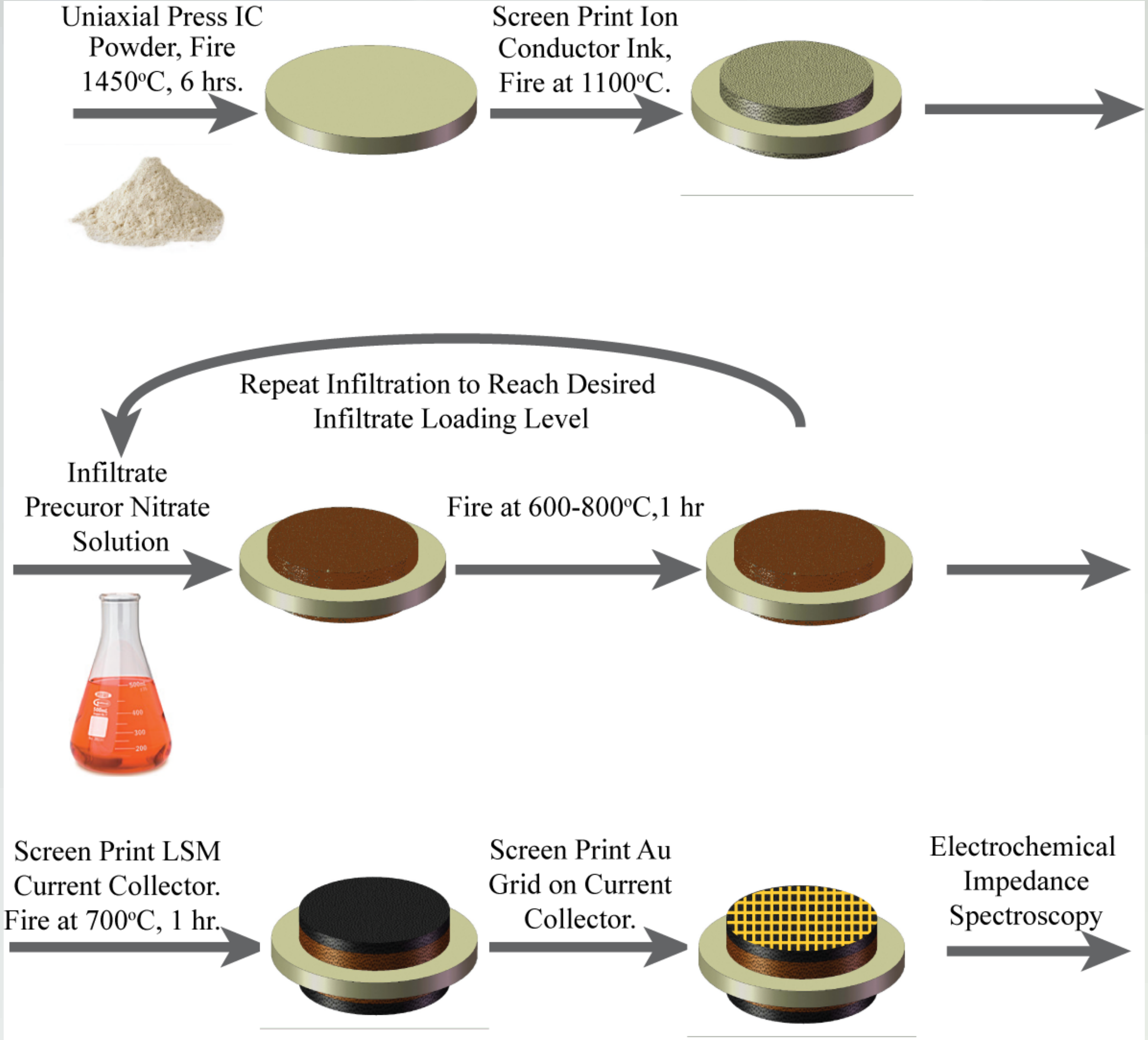
SOFC Cathode Reaction: $1/2O_{2\,(g)} + 2e^{-} + V_{o}^{**} = O_{o}$



Material	Oxygen Surface Exchange Coefficient (k)	Bulk Oxygen Ion Diffusivity (D)	Electronic Conductivity (σ_e)
Mixed Ionic Electronic Conductor (MIEC)	High	Low	High
Ionic Conductor (IC)	Low	High	Low

Burye and Nicholas, J Power Sources, 276, 54-61 (2015)

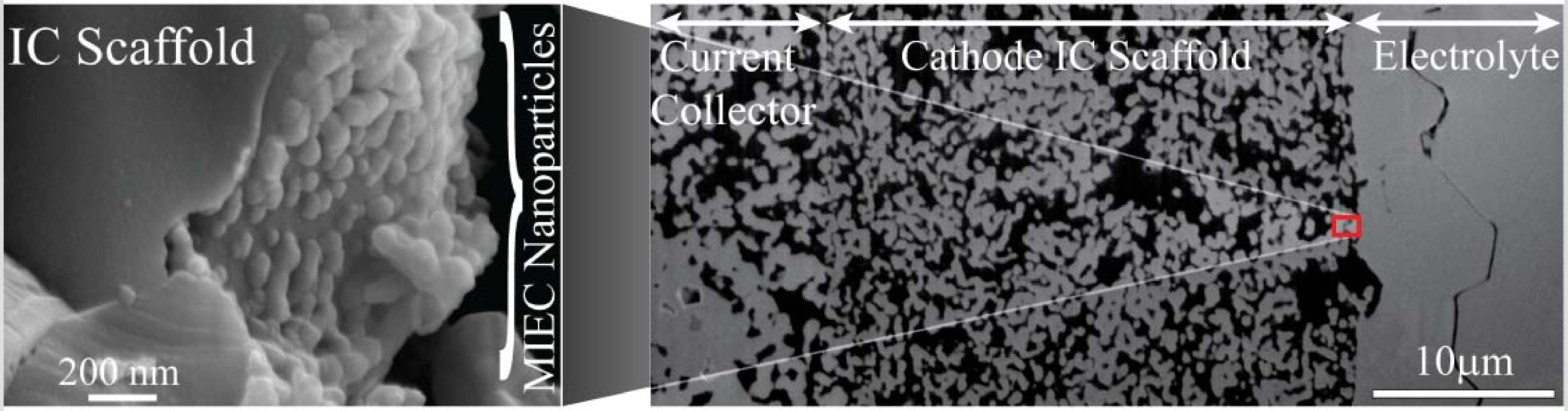
Standard Nano-Composite Cathode Fabrication



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

Motivation for MIEC on IC Nano-Composite SOFC Cathodes

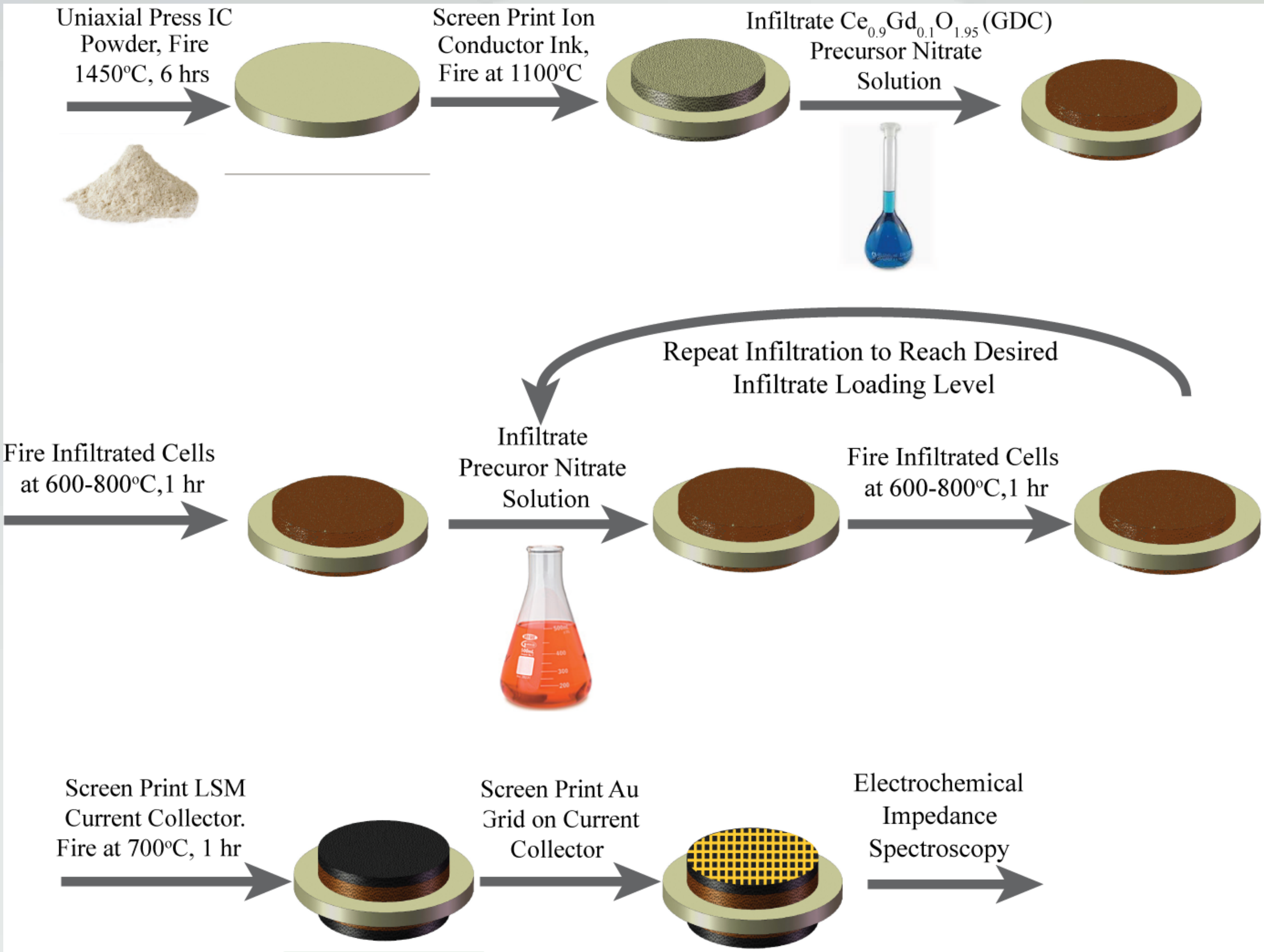
SOFC Cathode Reaction: $1/2O_{2\,(g)} + 2e^- + V_o^{**} = O_o$



Material	Oxygen Surface Exchange Coefficient (k)	Bulk Oxygen Ion Diffusivity (D)	Electronic Conductivity (σ_e)
Mixed Ionic Electronic Conductor (MIEC)	High	Low	High
Ionic Conductor (IC)	Low	High	Low

Burye and Nicholas, J Power Sources, 276, 54-61 (2015)

GDC Pre-Infiltrated Nano-Composite Cathode Fabrication



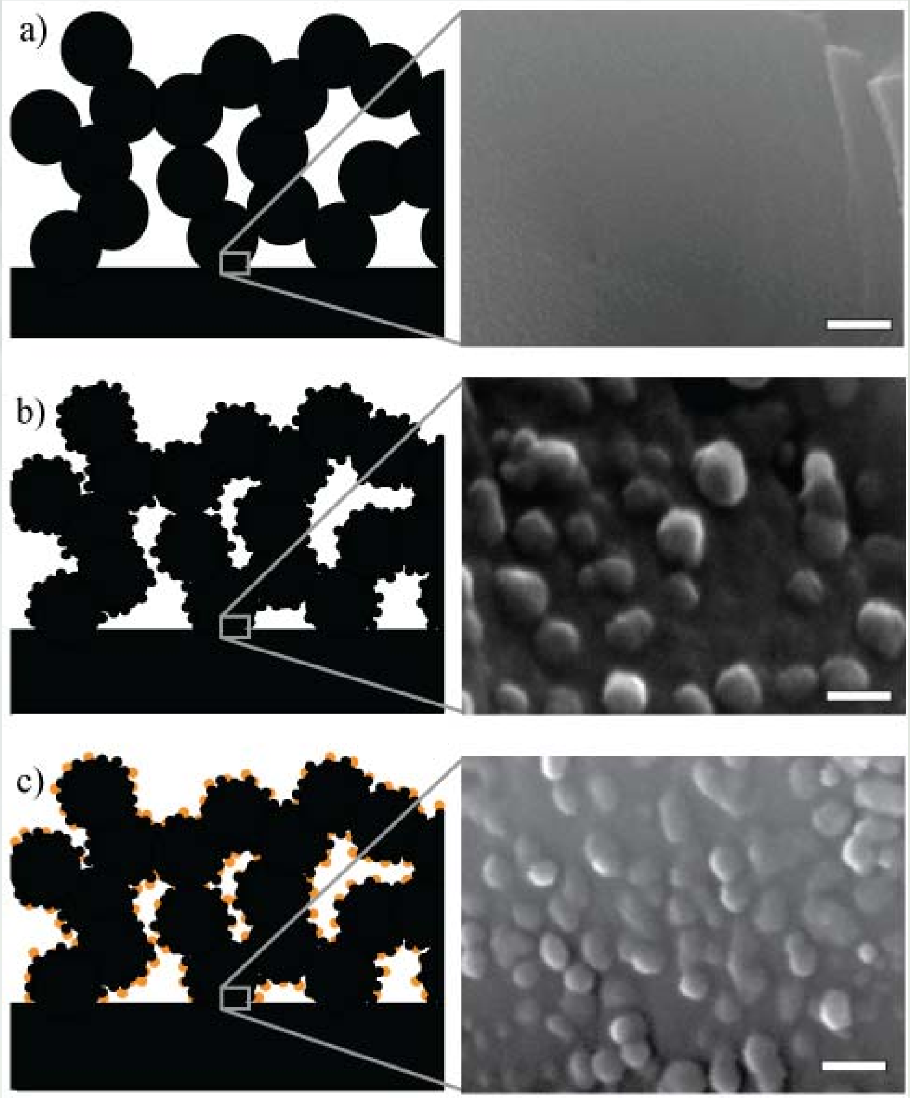
Burye and Nicholas, J Power Sources, 300, 402-412 (2015)

Nano-Composite Cathode Fabrication With Ceria Pre-infiltration

Uninfiltrated Surface

Ceria Pre-Infiltrated Surface

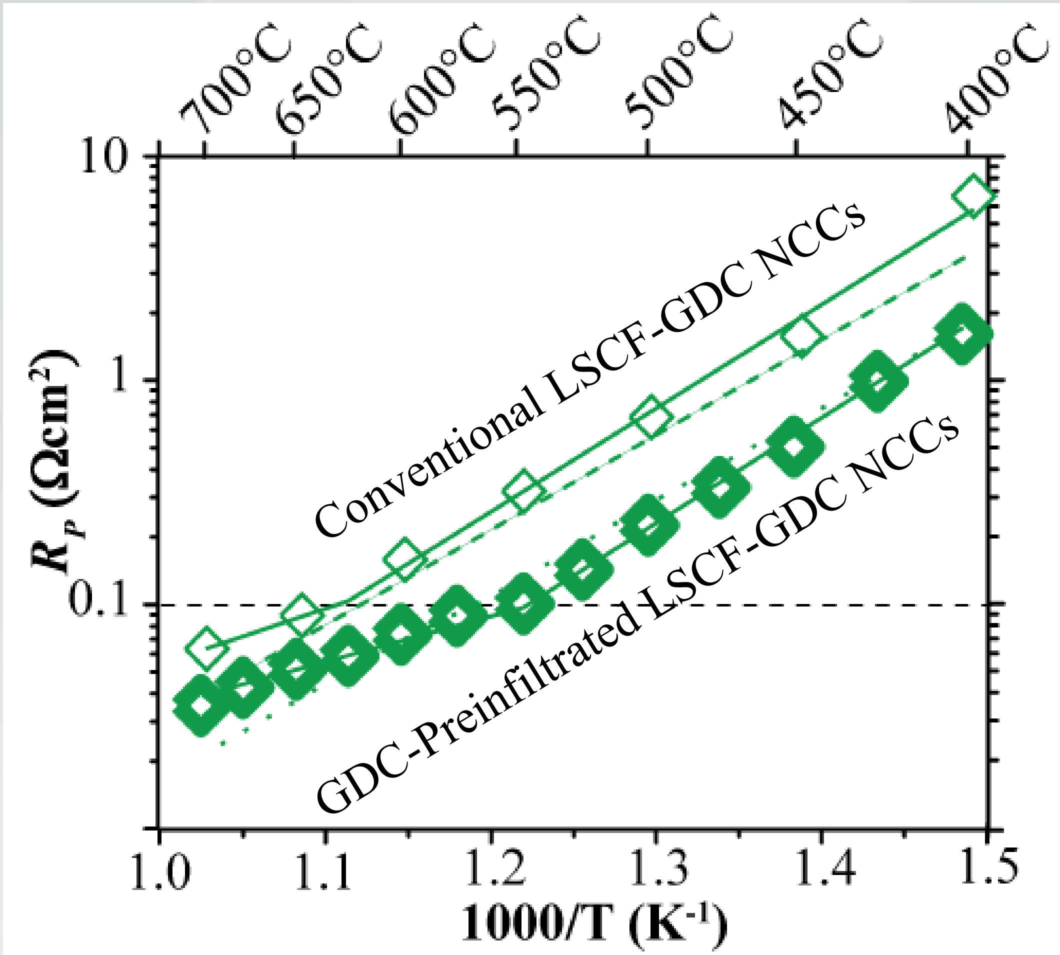
Ceria and LSCF Infiltrated Surface



All scale bars are 50 nm wide

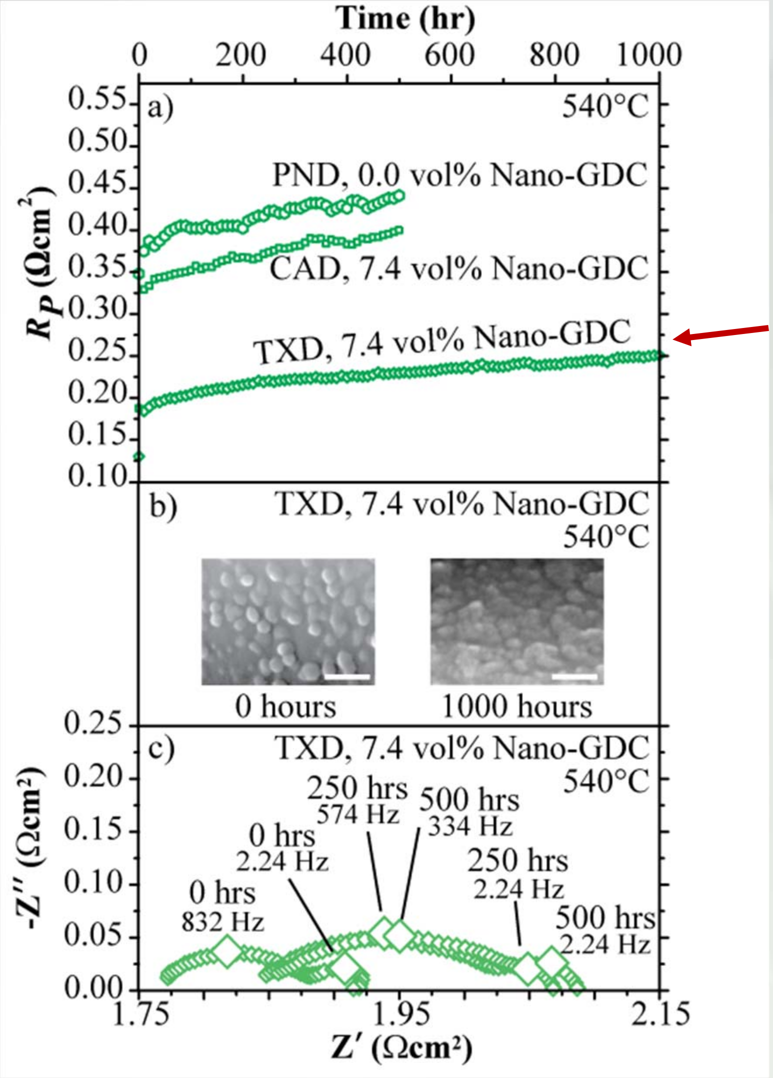
Burye and Nicholas, J Power Sources, 300, 402-412 (2015)

Standard LSCF-GDC Shows Decent Performance and GDC Pre-Infiltration Decreases Cathode Resistance



Burye and Nicholas, J Power Sources, 300, 402-412 (2015)

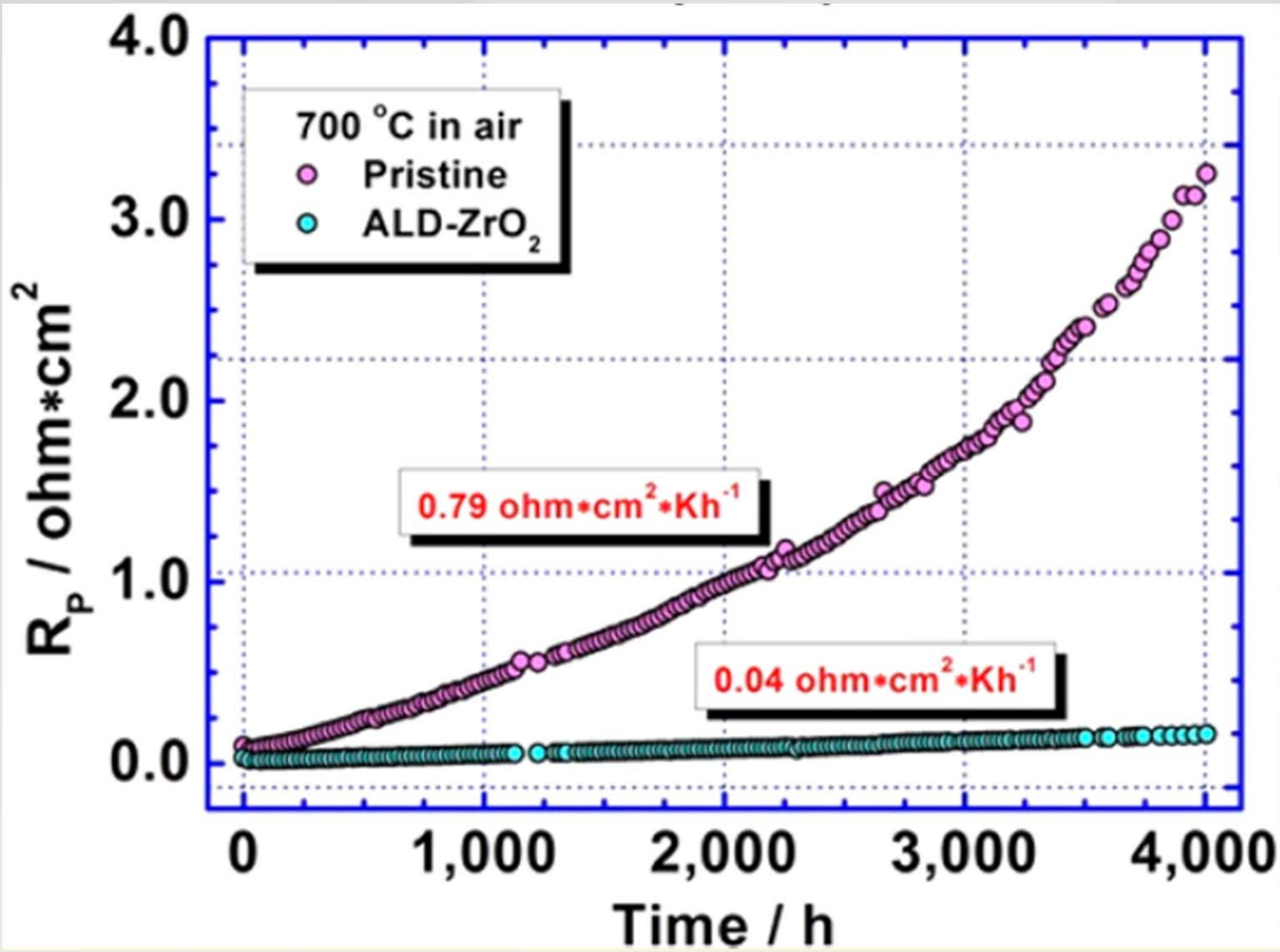
Uncoated GDC Pre-Infiltrated LSCF-GDC Cells Have Stability Problems at 550°C Under Open Circuit Conditions



39 %/khrs after initial "break-in"

Burye and Nicholas, J Power Sources, 300, 402-412 (2015)

ZrO_2 Thin Film Deposited by ALD Could Greatly Improve the Stability of SOFC NCCs



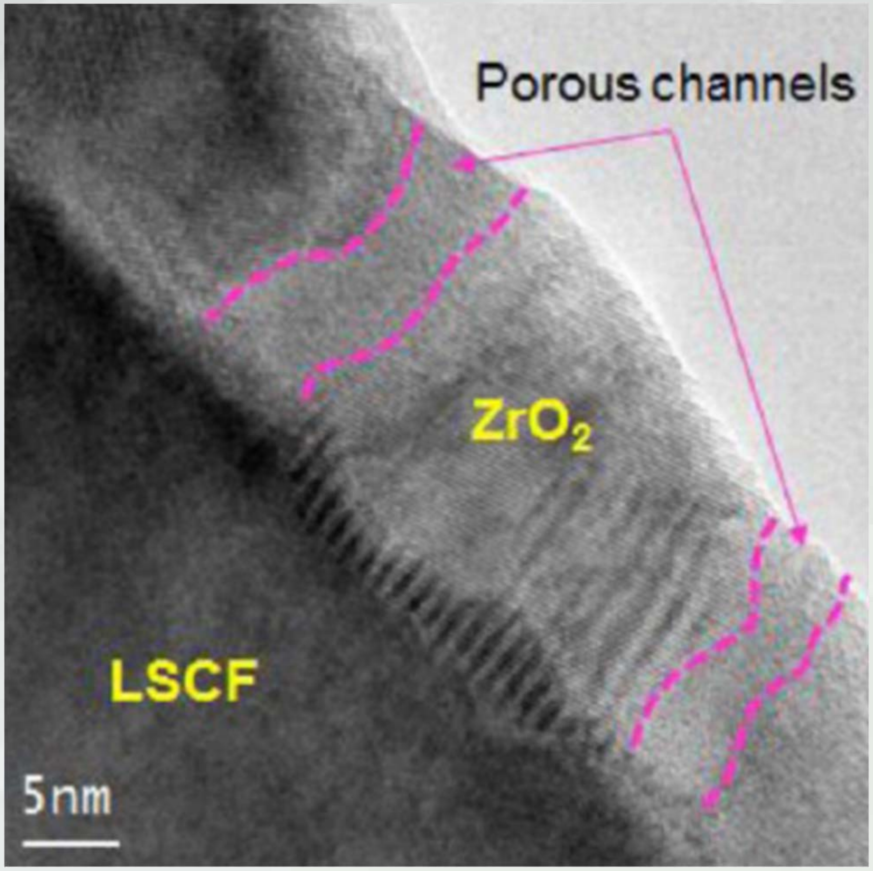
Standard LSC-LSGM

5nm ZrO_2 overcoated LSC-LSGM

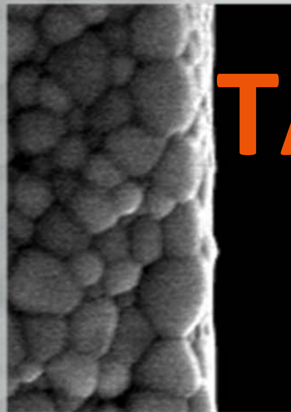
LSC ($La_{0.6}Sr_{0.4}CoO_{3-\delta}$) nanoparticles supported on a porous LSGM ($La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-\delta}$) scaffold

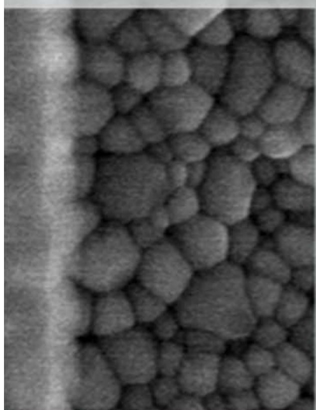
Gong *et al*, Nano letters, 13.9 (2013)

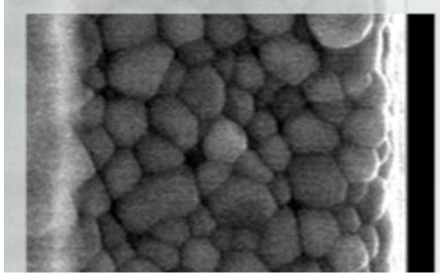
The Morphology of the ALD Coatings Grown by the Huang Group is More Porous than the Dense Conformal Coatings Reported by Other Groups



Gong *et al*, Chem. Materials, 25, 4224 (2013)







TALK Outline

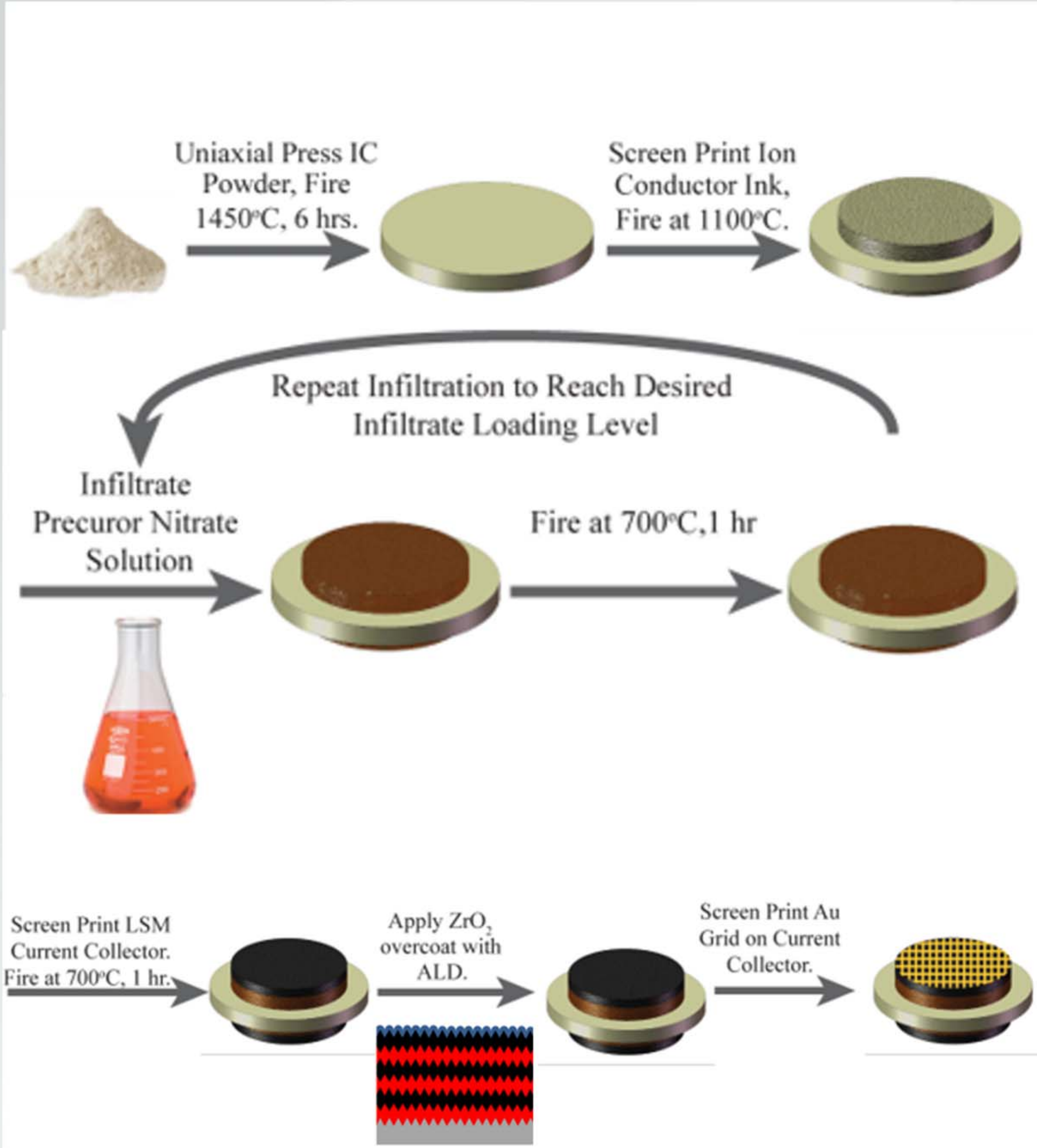
ALD-Stabilized Nano-Composite Cathodes

1. Motivation
2. **Experimental Methods**
3. Results and Discussion

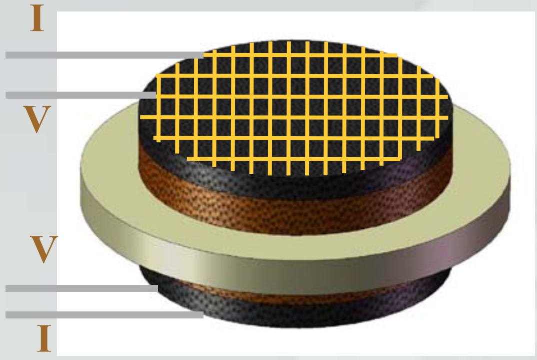
Ni-Ag Circuits Pastes

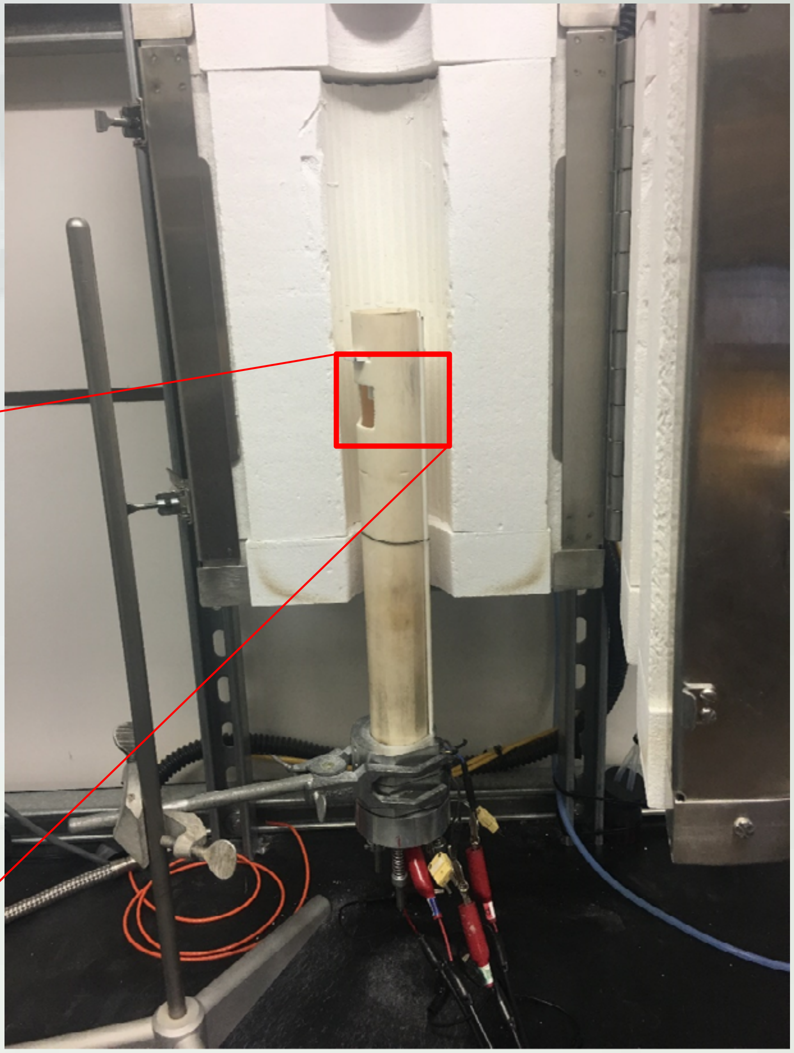
1. Motivation
2. Experimental Methods
3. Results and Discussion

ZrO_2 Coated Nano-Composite Cathode Fabrication

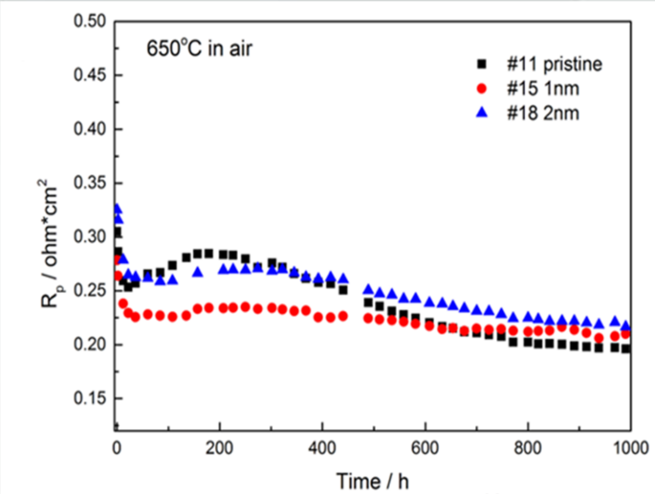


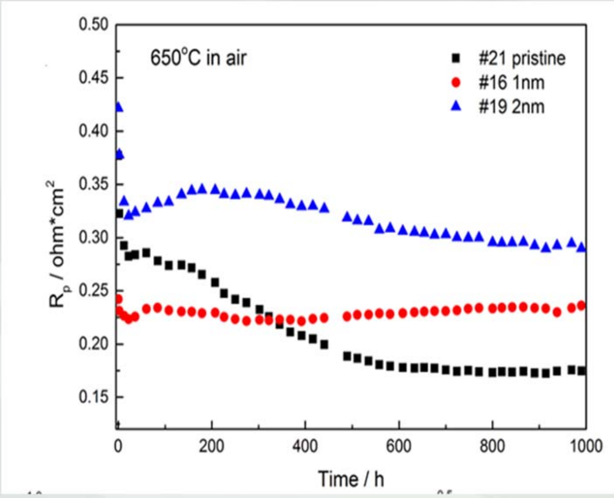
Gold Current Collector Grids with Platinum Plate Push-Contacts were Used for the Measurements Here

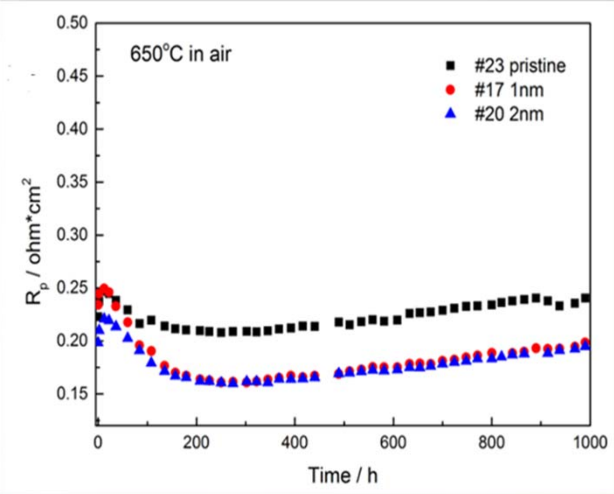




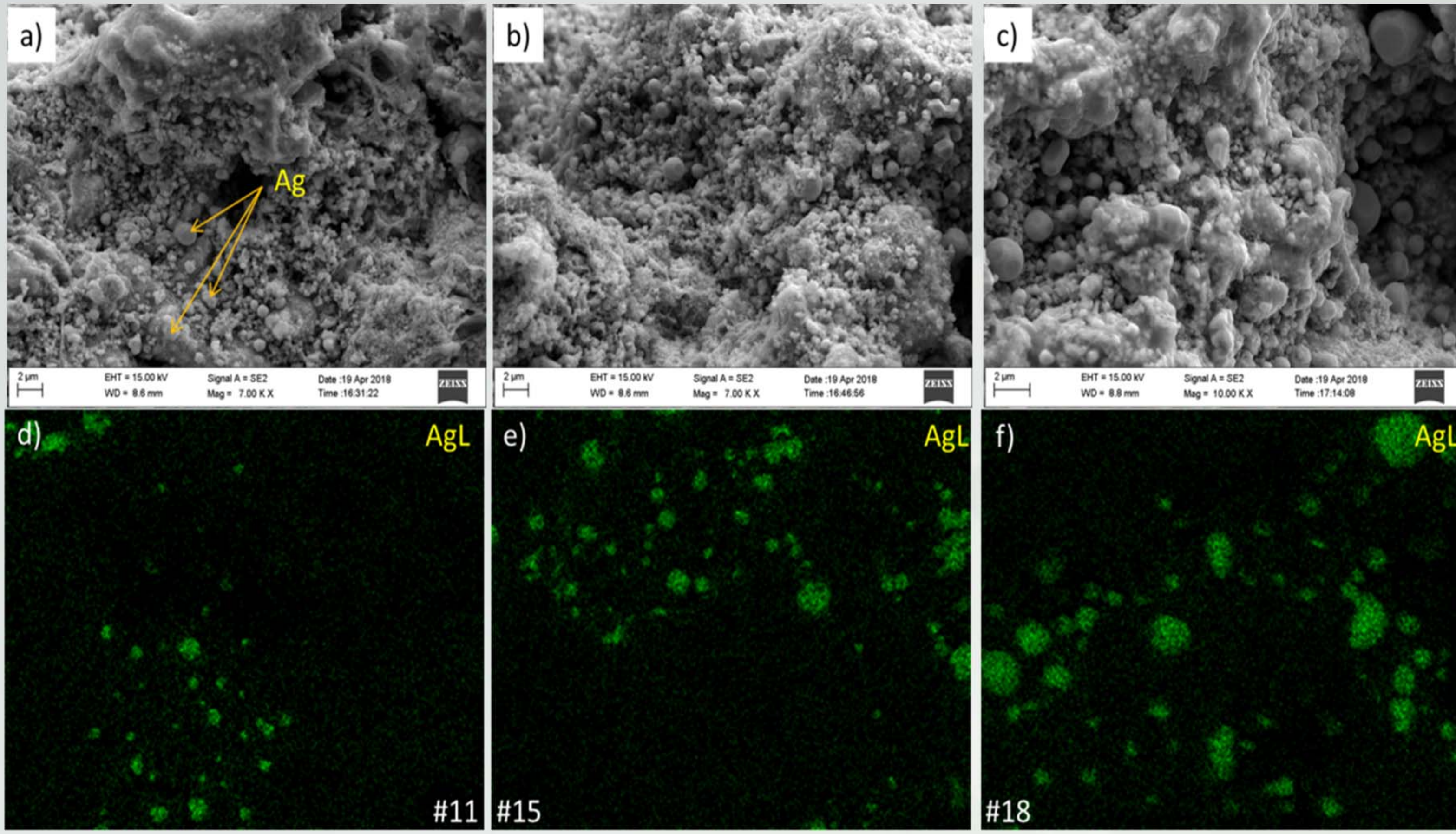
Silver Current Collectors Result in Strange, Unreproducible R_p Behavior at Elevated Temperatures







Silver Should NOT Be Used as Current Collector Because of Its Migration at Elevated Temperature

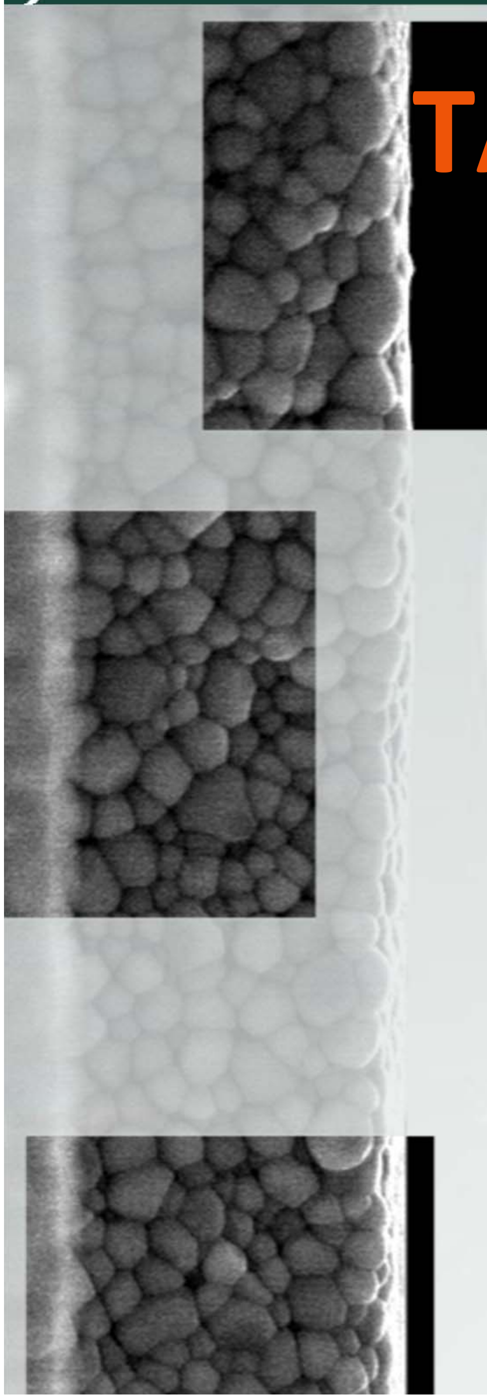


Electrode

Electrolyte

Electrode

Electrolyte



TALK Outline

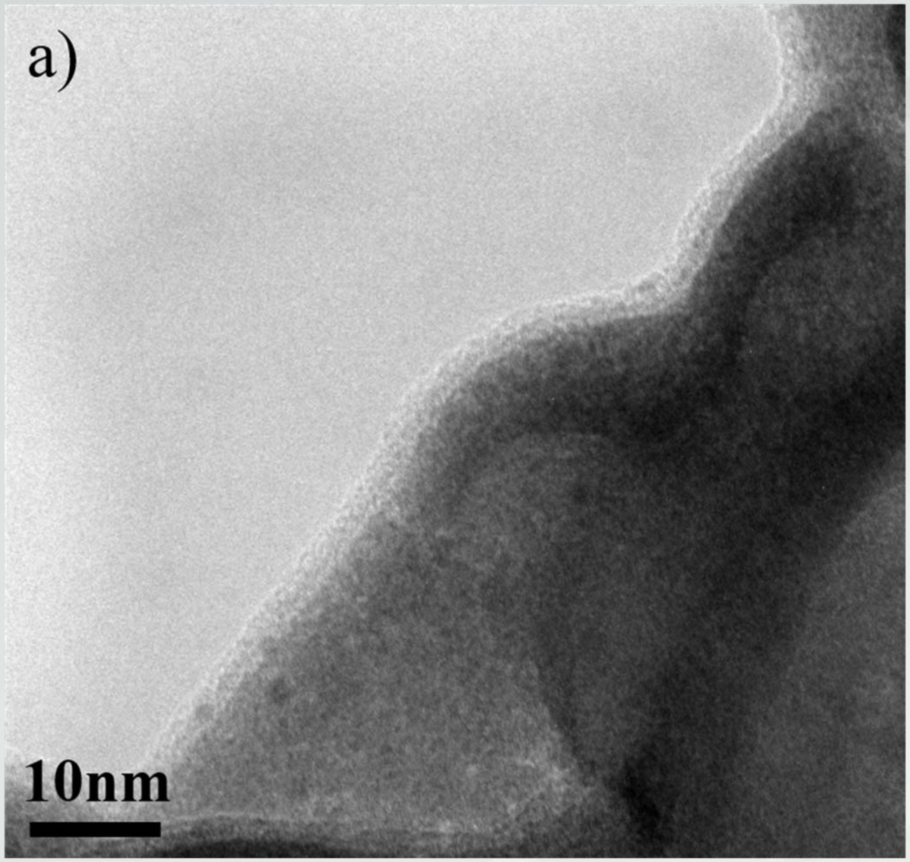
ALD-Stabilized Nano-Composite Cathodes

1. Motivation
2. Experimental Methods
3. **Results and Discussion**

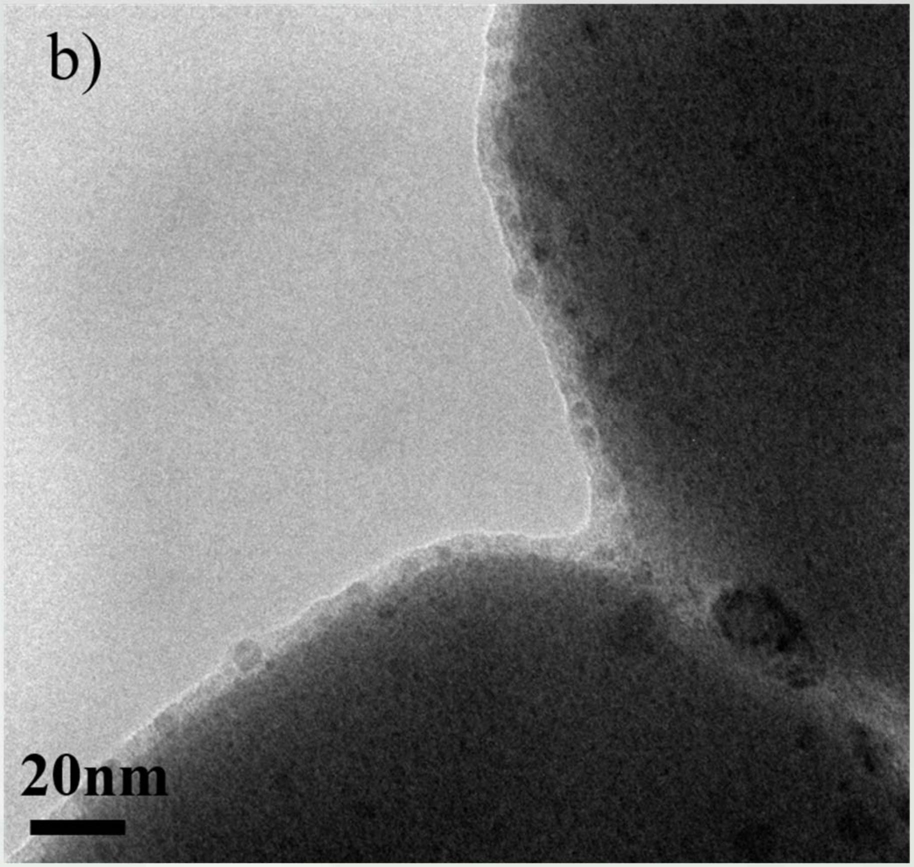
Ni-Ag Circuits Pastes

1. Motivation
2. Experimental Methods
3. Results and Discussion

ZrO_2 Overcoat Maintained Conformal Target Thickness After 1000 Hours at 650°C

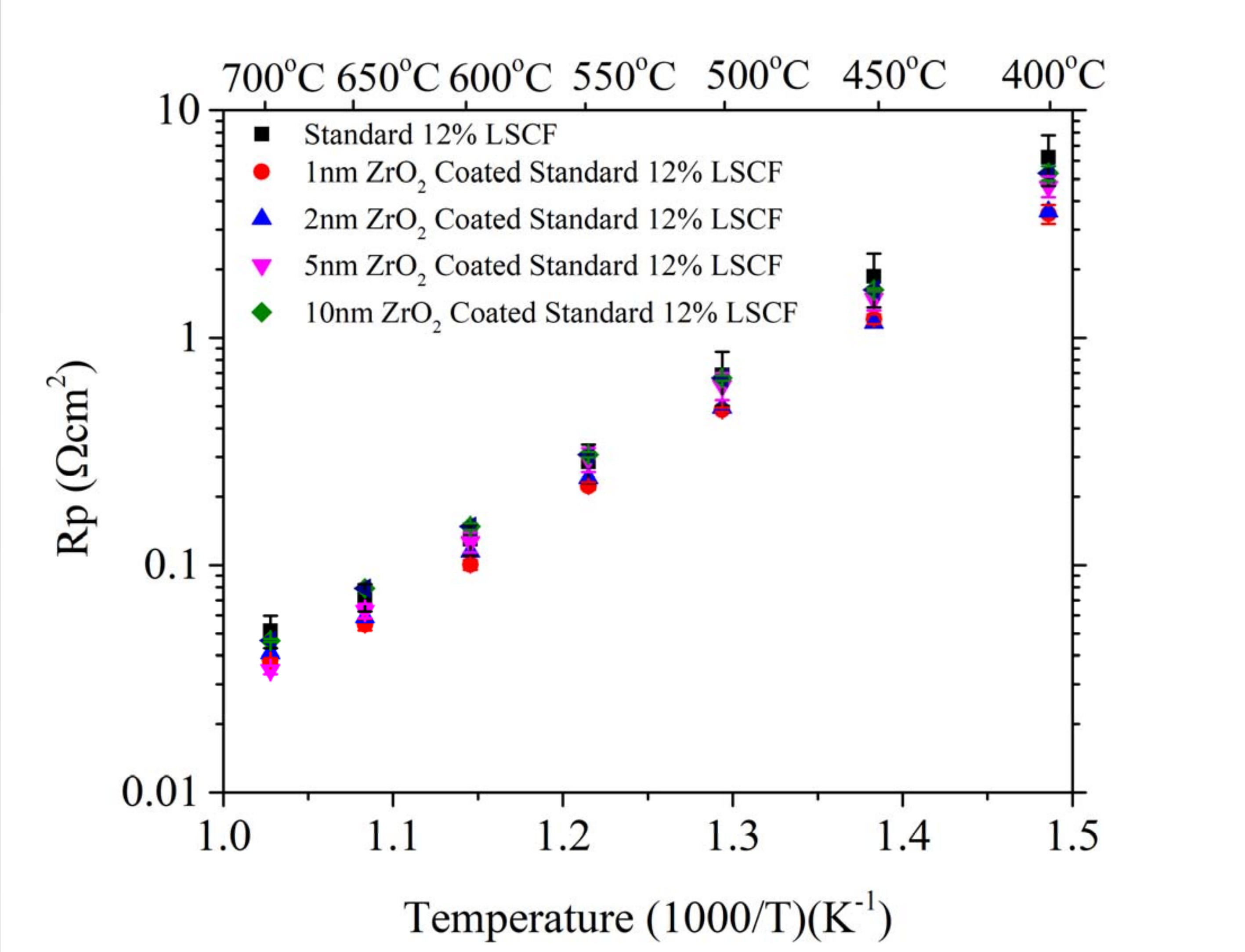


Tested cell with 3nm ZrO_2 overcoat (actual thickness ~3.2nm)



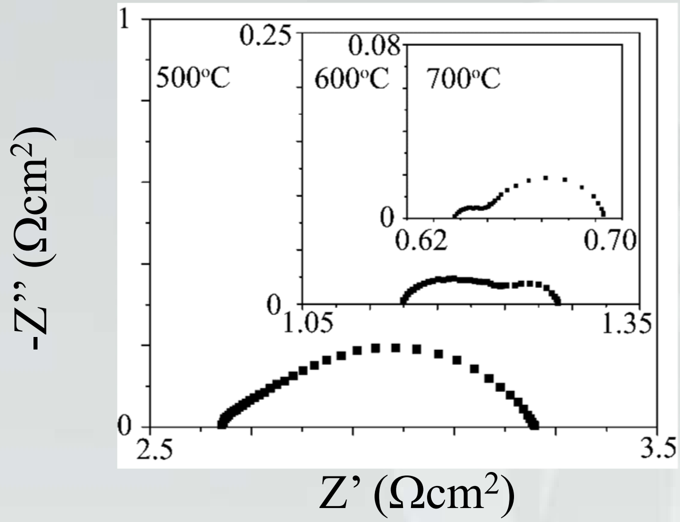
Tested cell with 5nm ZrO_2 overcoat (actual thickness ~5.3nm)

1-10 nm Thick Zirconia Overcoats Don't Dramatically Affect Conventional LSCF-GDC NCC Performance

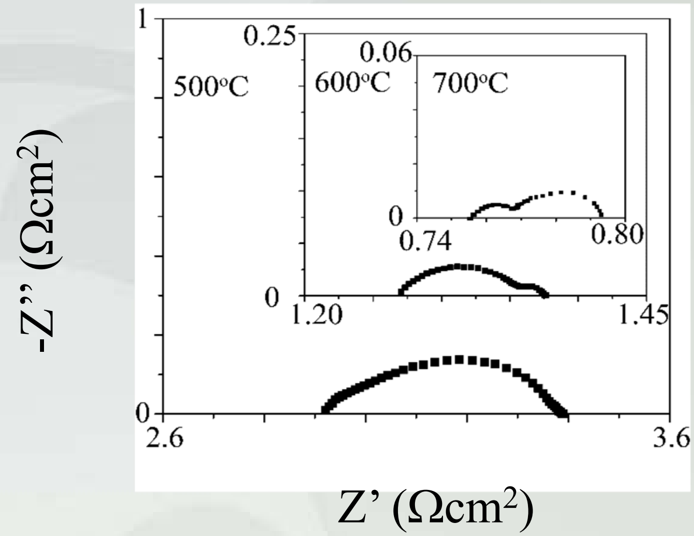


1-10 nm Thick Zirconia Overcoats Don’t Dramatically Affect Conventional LSCF-GDC NCC Performance

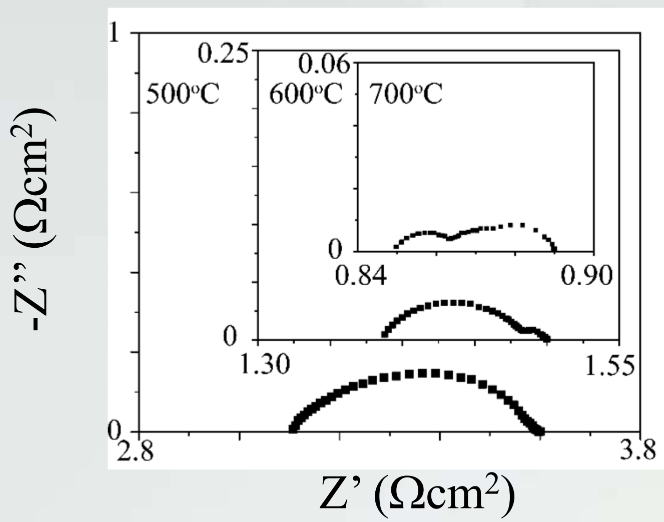
Standard LSCF-GDC



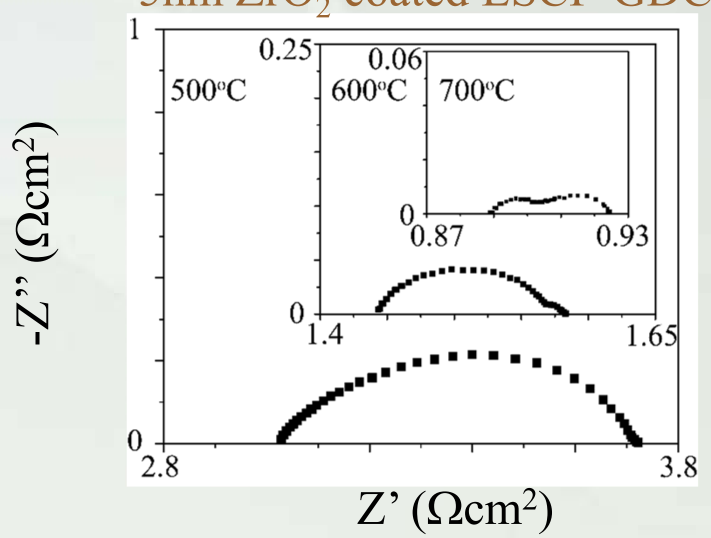
$1nm\ ZrO_2$ coated LSCF-GDC



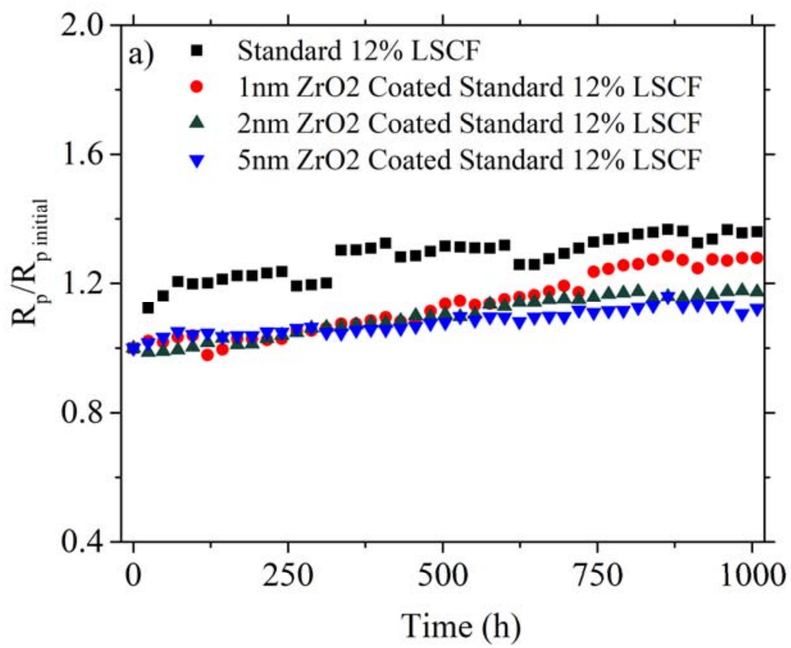
$2nm\ ZrO_2$ coated LSCF-GDC

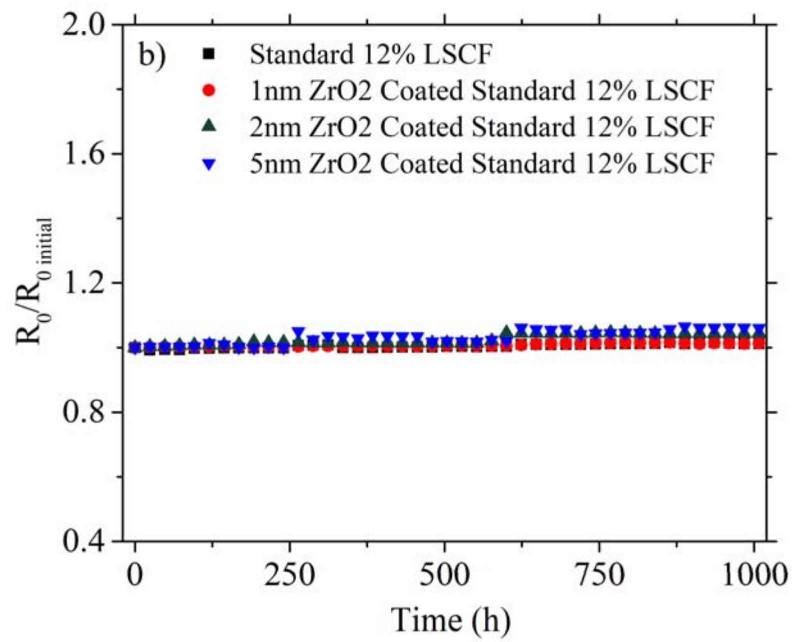


$5nm\ ZrO_2$ coated LSCF-GDC



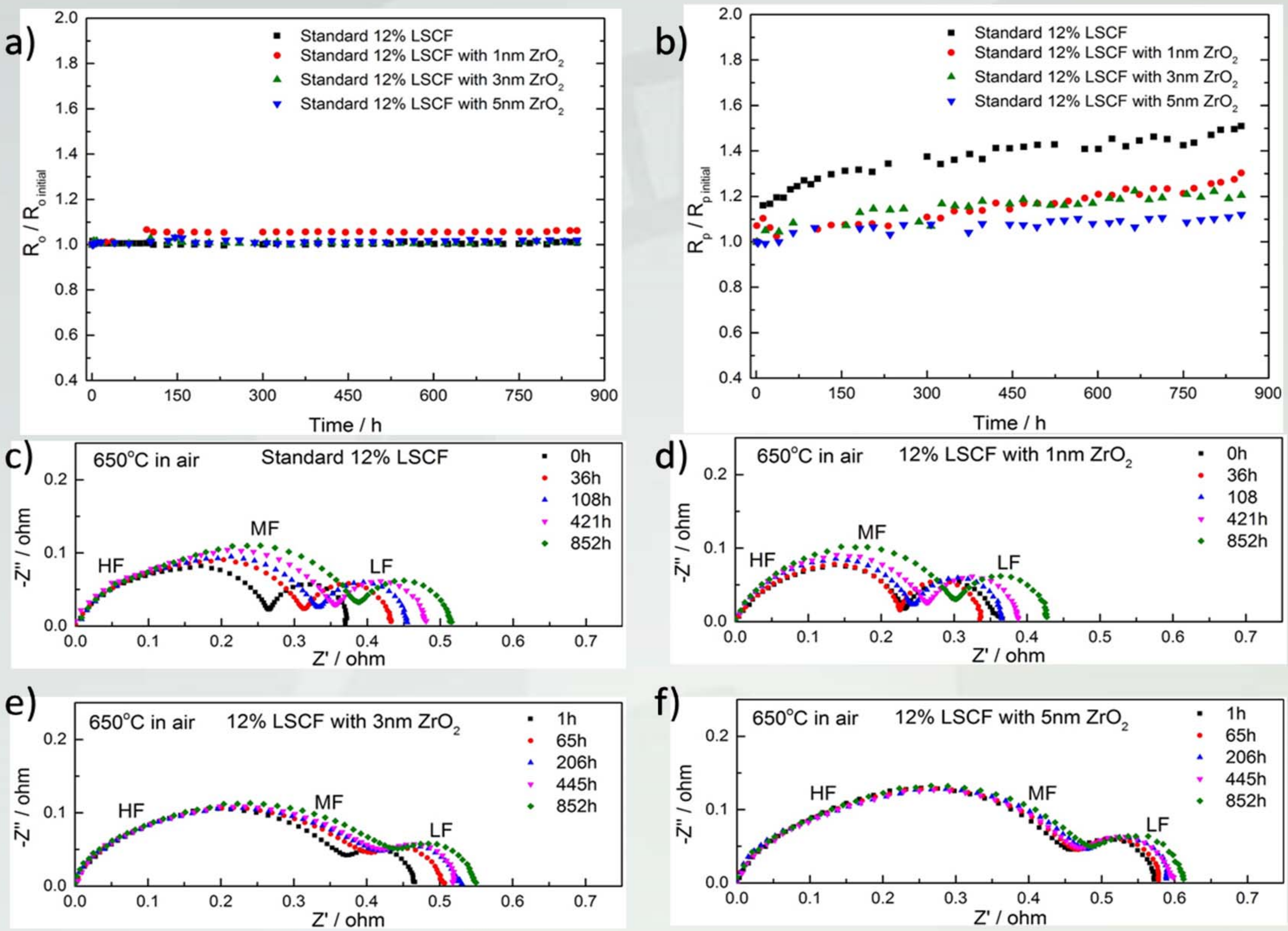
Thicker Zirconia Overcoats Result in Lower 650°C *Rp* Degradation Rates



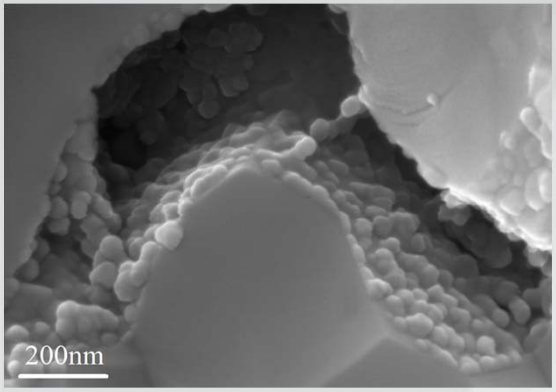


	R_p degradation rate (/khrs)	R_0 degradation rate (/khrs)
12% Standard LSCF	36.1% (0.043Ωcm²/khrs)	1.9%
1nm ZrO_2 coated 12% LSCF	28% (0.015Ωcm²/khrs)	1.4%
2nm ZrO_2 coated 12% LSCF	18% (0.015Ωcm²/khrs)	4.2%
5nm ZrO_2 coated 12% LSCF	12% (0.011Ωcm²/khrs)	6.3%

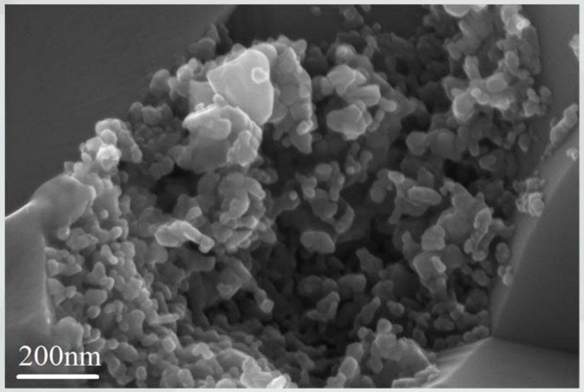
Independent 650°C Degradation Tests at the University of South Carolina Showed Similar Results



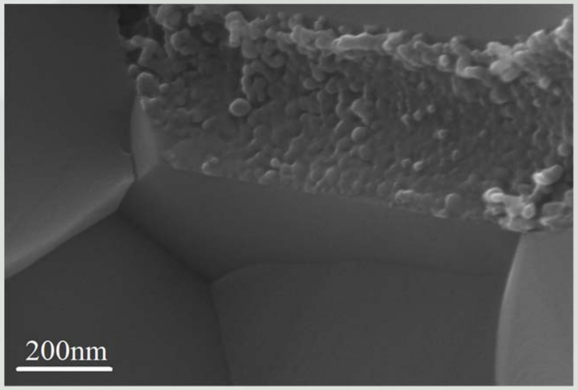
No Obvious Particle Coarsening Was Observed for All Cells after 1000h Degradation at 650°C



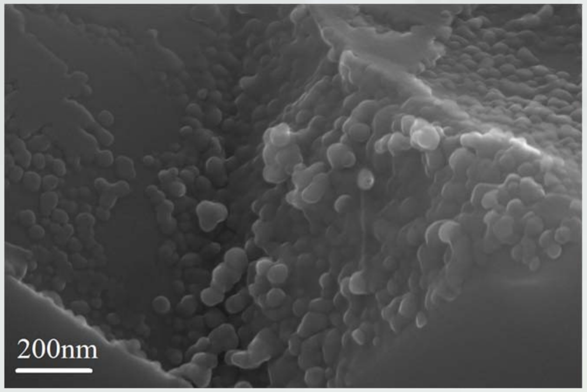
As-produced 12% standard LSCF-GDC NCC



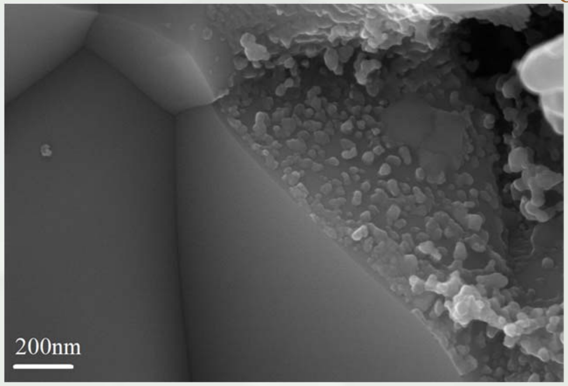
12% standard LSCF-GDC NCC after 1000h at 650°C



1nm ZrO_2 coated 12% standard LSCF-GDC NCC after 1000h at 650°C

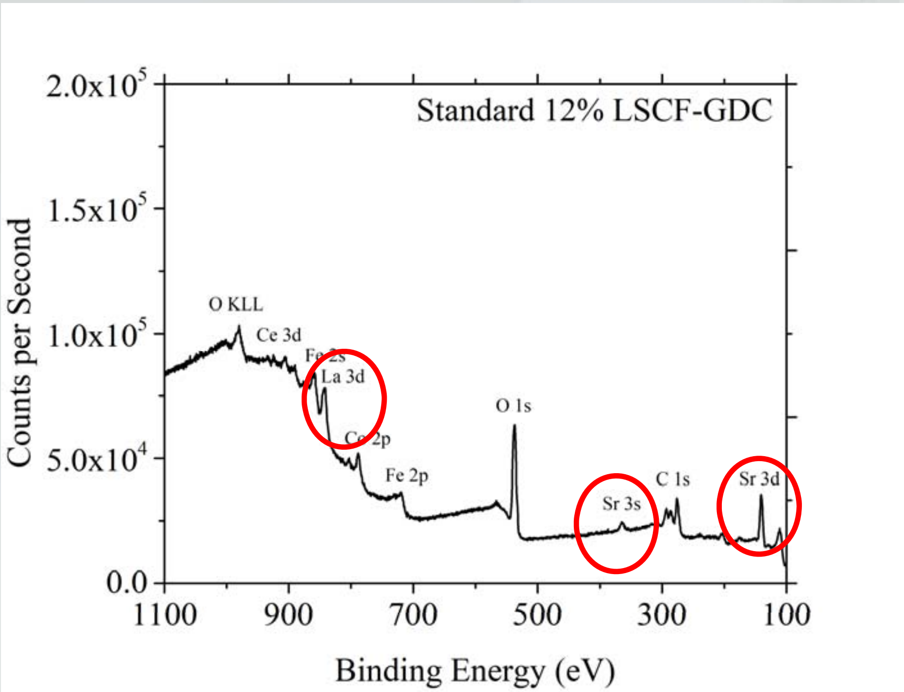


2nm ZrO_2 coated 12% standard LSCF-GDC NCC after 1000h at 650°C



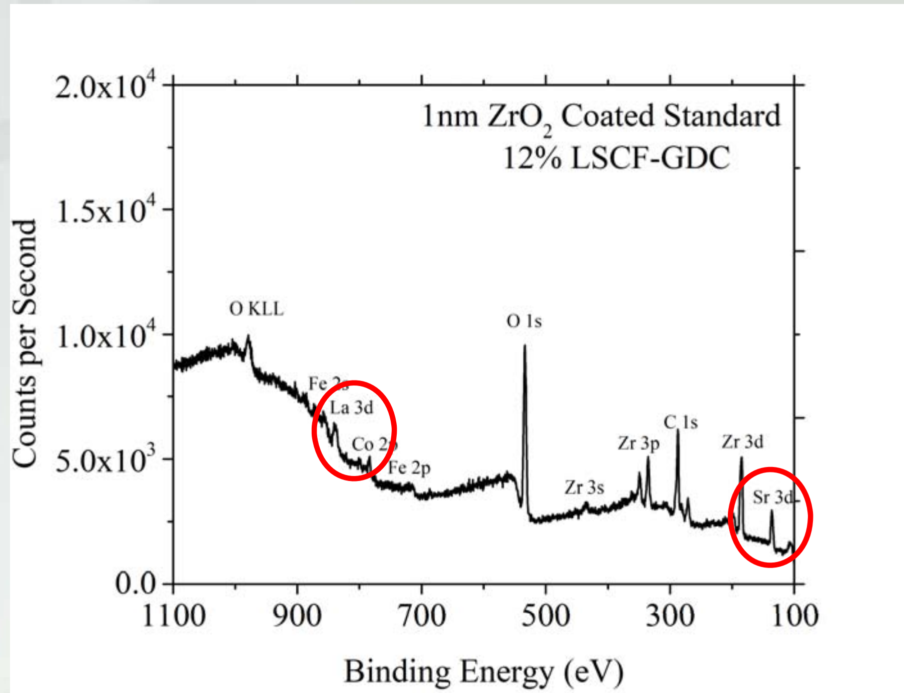
5nm ZrO_2 coated 12% standard LSCF-GDC NCC after 1000h at 650°C

Suppression of Sr Segregation Is Suspected to Contribute to the LSCF-GDC NCC Performance Improvement with ZrO_2 Overcoat



Standard 12% LSCF

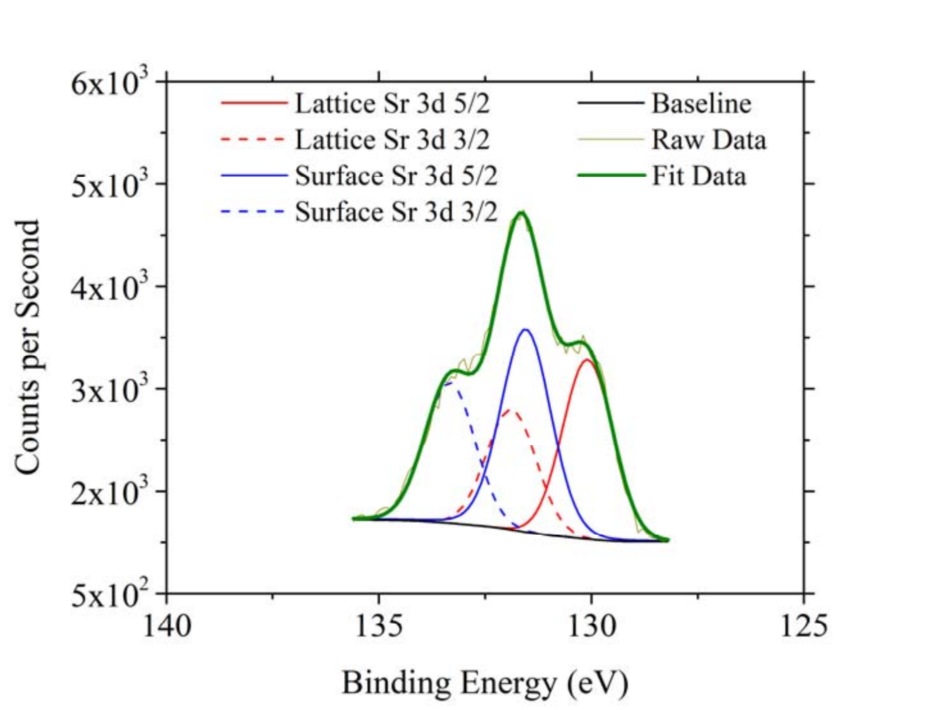
[Sr]/[La+Sr+Co+Fe]=51%

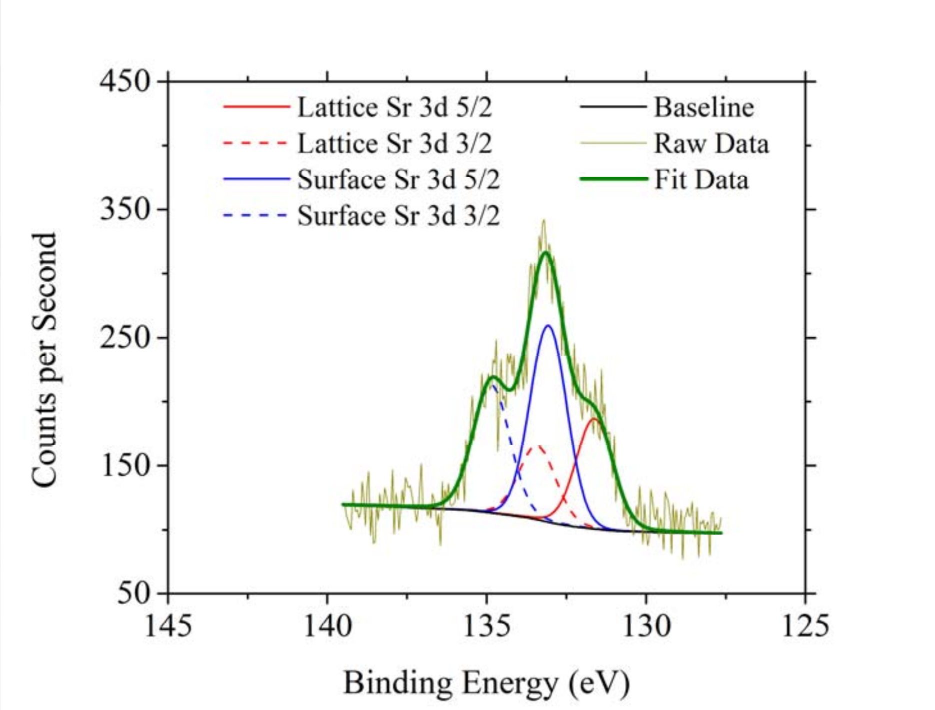


1nm ZrO_2 Coated Standard 12% LSCF

[Sr]/[La+Sr+Co+Fe]=42%

XPS Deconvolution Suggests There is Not Much Change in the Partition Between Sr Surface Sites with ALD Overcoat





Standard 12% LSCF

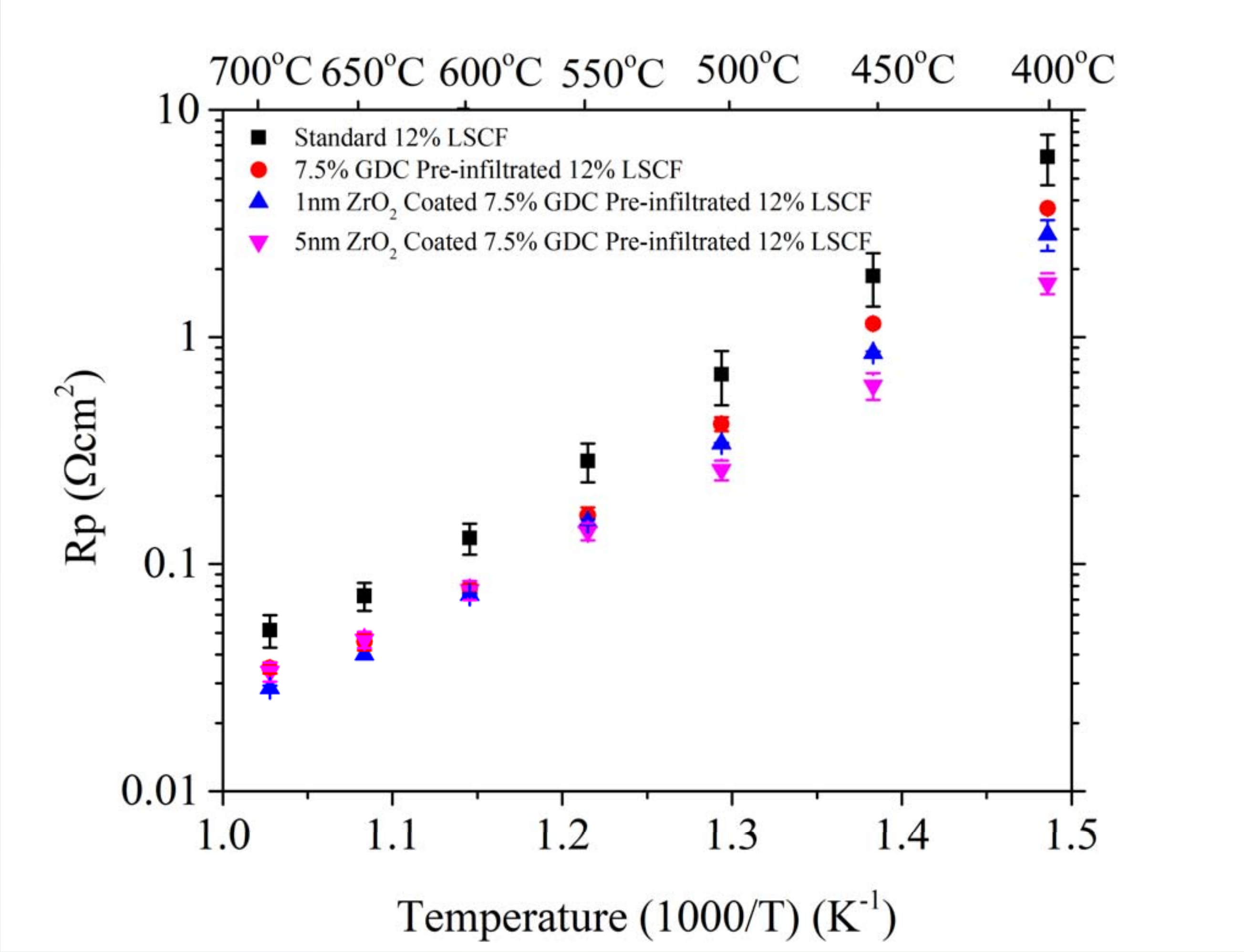
Surface Sr-- 57%

1nm ZrO_2 Coated Standard 12% LSCF

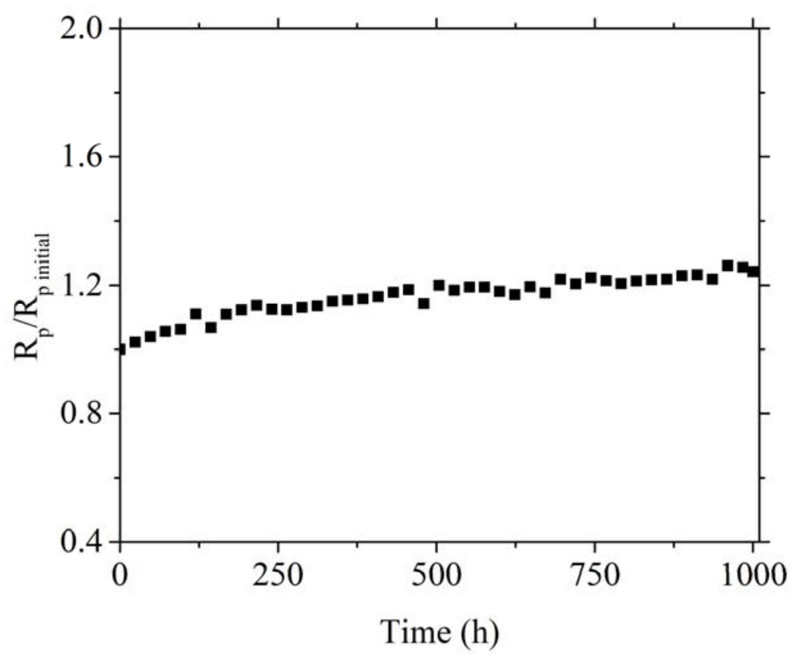
Surface Sr--63%

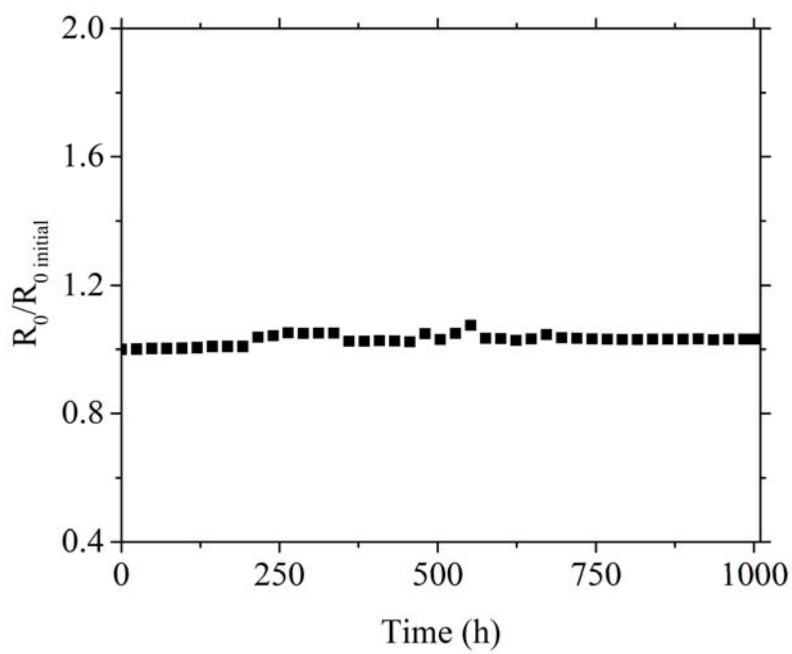
Using Peak Assignments found in Crumlin, Ethan J., et al. Energy & Environmental Science 5.3 (2012)

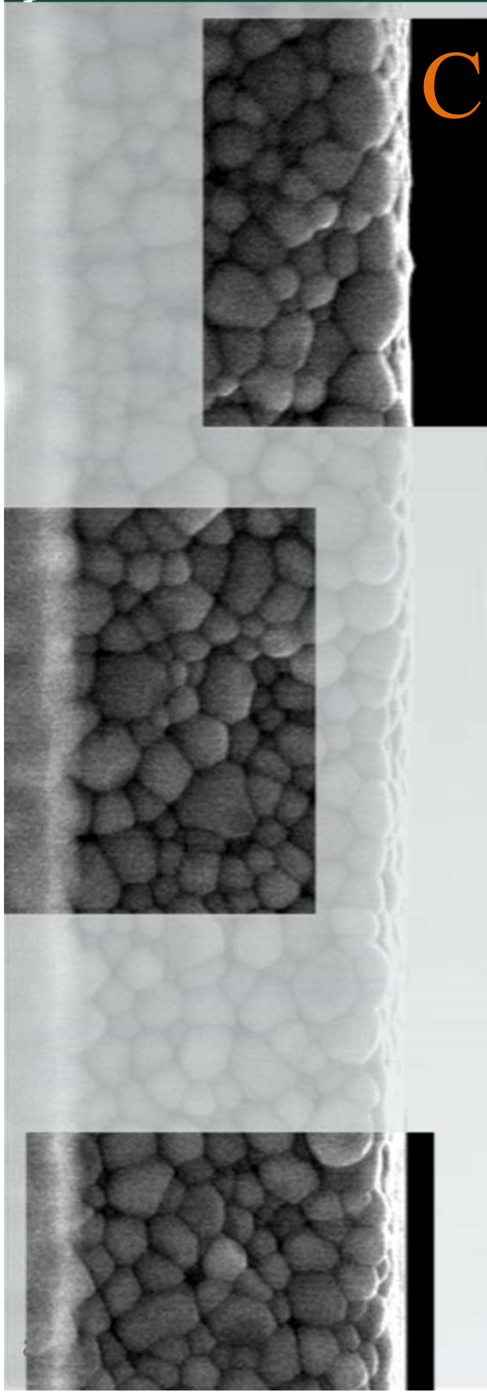
R_p Improvement in the Low Temperature Region Was Observed for Coated GDC Pre-infiltrated LSCF-GDC NCCs



5nm ZrO_2 Coated 7.5% GDC Pre-infiltrated 12% LSCF Showed *Rp* Degradation Rates of ~22%/khrs







Conclusions

1. ZrO_2 ALD overcoats of 1-5 nm in thickness improved the long-term stability of standard LSCF-GDC NCCs without significantly altering the 400-700°C LSCF-GDC R_p.

2. A possible reason for the improved R_p is Sr surface segregation alterations induced by the zirconia overcoat.

3. ALD overcoats reduced the activation energy for oxygen incorporation into the GDC-preinfiltrated LSFC-GDC NCCs.

4. Although the results are promising, more work is needed to realize cathode degradation rates meeting DOE targets of <1%/khrs.

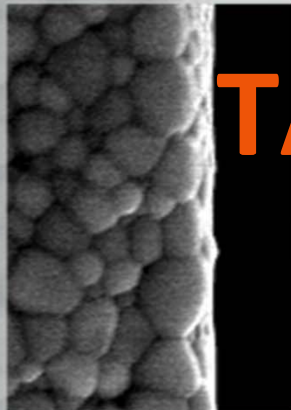
High Performance Circuit Pastes for Solid Oxide Fuel Cell Applications

6 Month Update

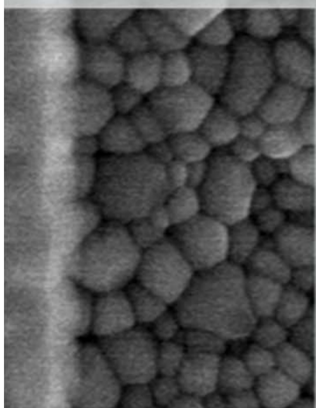
Mr. Genzhi Hu, Ms. Aishwarya Bhatlawande, Ms. Jiyun Park, Mr. Robert Termuhlen, Dr. Yue Qi, Dr. Thomas Beiler, Dr. Timothy Hogan, Dr. Hui-Chia Yu, and Dr. Jason D. Nicholas

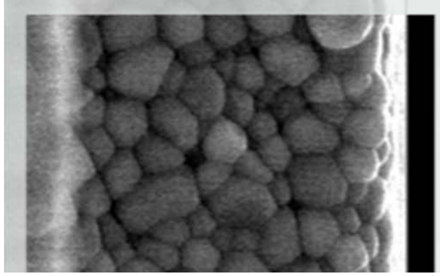
Funded by the Department of Energy Solid Oxide Fuel Cell Core Technology Program through Agreement Number DE-FE0031250

Program Manager: Venkat Venkatraman



TALK Outline





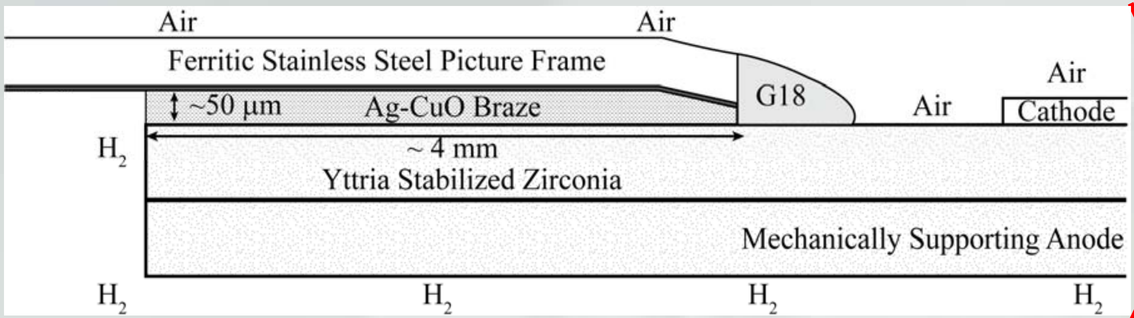
<u>ALD-Stabilized Nano-Composite Cathodes</u>

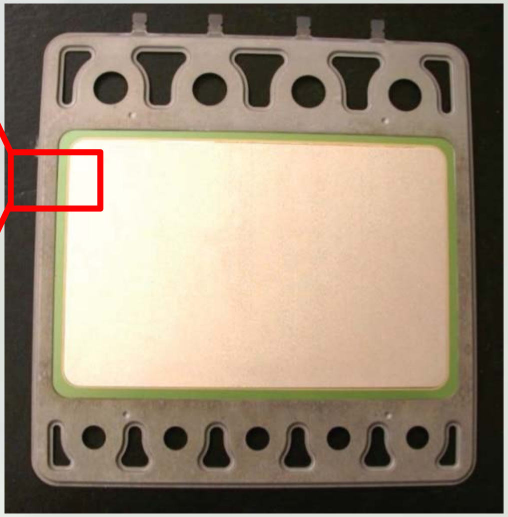
1. Motivation
2. Experimental Methods
3. Results and Discussion

<u>Ni-Ag Circuits Pastes</u>

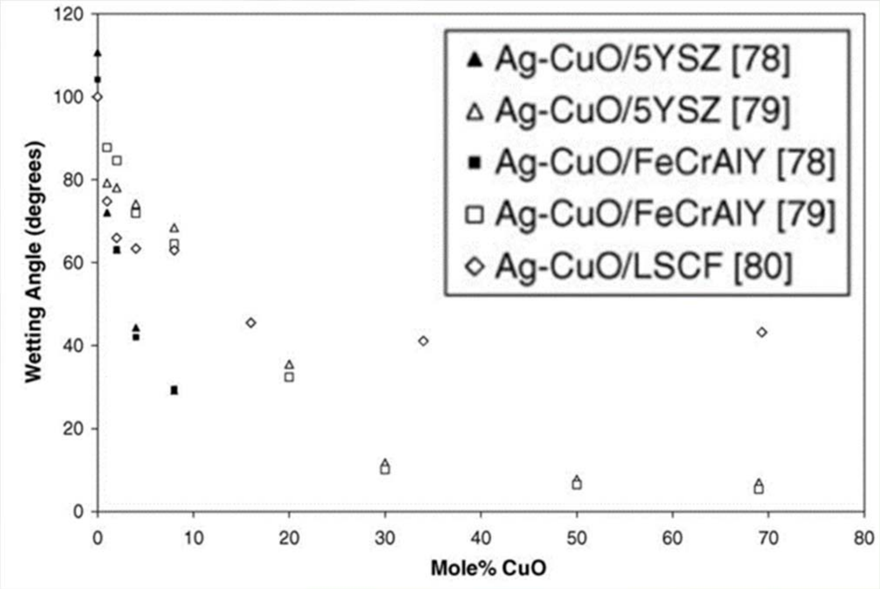
1. **Motivation**
2. Experimental Methods
3. Results and Discussion

Conventional Silver-Copper Oxide Reactive Air Brazes Have many Benefits





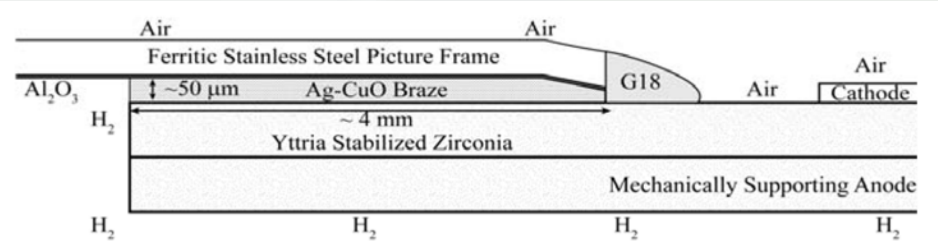
- Brazes are less Permeable to H_2 and O_2 than Glass Seals
- Brazes are more ductile than glass seals, so CTE Mismatch is not a concern
- Reactive air brazing can be performed in air
- The enhanced wetting provided by CuO allows Ag-CuO brazes to be used on a variety of ceramics



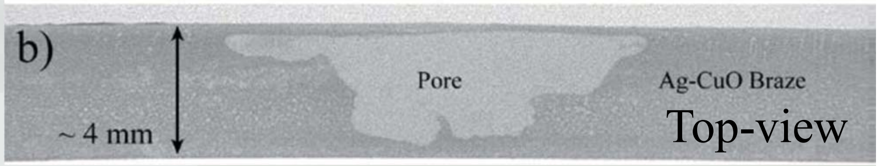
Delphi Technologies Inc, U.S. Patent No US7855030B2
Kim, J.Y., J.S. Hardy, and K.S. Weil, Journal of the American Ceramic Society, 2005. 88 (9): p. 2521-2527.

Reactive Air Brazes Have Several Fatal Flaws

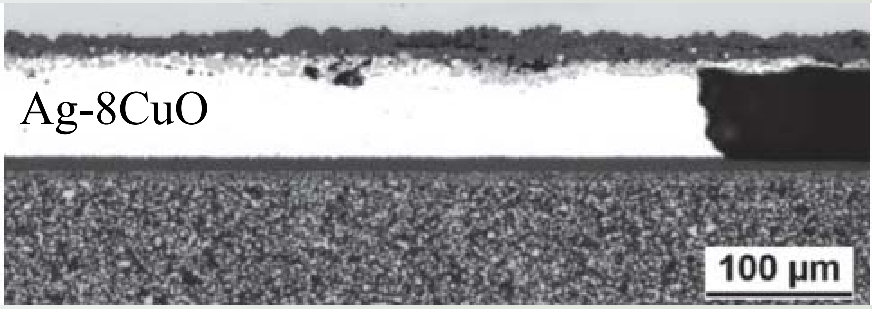
1. Braze joint will be exposed to dual atmospheres (H_2/Air) in SOFC operation.



2. Reactive air silver brazes are only partially wetting, resulting in occasional manufacturing defects (**Type I Pores**);



3. Reduction of reactive air additions (CuO) by hydrogen during SOFC operation can result in **Type II Pores;**



4. **Type III pore** formation due to H_2 and O_2 reaction. CuO additions do not prevent the formation of **Type III Pores** produced when hydrogen and oxygen dissolved in the braze meet and form water pockets.

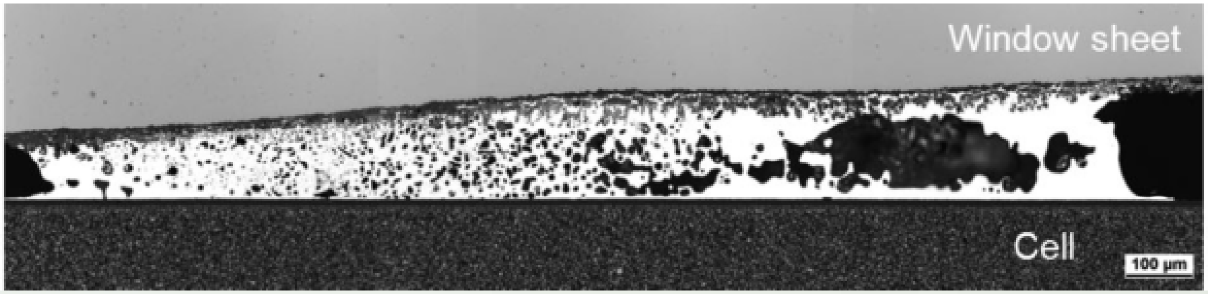
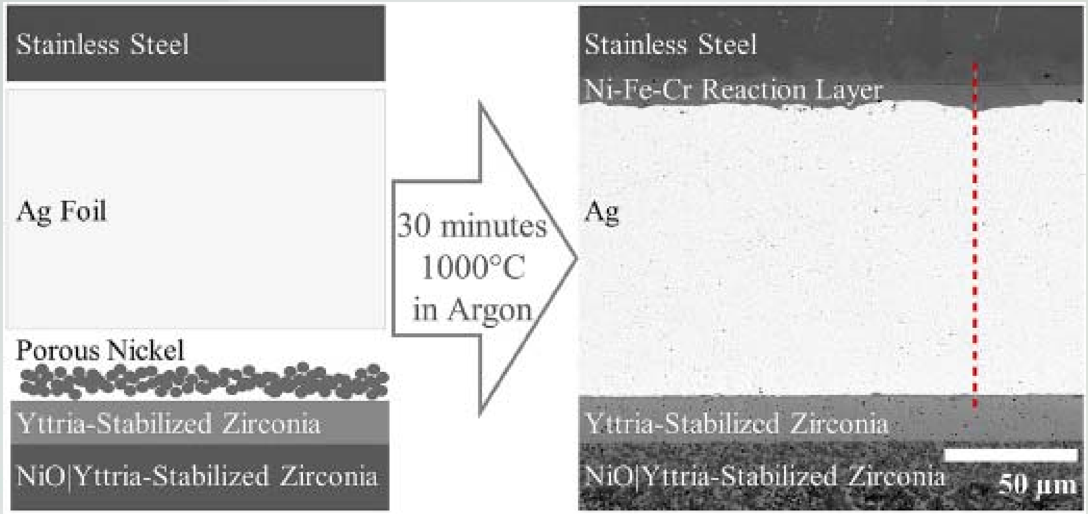
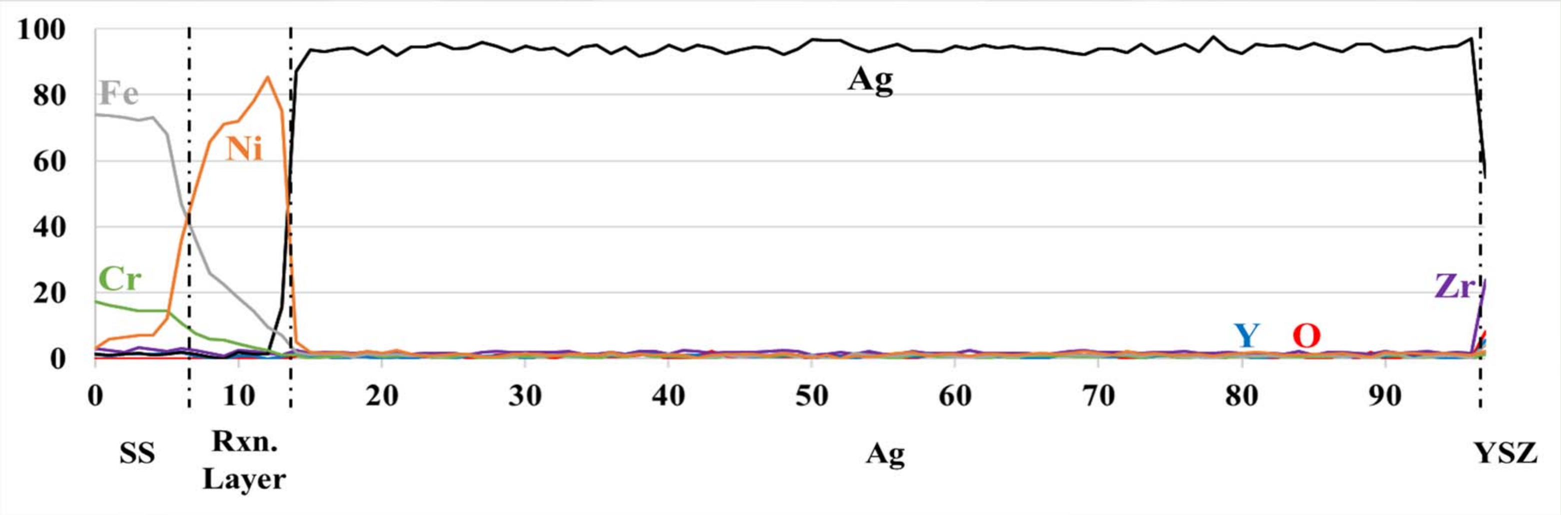


Image b) Courtesy of Delphi Automotive.

Bause, T., et al., Damage and Failure of Silver Based Ceramic/Metal Joints for SOFC Stacks. Fuel Cells, 2013. 13 (4): p. 578-583.

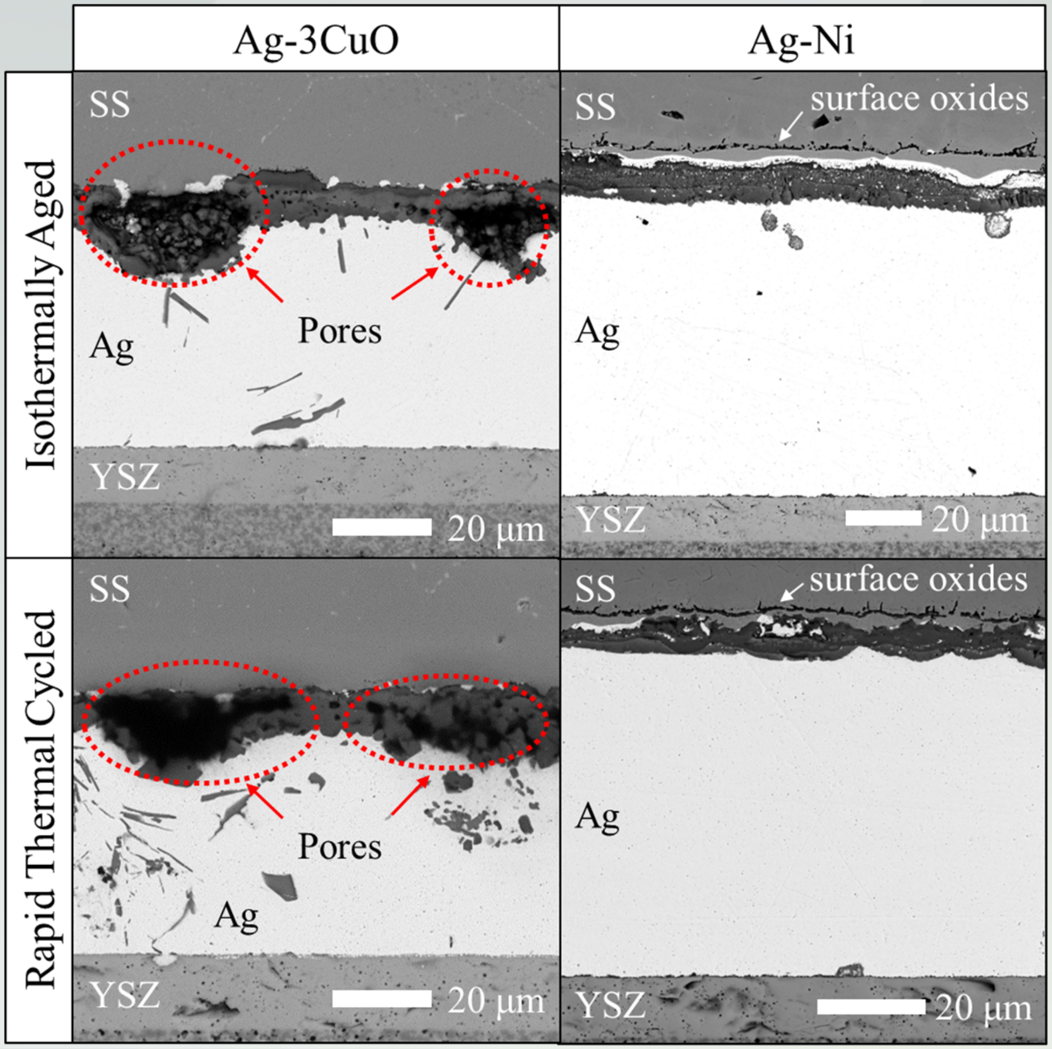
Dense Braze Joints Can be Produced and the Porous Nickel Layer is Transient



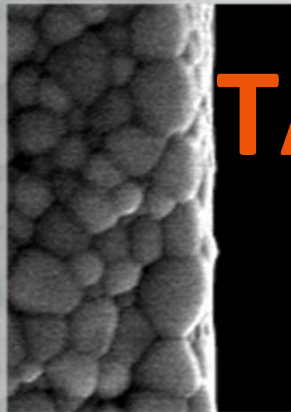


Zhou, Q., T. R. Bieler and J. D. Nicholas. "Transient Porous Nickel Interlayers for Improved Silver-Based Solid Oxide Fuel Cell Brazes." *Acta Materialia* **148**: 156-162, http://dx.doi.org/10.1016/j.actamat.2018.01.061 (2018)

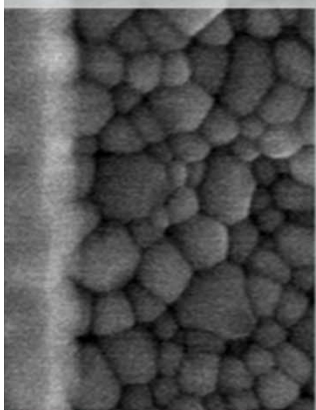
Ag-Ni Brazes Show Superior Dual Atmosphere tolerance After 300 hrs of Isothermal 750°C Aging, or 300 25°C/min 35-830°C Rapid Thermal Cycles



Zhou et al., Dual Atmosphere Isothermal Aging and Rapid Thermal Cycling of Ag-Ni and Ag-CuO Stainless Steel to Zirconia Braze Joints, Intl. J. Hydrogen Energy, Submitted (2019).



TALK Outline

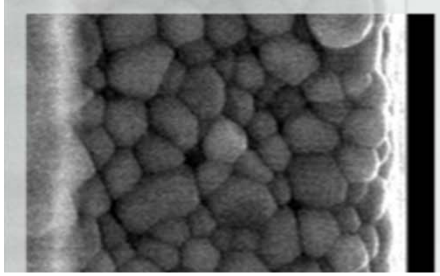


<u>**ALD-Stabilized Nano-Composite Cathodes**</u>

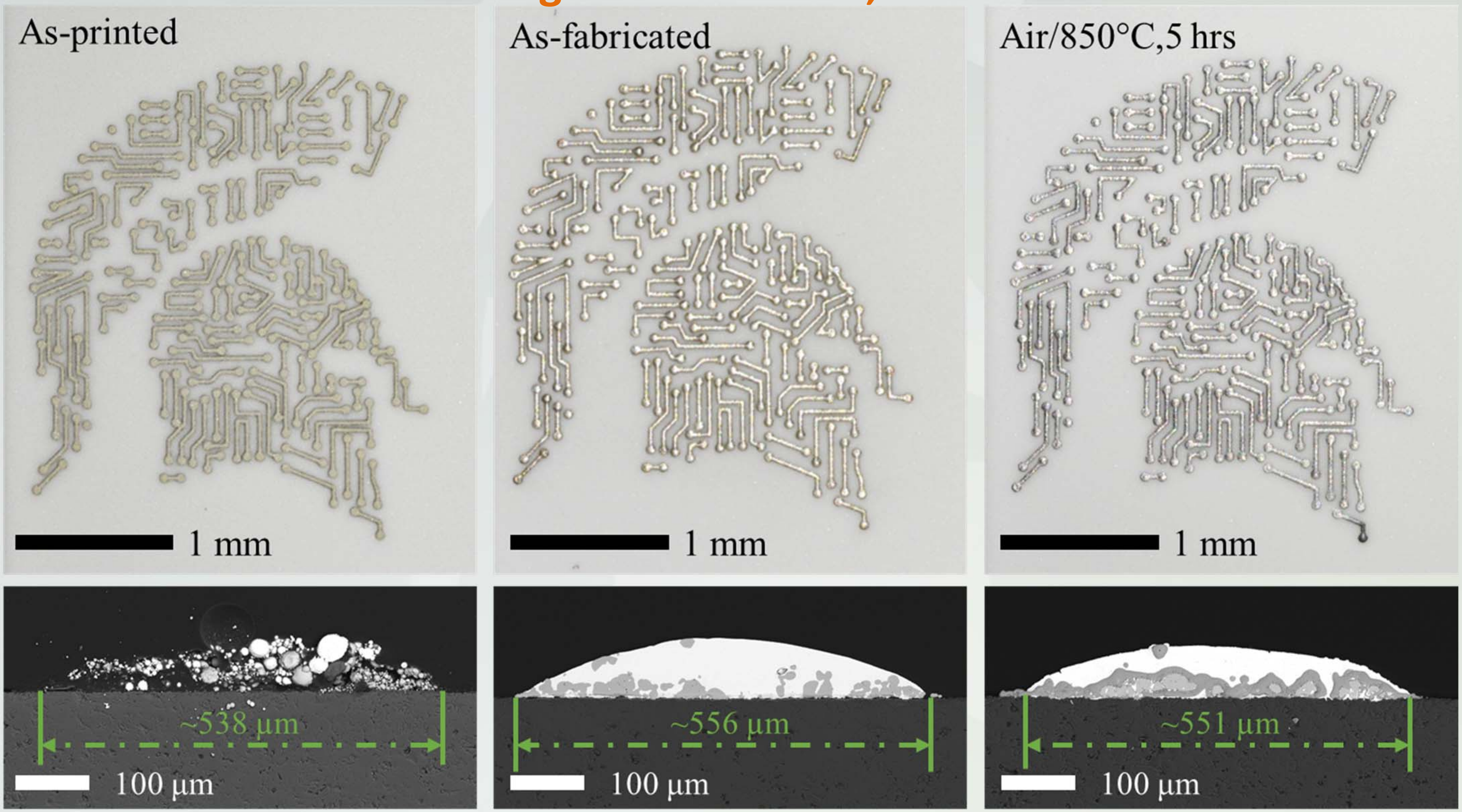
1. Motivation
2. Experimental Methods
3. Results and Discussion

<u>**Ni-Ag Circuits Pastes**</u>

1. Motivation
2. **Experimental Methods**
3. Results and Discussion

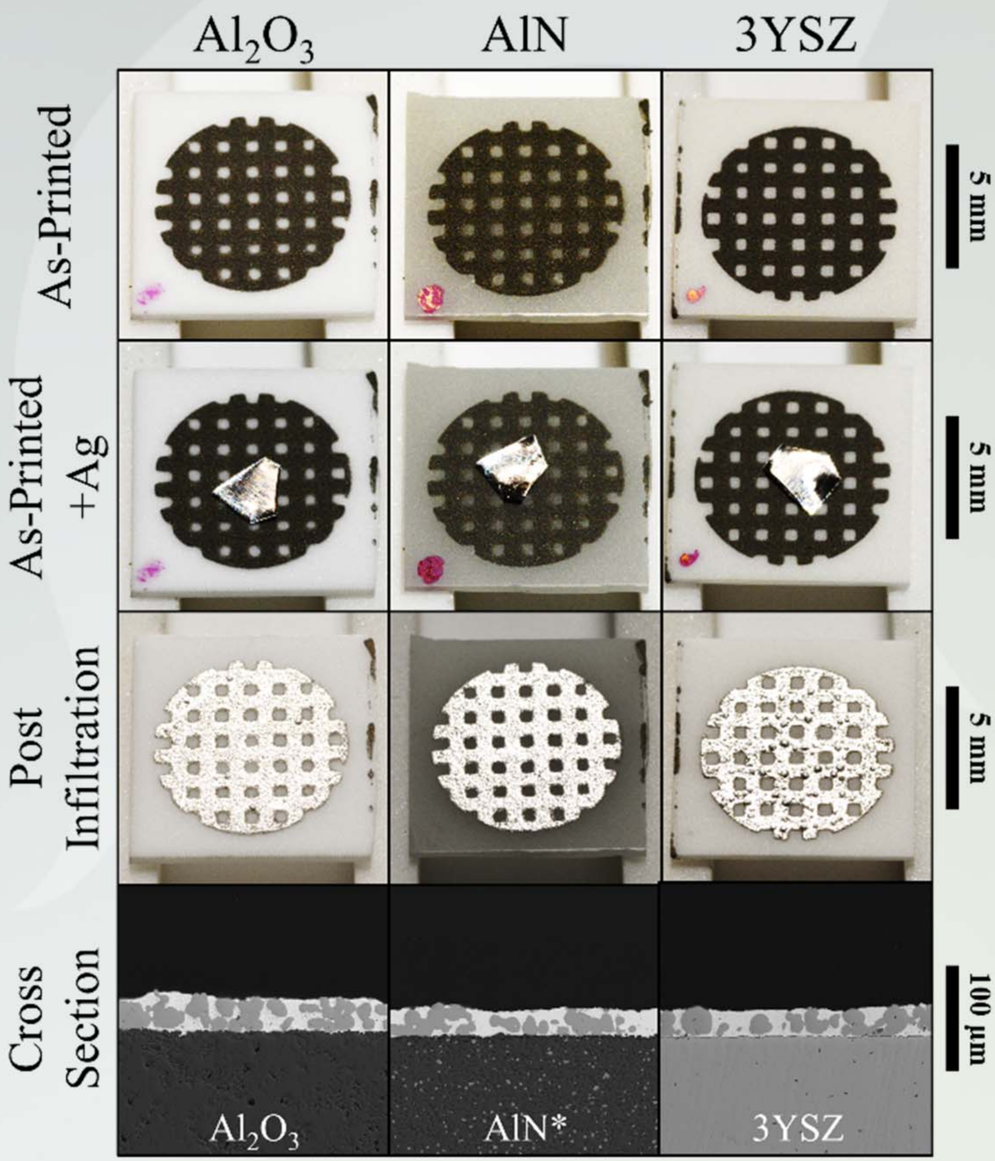


The Controlled Wetting and Spreading of Ag can be used for High Temp Semiconductors, High Power SOFCs, Etc.



Zhou et al., Controlled Wetting and Spreading of Metals on Substrates Using Porous Interlayers and Related Articles, USPTO Provisional Patent (Submitted April 17, 2018)
Zhou et al., Controlled Wetting and Spreading of Ag on Various Ceramic Substrates with Porous Ni Interlayers, Scr. Mater, 2018. (In Preparation)

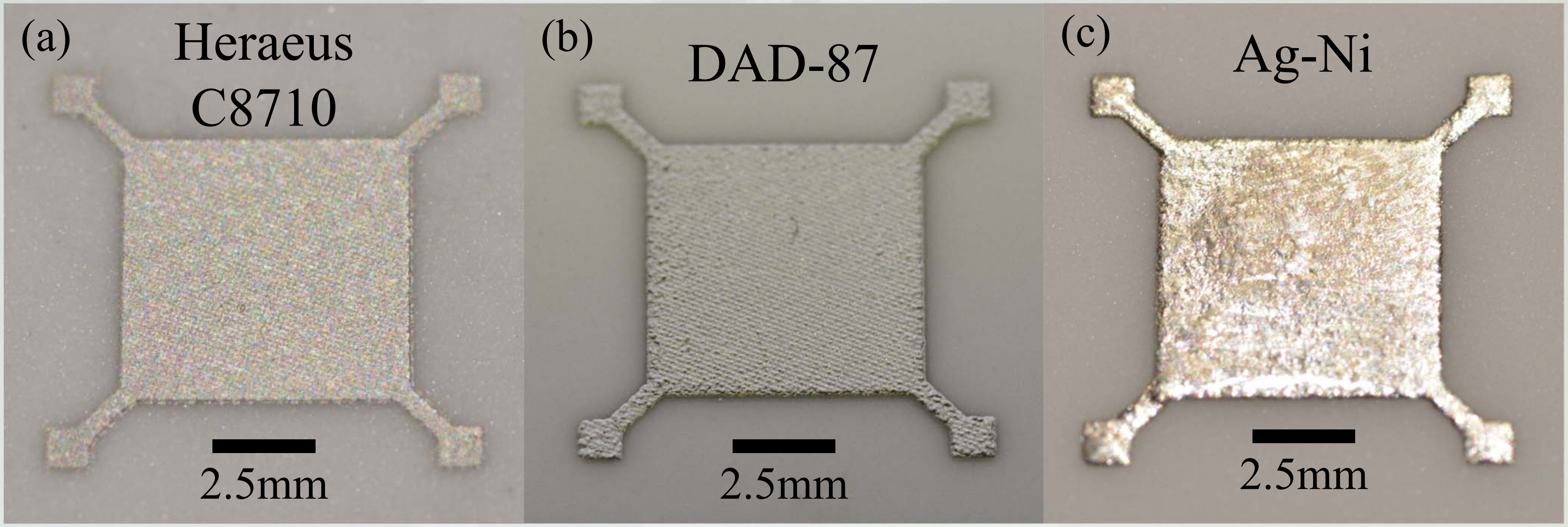
Molten Ag Will Also Infiltrate and Spread Through a Contiguous Ni Pattern



Zhou et al., Controlled Wetting and Spreading of Metals on Substrates Using Porous Interlayers and Related Articles, USPTO Provisional Patent (Submitted April 17, 2018)

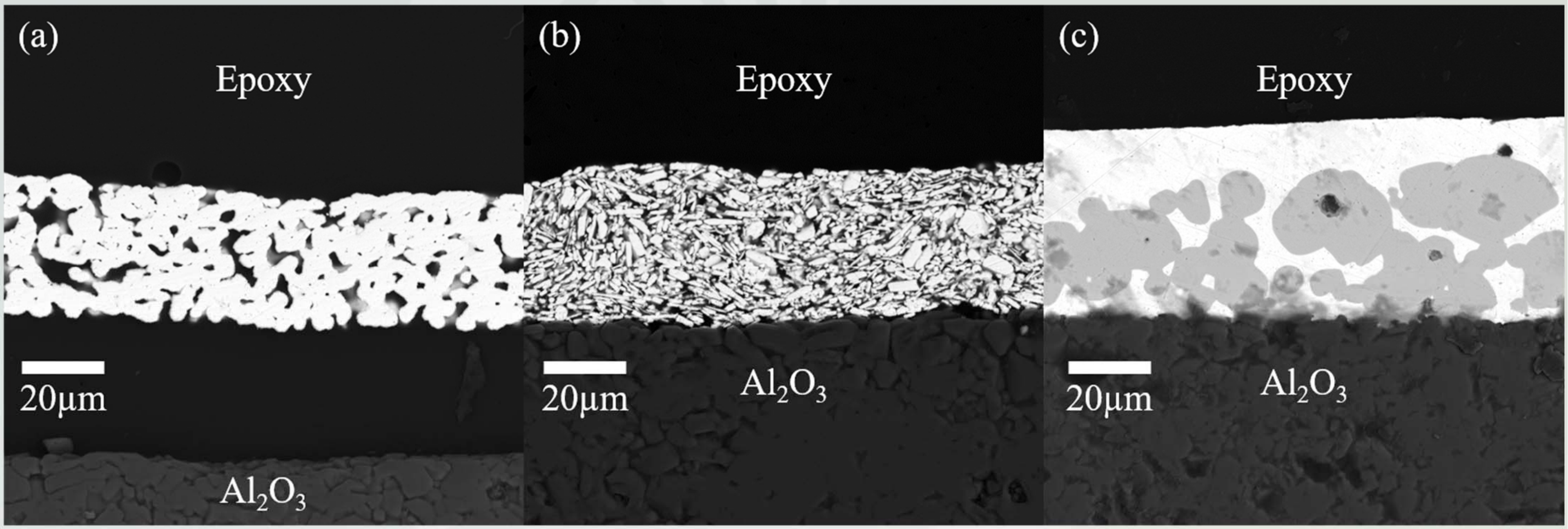
Zhou et al., Controlled Wetting and Spreading of Ag on Various Ceramic Substrates with Porous Ni Interlayers, Scr. Mater, 2018. (In Preparation)

The Electrical and Adhesion properties of Ag-Ni Circuit Pastes are Being Compared to Conventional Circuit Pastes



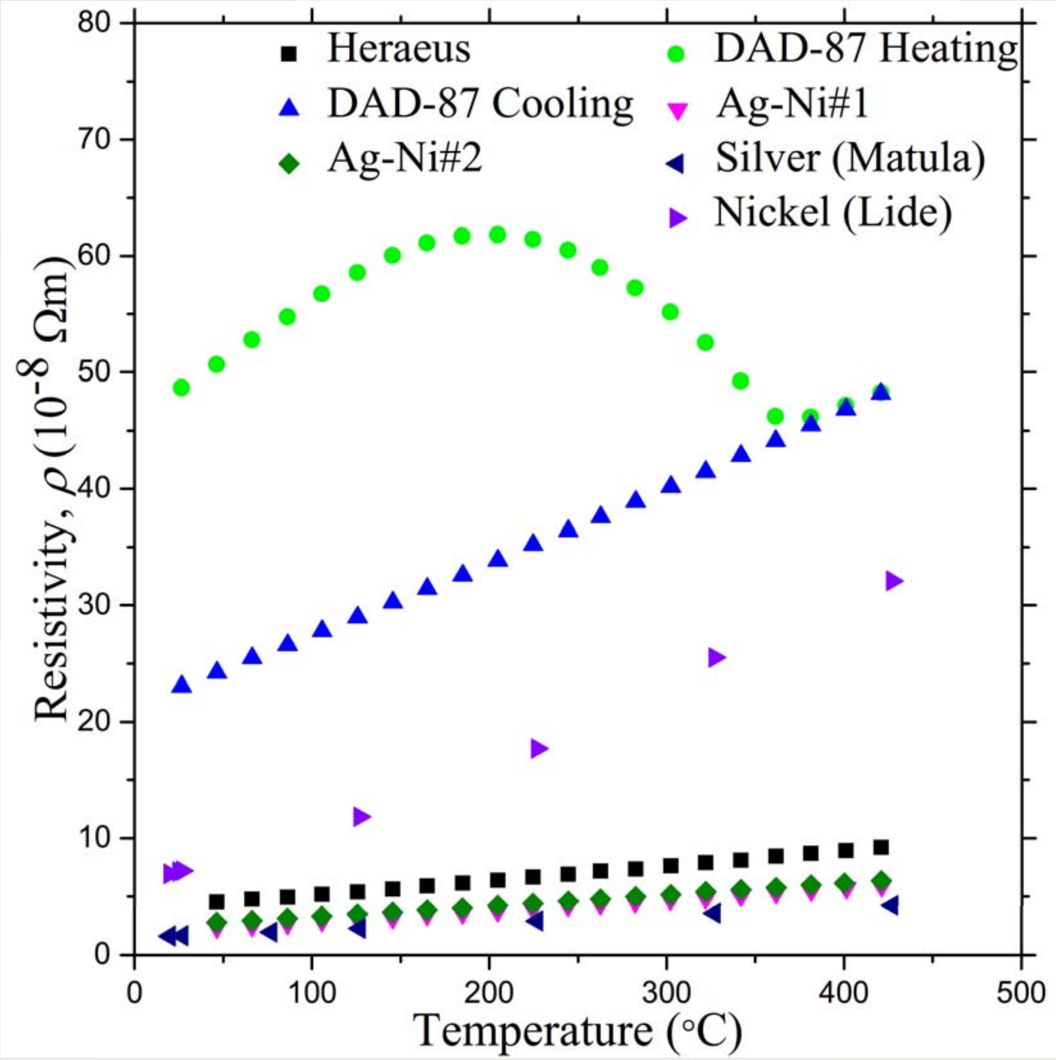
Screen printed samples for sheet resistance measurements

Following Manufacturer Suggested fabrication Procedures Results in Heraeus C870 Circuits that are delaminated, DAD-87 Circuits that are Nanoporous, and Ag-Ni Circuits that are Dense and Well Adhered



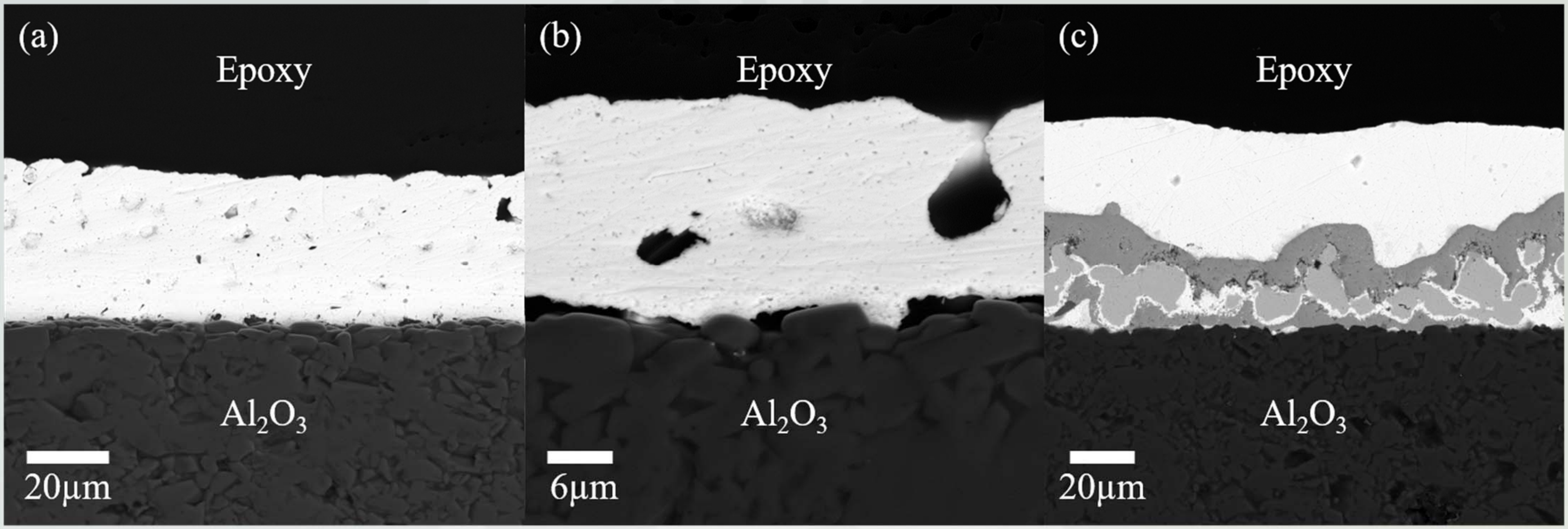
Heraeus C8710 DAD-87 Ag-Ni

The Ag-Ni Circuits Have a Resistivity Close to that of Pure Silver, as Expected



Matula, R.A., Electrical resistivity of copper, gold, palladium, and silver, J. Phys. Chem. Ref. Data, 1979. 8(4): p. 1147-1298.
Lide, D.R., CRC Handbook of Chemistry and Physics, Internet Version. 2005: CRC Press, Boca Raton, FL.

10 Hours of 750°c Isothermal Aging Produces Dense, partially delaminated Heraeus C8710 Porous, Well-Adhered DAD-87, and Dense, Well-adhered Ag-Ni with lots of Brittle NiO



Heraeus C8710 DAD-87 Ag-Ni

Note, the Heraeus C8710 is delaminated elsewhere

Conclusions

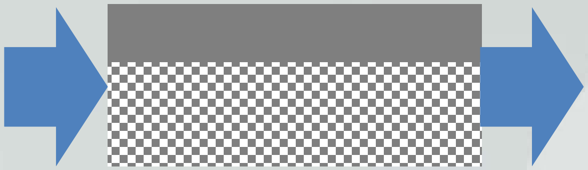
1. Conventional silver circuit pastes have significant delamination and/or conductivity problems

2. Ag-Ni circuits are one of the few ways to make dense, thick-film, well-bonded, low resistivity circuits for SOFCs, power electronics and other applications.

3. Techniques to eliminate NiO is needed in Ag-Ni circuits

Backup Slides

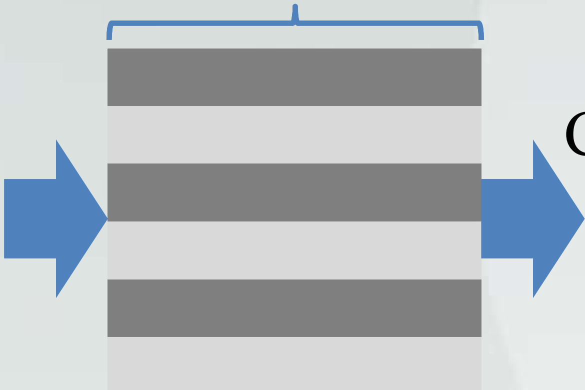
Theoretical Resistivity of Ag-Ni Circuit



Two layers

Pure silver and silver-nickel mixture

Voltage, U



Current, I

Mixture layer minimum case

I, current through the circuit cross section

U, voltage between two ends

R, resistance

ρ, resistivity

A, area

l, length

f, area fraction

$$R = \rho \frac{l}{A}$$

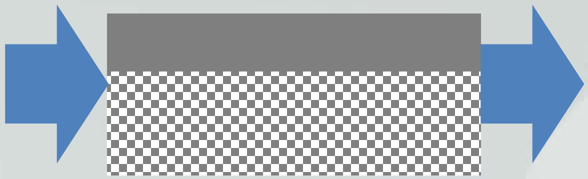
$$I = U\left(\frac{1}{R_{Ag}} + \frac{1}{R_{Ni}}\right)$$

$$\frac{1}{R_{mix}} = \frac{1}{R_{Ag}} + \frac{1}{R_{Ni}}$$

$$\frac{A}{\rho_{mix} l} = \frac{f_{Ag} A}{\rho_{Ag} l} + \frac{f_{Ni} A}{\rho_{Ni} l}$$

$$\frac{1}{\rho_{mix}} = \frac{f_{Ag}}{\rho_{Ag}} + \frac{f_{Ni}}{\rho_{Ni}}$$

Theoretical Resistivity of Ag-Ni Circuit

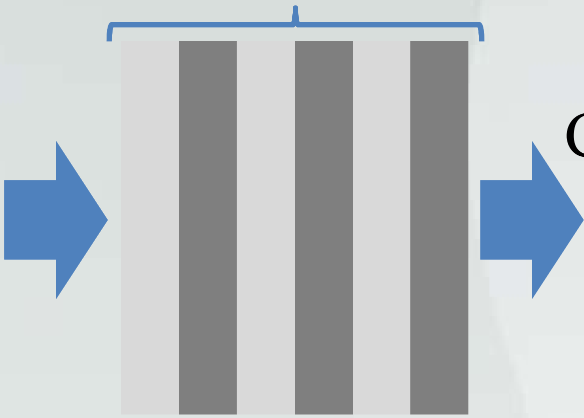


Two layers

Pure silver and silver-nickel mixture

$$R = \rho \frac{l}{A}$$

Voltage, U



Current, I

Mixture layer maximum case

$$U = IR_{Ag} + IR_{Ni}$$

I, current through the circuit cross section

U, voltage between two ends

R, resistance

ρ, resistivity

A, area

l, length

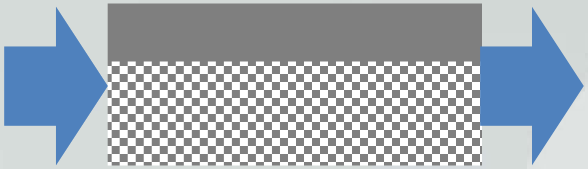
f, area fraction

$$R_{mix} = R_{Ag} + R_{Ni}$$

$$\rho_{mix} \frac{l}{A} = \rho_{Ag} \frac{l f_{Ag}}{A} + \rho_{Ni} \frac{l f_{Ni}}{A}$$

$$\rho_{mix} = \rho_{Ag} f_{Ag} + \rho_{Ni} f_{Ni}$$

Theoretical Resistivity of Ag-Ni Circuit



Two layers
Pure silver and silver-nickel mixture

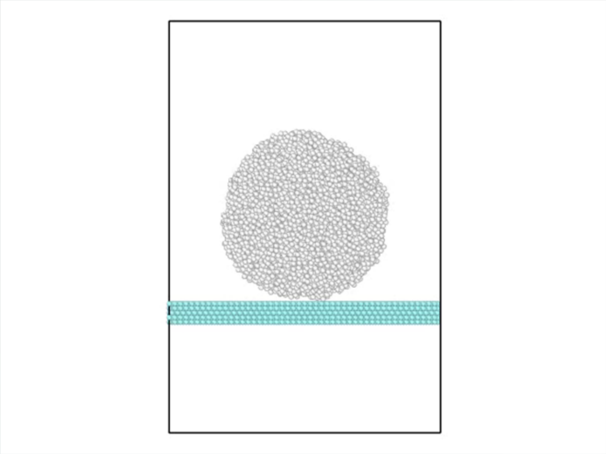
Overall circuit minimum case

$$\frac{1}{\rho_{overall}} = \frac{f_{Ag} f_{mix}}{\rho_{Ag}} + \frac{f_{Ni} f_{mix}}{\rho_{Ni}} + \frac{f_{pure}}{\rho_{Ag}}$$

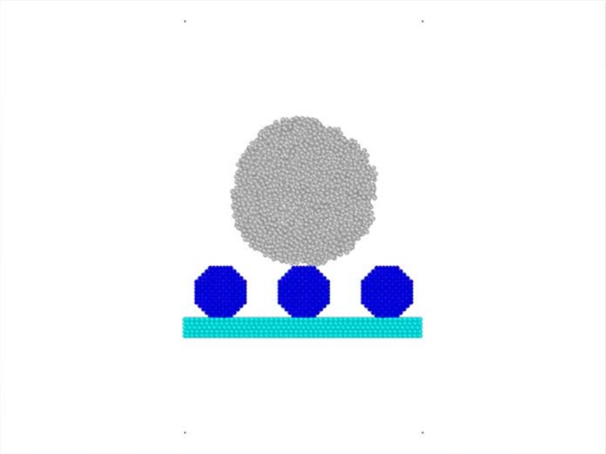
Overall circuit maximum case

$$\frac{1}{\rho_{overall}} = \frac{f_{mix}}{\rho_{Ag} f_{Ag} + \rho_{Ni} f_{Ni}} + \frac{f_{pure}}{\rho_{Ag}}$$

Ni Particles Improve Ag Wetting on YSZ

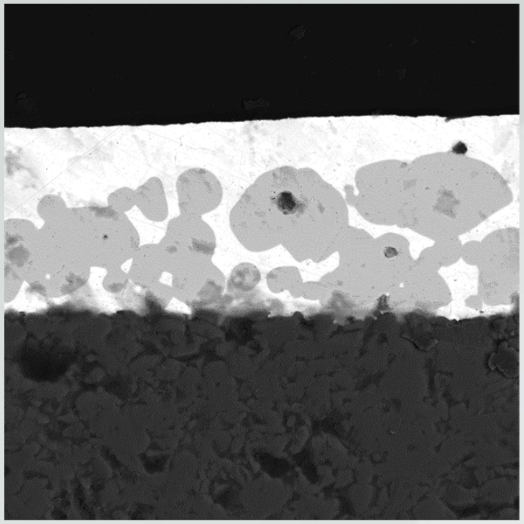


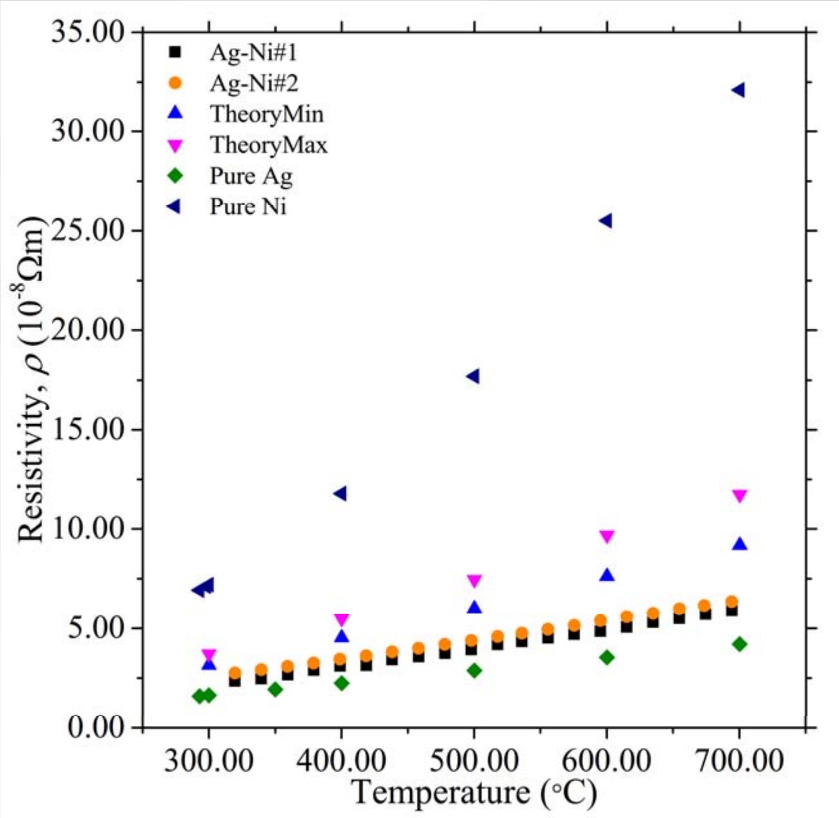
Ag on bare YSZ



Ag on YSZ with Ni particles

Theoretical Resistivity of Ag-Ni Circuit

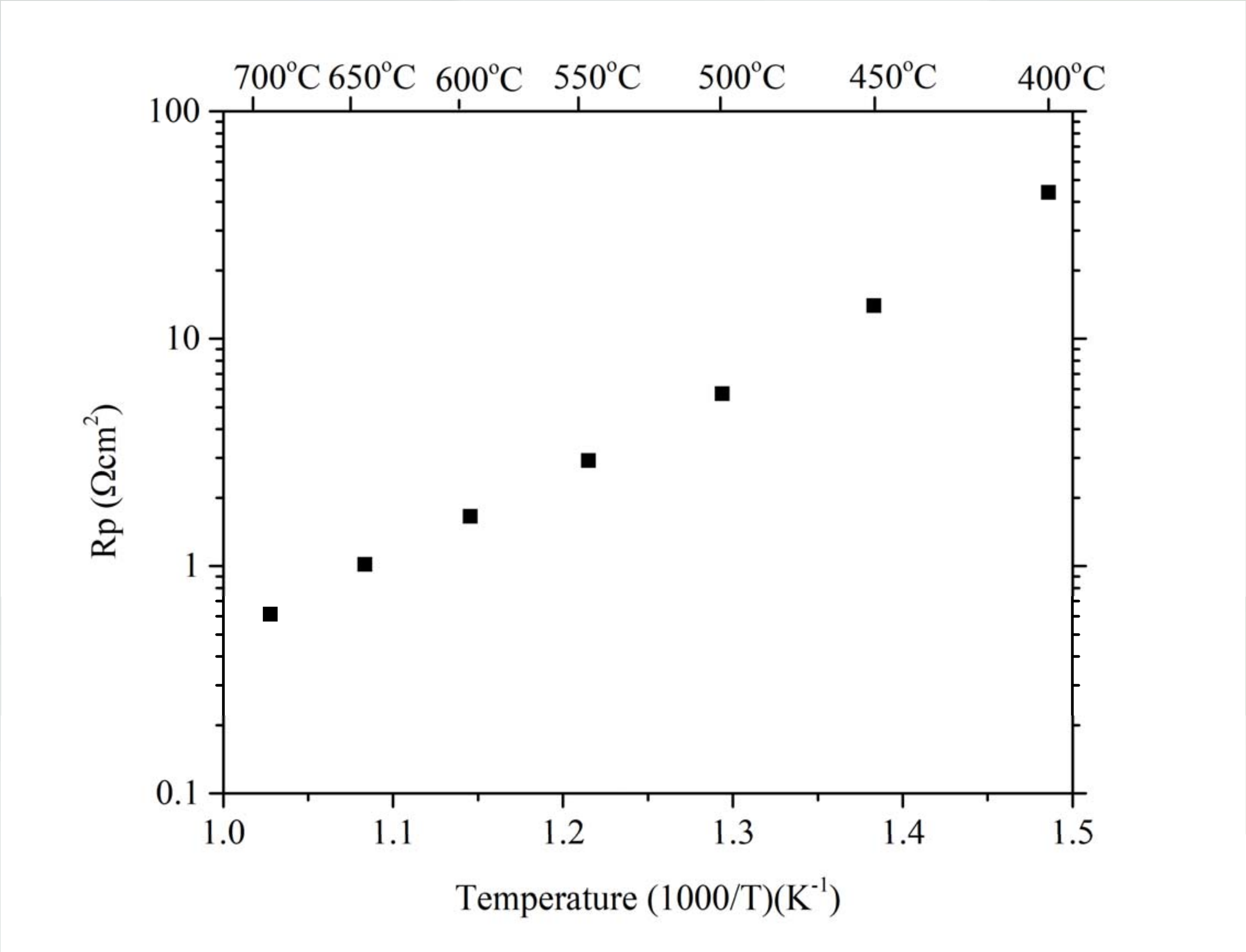




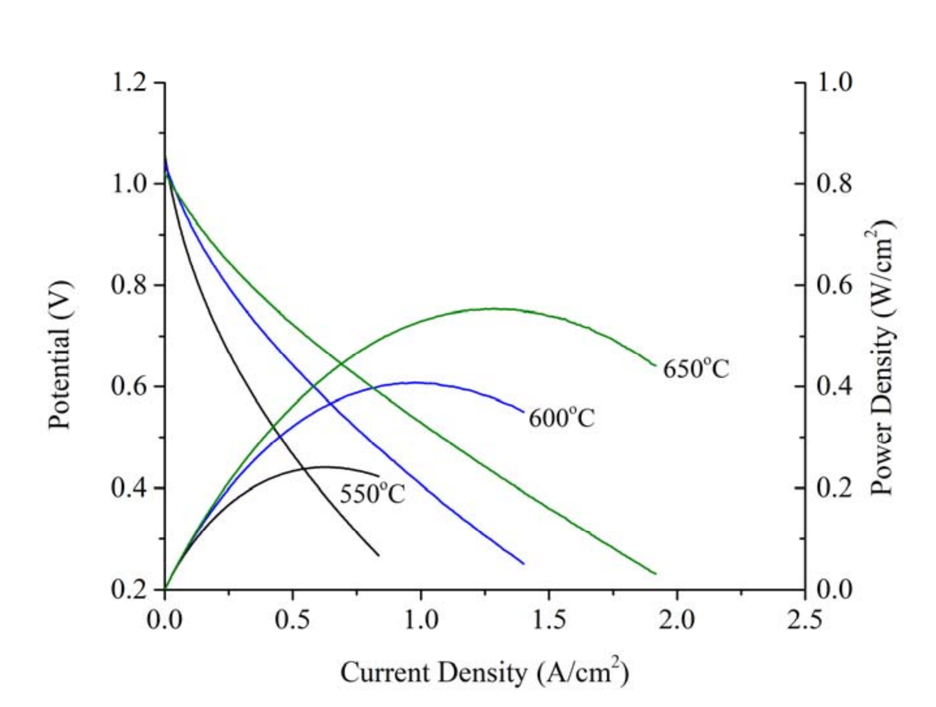
In calculation, area fraction is transformed to atomic fraction.

Explanation for deviation of theory: the fractions of Ag and Ni are measured in local areas, different from the overall relationship between Ag-Ni in the circuit.

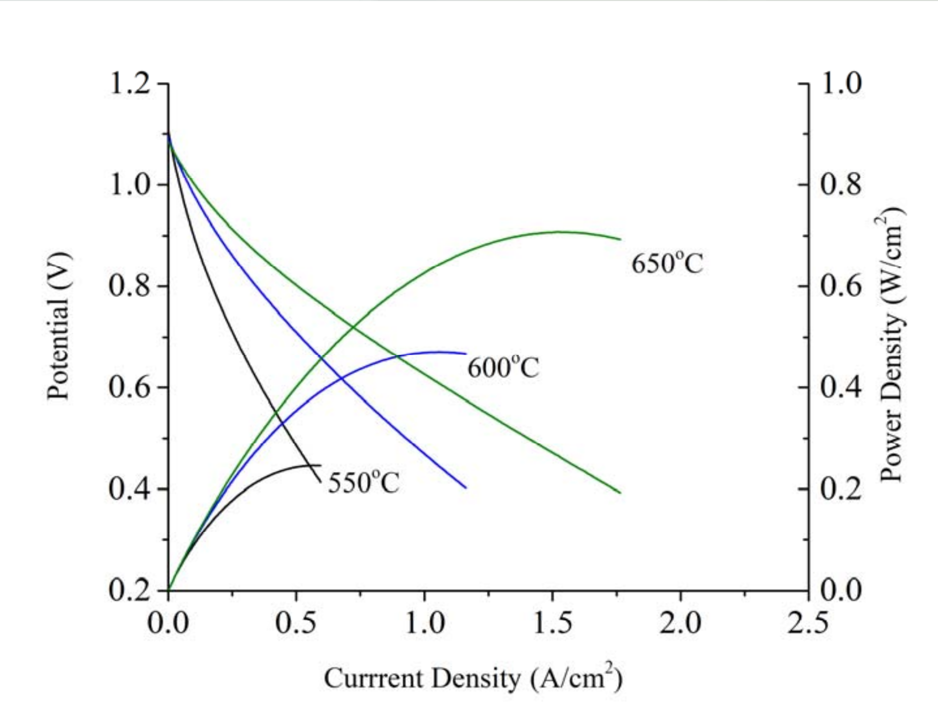
R_p for Infiltrated Co_3O_4-GDC Is Not Satisfactory



Anode NiO Infiltration Saw an Improvement in I-V Performance for LSCF-GDC NCC/YSZ/Ni-YSZ



12% LSCF-GDC NCC/YSZ/Ni-YSZ



12% LSCF-GDC NCC/YSZ/Ni-YSZ with ~8% NiO anode infiltration