Scalable and Cost Effective Barrier Layer Coating to Improve Stability and Performance of SOFC Cathode

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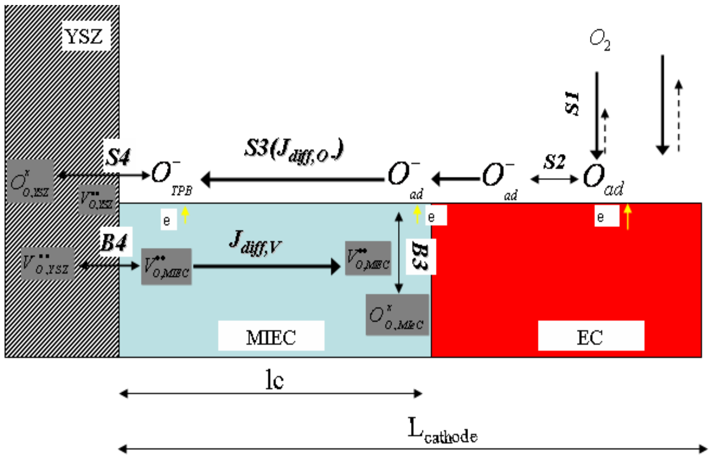
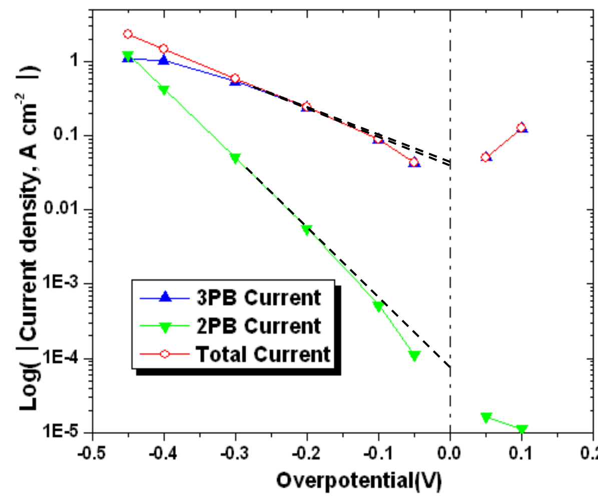
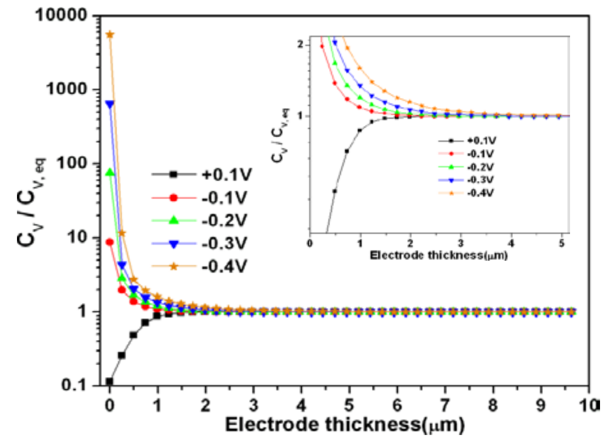
Oxygen Reduction Reaction on SOFC Cathode





- Important Factors: K, D, δe, etc.
- Un-settled Issues: ORR Details
- Implications to Industrial Applications



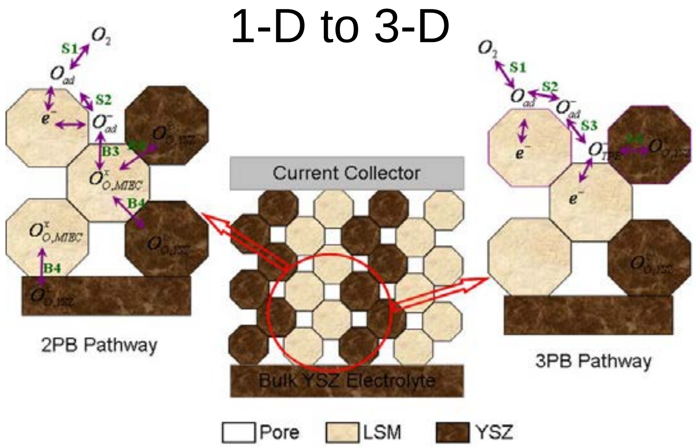
H. Zhang, K. Gerdes, **X. Liu*:** *Journal of Electrochemical Society 161 (2014) F983-990*

M. Gong, R. Gemmen, D. Mebane, K. Gerdes, **X. Liu***, *Journal of Electrochemical Society, 162 (2014) F344-F353*

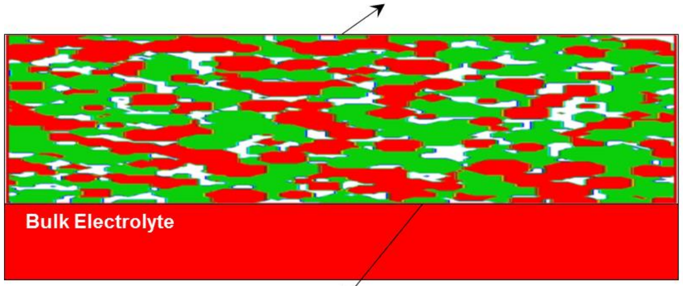
M. Gong, R. Gemmen, **X. Liu***, *Journal of Power Sources 201 (2012) 204-218*

Realistic Composite Cathodes, Effects of Morphology

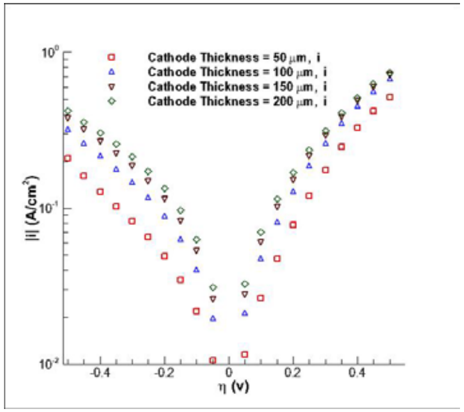
- Porosity
- Surface area
- Grain size
- Grain boundary
- MIEC/IC ratio
- Etc.

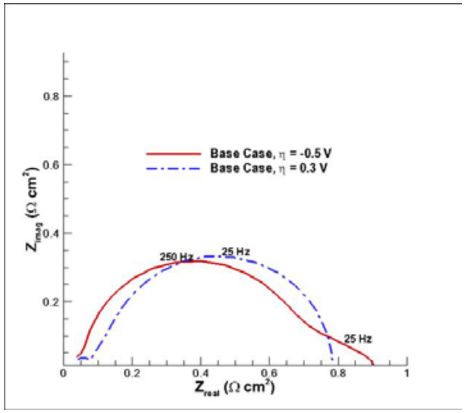


C/Air interface
Ionic current = 0, Electronic potential prescribed, Oxygen concentration prescribed, and flux of all Other species (coverages and vacancies) is zero



C/E Interface
Electronic current = 0, Ionic potential prescribed, YSZ oxygen vacancy is prescribed, All other fluxes are zero





Performance and Durability Implications

- Microstructural changes (loss effective TPB area)
  - Grain growth
  - Coarsening of the particles
  - Surface re-construction
- Chemical reaction with YSZ electrolyte.

$$La_2O_3(s)+2ZrO_2(s)\rightarrow La_2Zr_7O_3(s) \qquad SrO(s)+ZrO_2(s)\rightarrow SrZrO_3(s)$$

- Strontium segregation related issues

$$2Sr_{La}^{'}+V_{O,LSCF}^{\bullet\bullet}+2O_O^x \leftrightarrow 2SrO(s)$$

- Poisoning of the cathode (e.g. by chromium species etc.)

$$SrO(s)+H_2O(g)\rightarrow Sr(OH)_2(s) \qquad SrO(s)+CO_2(g)\rightarrow SrCO_3(s)$$

- Etc.

Approaches for Degradation Mitigation

- Microstructural changes (loss effective TPB area)
  - Grain growth
  - Coarsening of the particles
  - Surface re-construction
- No easy solutions

- Chemical reaction with YSZ electrolyte.
- Barrier Layers

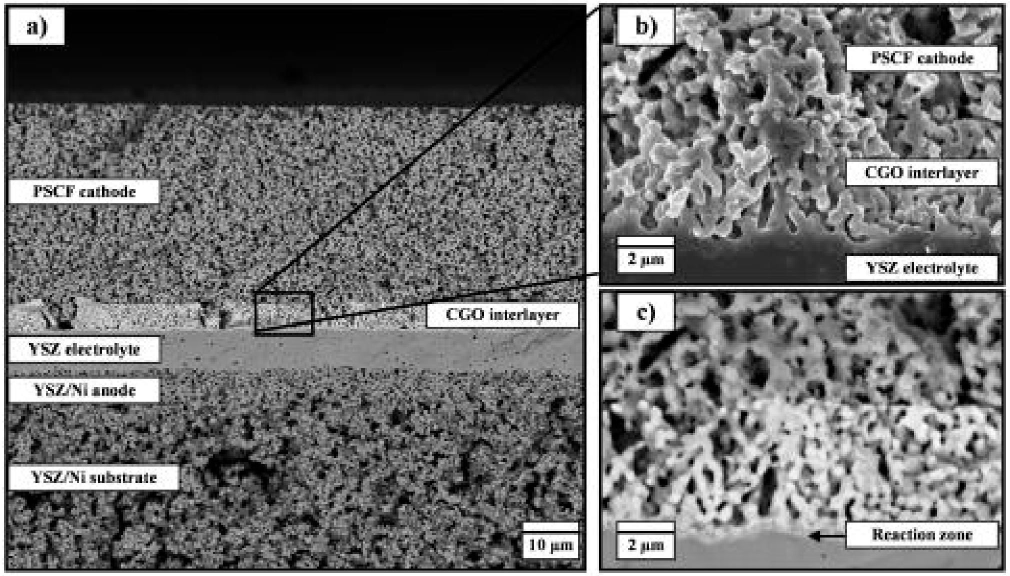
- Strontium segregation related issues
- Coating, Infiltration, Sr-free cathodes (maybe)

- Poisoning of the cathode (e.g. by chromium species etc.)
- Interconnect coatings, impurity tolerant cathodes etc.

Operation Parameters
Temperature, Overpotential, Environments, etc.

SOFC Cathode Barrier Layers

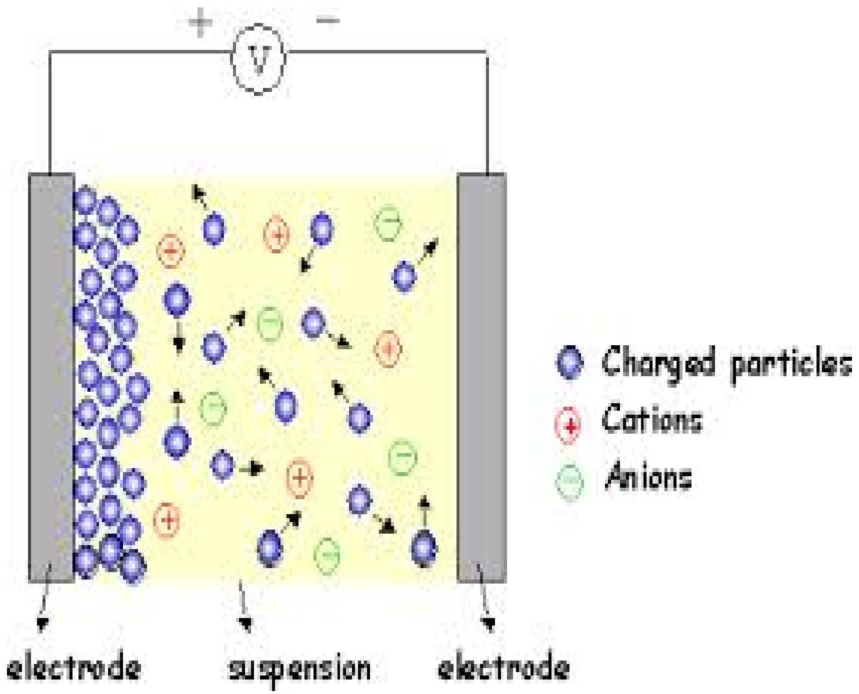
- **Chemical Compositions (GDC, SDC, etc.)**
- **Coating Methods (Screen Printing + Sintering)**
- **Functions**
  - Avoid Zirconate Formation
  - Improve ORR
- **Current Issues**
  - Porosity
  - Thickness



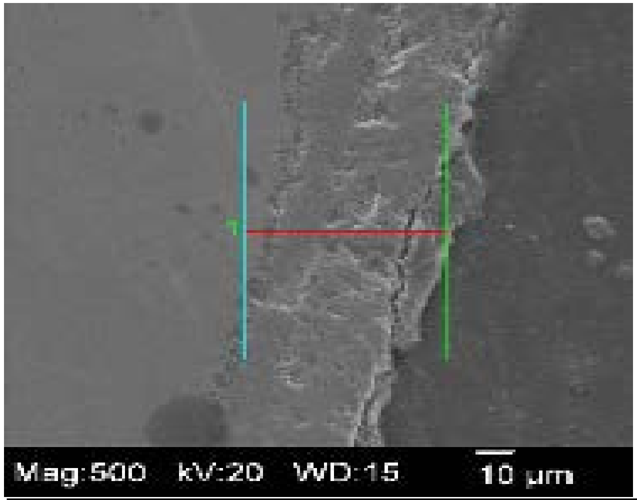
Project Objectives

- **Aim 1:** To develop a scalable and cost-effective electrophoretic deposition (EPD) coating process to achieve a dense barrier layer between an YSZ electrolyte and the cathode in a solid oxide fuel cell (SOFC) to significantly improve both stability and performance of SOFC cathodes
- **Aim 2:** To systematically investigate the interaction between doped ceria barrier layers and $(La,Sr)(Co,Fe)O_3$ (LSCF) cathode and the effects on oxygen reduction reaction (ORR) kinetics, electrochemical performance, and long-term stability of cathodes
- **Aim 3:** To achieve optimal barrier layer thickness.

Aim 1: Electrophoretic Deposition (EPD)



Sketch of EPD Process



Cross-section of EPD $(Mn,Co)_3O_4$ coating on 441 stainless steel developed by WVU.

H. Zhang, Z. Zhan, **X. Liu***: *Journal of Power Sources 196 (2011) 8041-8047*

Aim 1: EPD vs. Other Possible Coating Methods

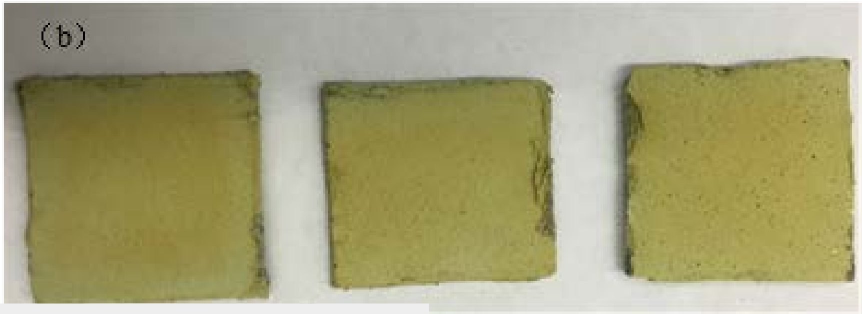
Method	Screen Printing	Dip Coating	Spin Coating	Electroplating	Thermal Spray
Green-body Porosity	High	High	High	Low	Medium
Coating time (~5µm)	Seconds/ minutes	Seconds/ minutes	Seconds/ minutes	Minutes/hours	Seconds
Cost	Low	Low	Low	Low	Medium
Scalable	Yes	Yes	Difficult	Yes	Yes
Composition Control	Easy	Easy	Easy	Moderate	Easy
Thickness Control (~5µm)	Easy	Easy/ moderate	Easy/ moderate	Moderate	Difficult
Coat on non-flat surface	Difficult	Easy	Moderate	Easy/moderate	Easy
Sintering	Required	Required	Required	Usually not	Usually not
Method	**Tape Casting**	**PLD**	**RF Sputtering**[1]	**CVD/ALD**	**EPD**[2]
Green-body Porosity	High	Low	Low	Low	Low
Coating time (~5µm)	Seconds/ minutes	Hours	Hours	Hours	Several minutes
Cost	Low	High	High	High	Low
Scalable	Yes	No	Yes	Yes	Yes
Composition Control	Easy	Moderate	Moderate	Moderate	Easy
Thickness Control (~5µm)	Easy	Moderate	Moderate	Easy/ moderate	Easy
Coat on non-flat surface	Easy	Easy/ moderate	Easy/ moderate	Easy/ moderate	Easy /moderate
Sintering	Required	Usually not	Usually not	Usually not	Required[3]

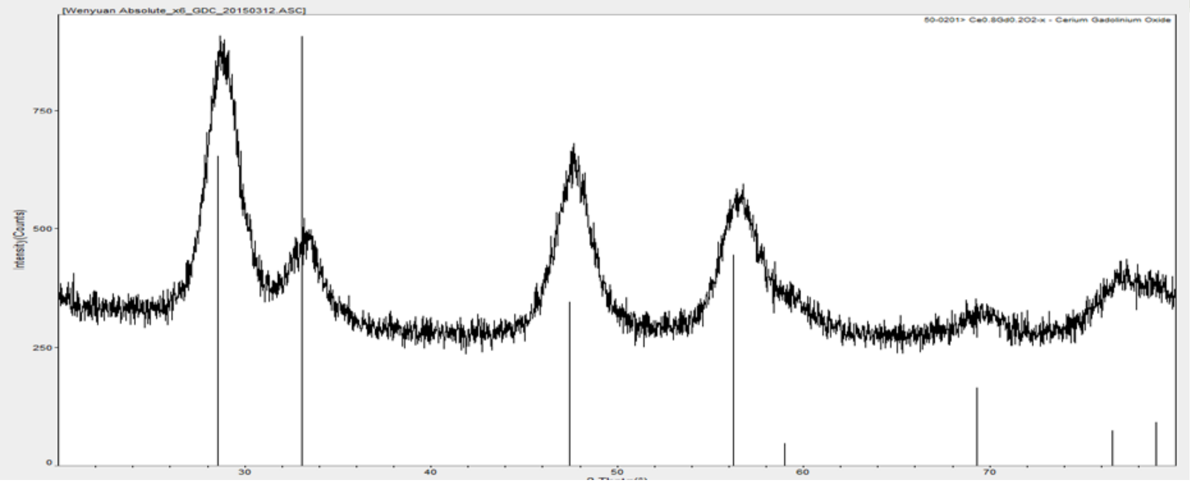
Aim 1: Major Technical Challenges for EPD

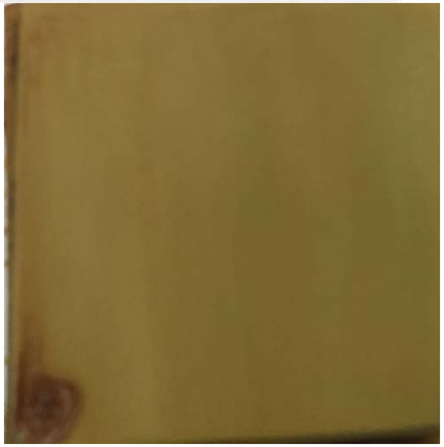
- **Suspension Issues**
  - Conductivity
  - Compatibility with particles & Substrates
  - Stability
- **Non-Conductive Substrates**
- **Sintering Optimization**
  - Sintering Temperature & Atmospheres
  - Sintering Aids

Aim 1: Preliminary Results - Suspension

Substrates: Stainless Steel, Graphite



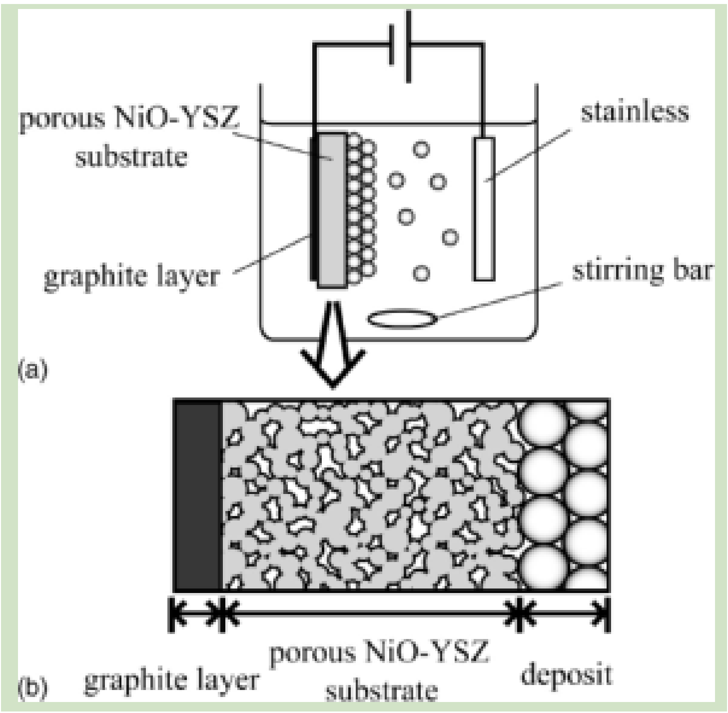


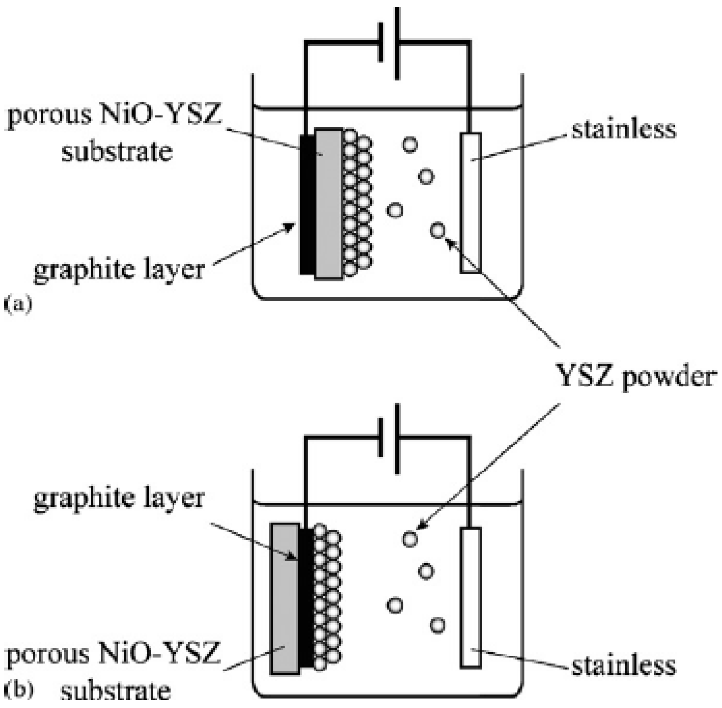


Results: Dense GDC layer formed on cathodic substrate; GDC particles in ethanol are positively charged

Aim 1: Preliminary Results – Non-Conductive Substrates

Possible Solutions: Carbon Coating vs. Porous Substrates



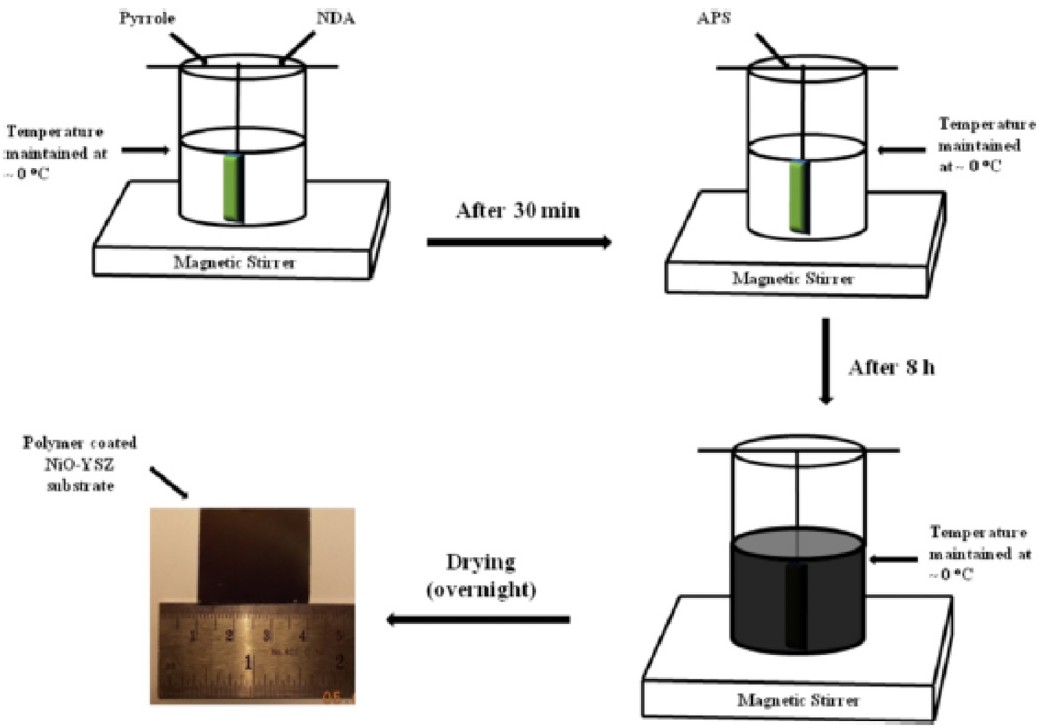


Preliminary Results: We coated a layer of carbon/graphite on YSZ pellet by spin coating, tap casting, spray, sputtering, but the preliminary results showed the cohesiveness of carbon/ graphite layer is very poor and the conductivity is low.

M. Matsuda, T. Hosomi, K. Murata, T. Fukui, M. Miyakea. Electrochem. Solid-State Lett.2005 8(1):A8-A11.

Aim 1: Preliminary Results – Non-Conductive Substrates

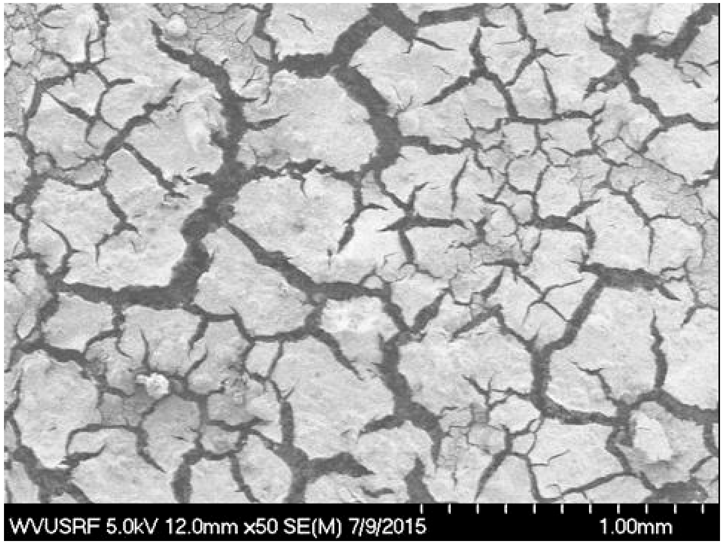
Possible Solutions: In-situ forming a conducting Polymer Layer

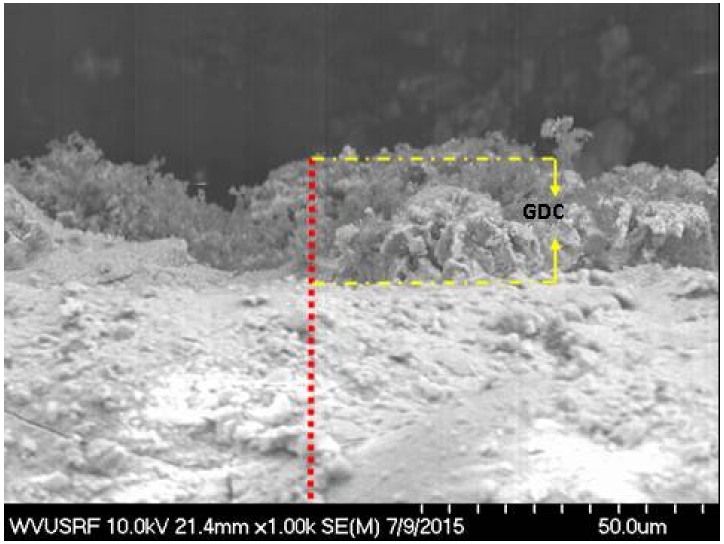


Dabasish. Das, Rajenda N. Basu. J.Am.Ceram.Soc.97[11] 3452-3457(2014).

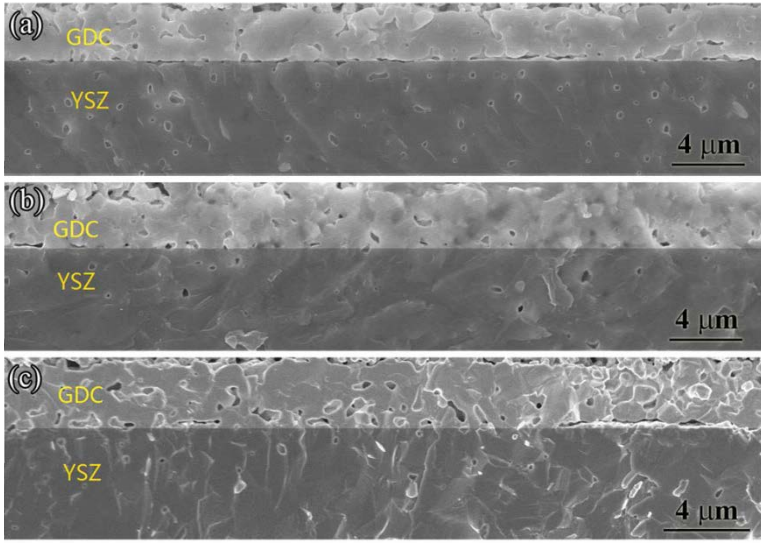
Aim 1: Preliminary Results – Non-Conductive Substrates

Possible Solutions: In-situ forming a conducting Polymer Layer

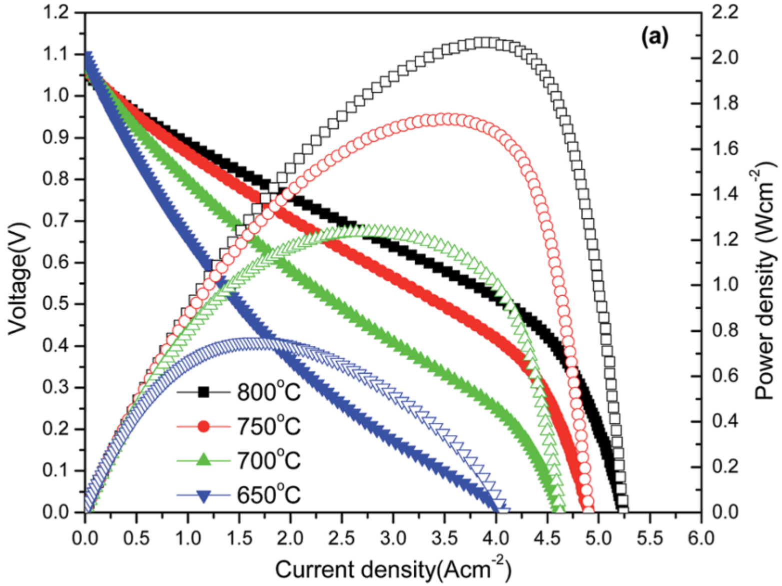




Aim 1: Preliminary Results – Reducing Sintering Temperature



Fracture cross sectional SEM images taken after testing of cells with 1 mol% Fe2O3 in the YSZ layers and GDC layers with 1 (a), 2 (b), or 3 (c) mol% Fe2O3.

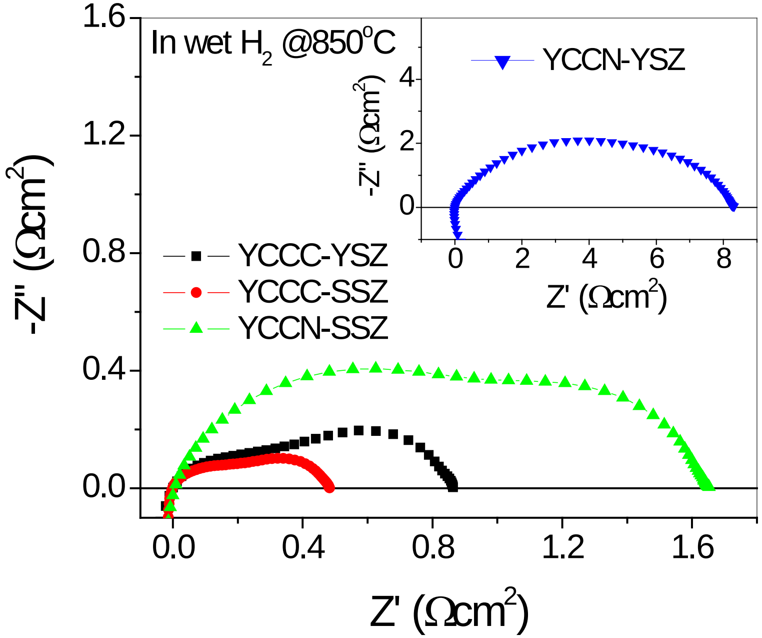


Voltage and power density versus current density, measured at different temperatures in air and humidified hydrogen.

Z. Gao, V. Zenou, D. Kennouche, L. Marks, S. Barnett, J. Mat. Chem. A (2015)

Aim 2: Electrolyte/Barrier Layer Effect on ORR Kinetics

Good performance for YCCC and YCCN



Combination of high electronic conductivity and activity from B site elements.

0.5 Ωcm² for YCCC on SSZ at 850°C

Two-arc profiles for all electrodes

Two electrolytes used: YSZ, SSZ → Better performance from SSZ/GDC?

W. Li, M. Gong, **X. Liu***, *Journal of Power Sources 241 (2013) 494-501*

Aim 2: Electrolyte/Barrier Layer Effect on ORR Kinetics

Table I. *R*, *C* and f_0 for HF and LF arcs of four electrodes after fitting at 850 °C, and the corresponding *E*a as well as reaction order (*n*) in the temperature and P_{H2} ranges used in the work.

In wet H_2 at 850 °C		*R* (Ωcm^2)	*C* (F/cm^2)	f_o (Hz)	*E*a (eV)	*n*
HF arc	YCCC-YSZ	0.65	5.2×10^{-5}	3500	1.0	0.25~0.33
	YCCC-SSZ	0.22	1.1×10^{-4}	2300	1.1	0.16~0.30
	YCCN-YSZ	5.2	5.3×10^{-5}	530	1.6	0.10~0.16
	YCCN-SSZ	0.96	8.3×10^{-5}	1900	1.6	0.10~0.28
LF arc	YCCC-YSZ	0.33	6.9×10^{-3}	70	0.8	0.34~0.50
	YCCC-SSZ	0.27	1.6×10^{-2}	70	0.6	0.46~0.60
	YCCN-YSZ	3.2	1.1×10^{-3}	45	0.6	0.18~0.37
	YCCN-SSZ	0.66	2.3×10^{-3}	100	0.9	0.51~0.70

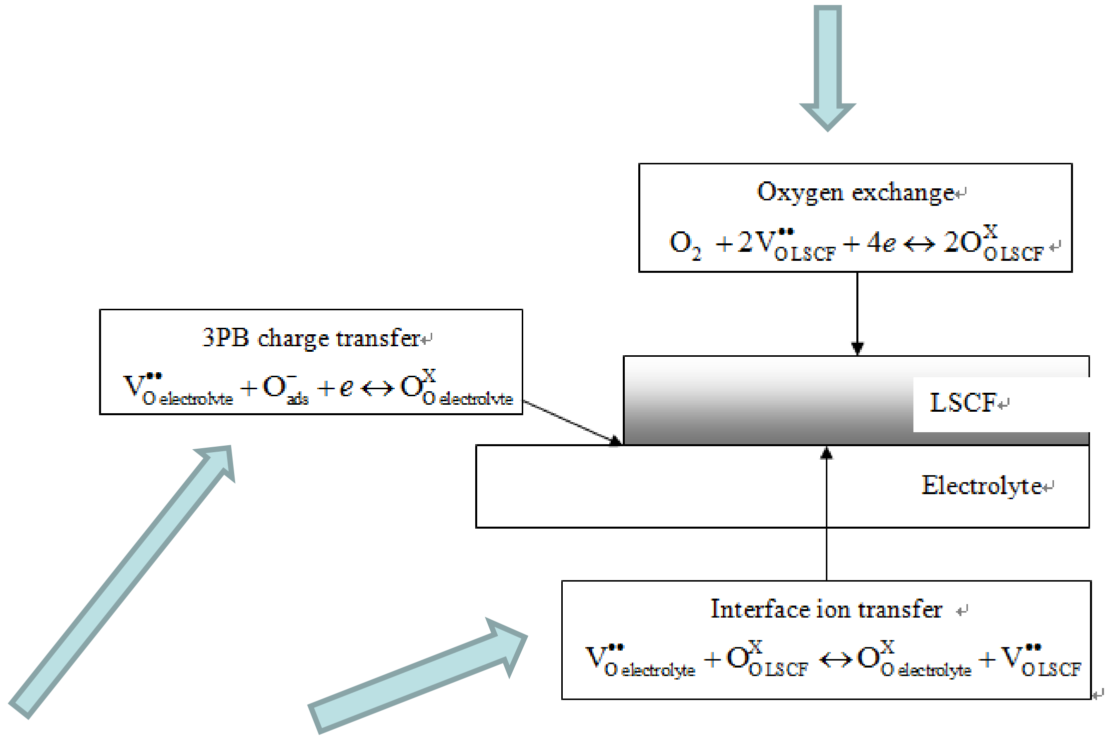
Table II. Summary of *R*, *C* and f_0 for these four electrodes tested in air at 850 °C, as well as *E*a in the temperature range of 650~850 °C.

In air at 850 °C		*R* (Ωcm^2)	*C* (F/cm^2)	f_o (Hz)	*E*a(eV)
YCCC-YSZ	Single arc	1.2	1.1×10^{-3}	112	2.0
YCCC-SSZ	Single arc	1.0	1.4×10^{-3}	50	2.0
YCCN-YSZ	Single arc	36.7	1.5×10^{-4}	30	2.0
YCCN-SSZ	HF arc	12.6	3.8×10^{-4}	32	2.1
	LF arc	8.7	1.2×10^{-3}	5	1.7

W. Li, M. Gong, **X. Liu***, *Journal of Electrochemical Society 161 (2014) F551-F560*

Aim 2: Electrolyte/Barrier Layer Effect on ORR Kinetics

Having no effect on reaction occurring here



2PB contribution

affect these two reactions

W. Li, M. Gong, **X. Liu***, *Journal of Electrochemical Society 161 (2014) F551-F560*

Aim 2: Electrolyte/Barrier Layer Effect on ORR Kinetics

How electrolyte improve the non-charge transfer processes?

B-V eqn. for charge transfer at cathode side:

$$j_{ct} = j_{ct}^{0}\{\frac{c_{O^-}}{c_{O^-}^{0}}\exp(-\alpha f\eta)-\exp[(1-\alpha)f\eta]\}$$

YSZ→SSZ/GDC

↓

Increased charge transfer exchange current

↓

Under the same overpotential, more O^- is consumed.

↓

Lowered concentration of O^- species right outside electrolyte

→

Gradient increases

↑

Gradient of O^- spread far away to recover reduction of O^-

↑

More areas are activated in O- adsorption and diffusion processes

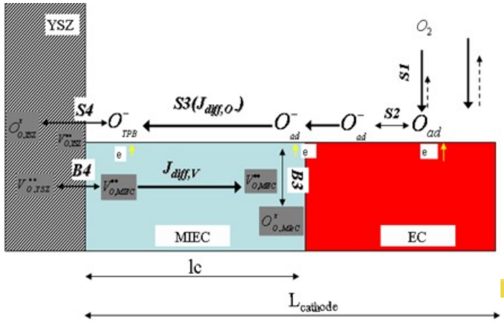
↑

O- stops reducing and bigger gradient built at the interface

→

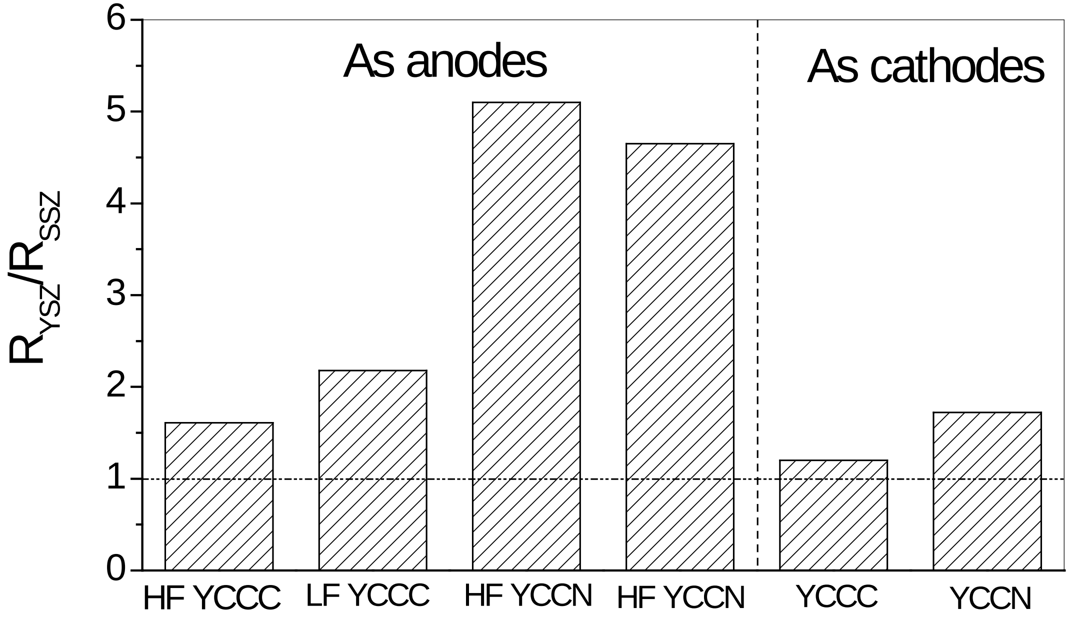
Current is steady but bigger at last

Not only charge transfer is increased, but active site for surface processes is also increased



W. Li, M. Gong, **X. Liu***, *Journal of Electrochemical Society 161 (2014) F551-F560*

Aim 2: Electrolyte/Barrier Layer Effect on ORR Kinetics



Improved charge transfer and surface processes on SSZ/GDC electrolyte

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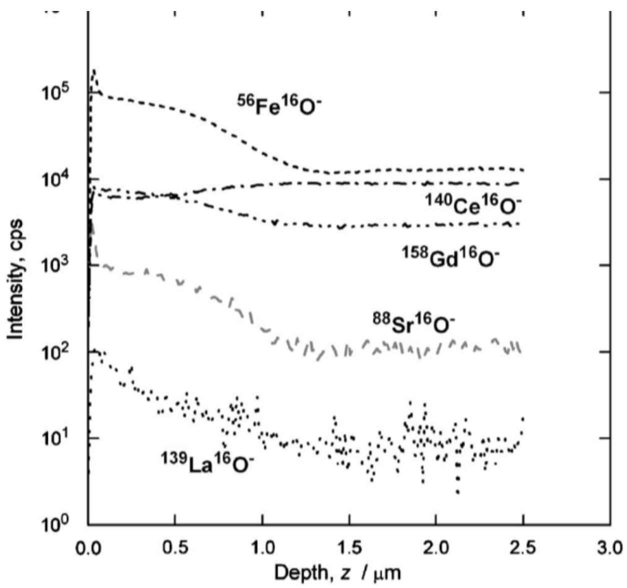
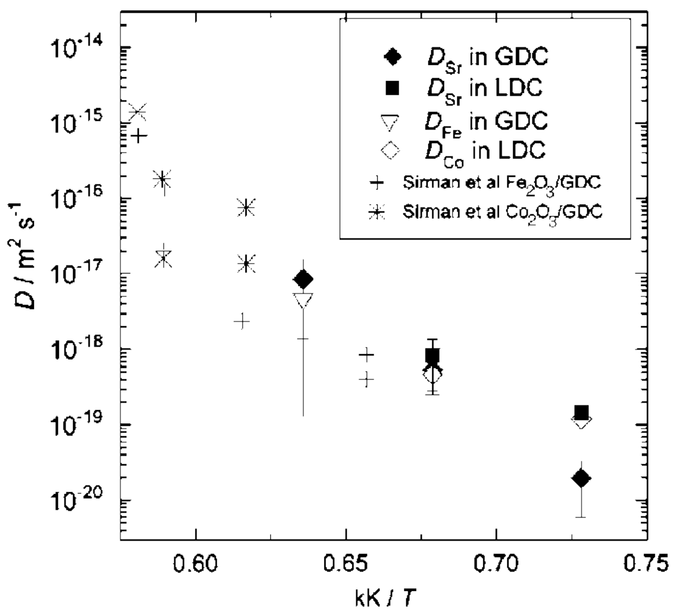
Aim 3: Optimized Barrier Layers Thickness



Diffusion profile observed in GDC that had been annealed at 1200° C for 115 h with LSF [Ref.1]



Bulk diffusivities as function of temperature [Ref. 2].

1. Sakai, N., Yokokawa, H., Miyachi, M., and Sawata, A., in *Solid Oxide Fuel Cells IX*, J. Mizusaki and S. C. Singhal, Editors, PV 2005-07, p. 1703, The Electrochemical Society Proceedings Series, Pennington, NJ _2005
2. Sakai, N., Kishimoto, H., Yamaji, K., Horita, T., Brito, M. E. & Yokokawa, H. Solid Oxide Fuel Cells 10 (SOFC-X), Pts 1 and 2 7, 389-398

Aim 3: Optimized Barrier Layers Thickness

Objectives: Understand Cation diffusion & Zirconate formation kinetics in the vicinity of barrier layer as function of temperature, overpotential, barrier layer thickness etc.

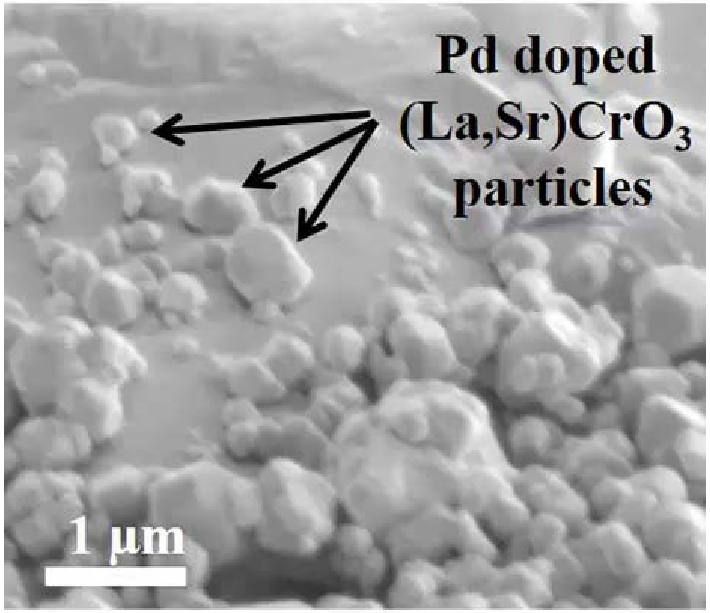
Approaches:

Secondary Ions Mass Spectroscopy (SIMS)

Cross-sectional transmission electron microscopy (XTEM)

3-D Atom-Probe Tomography (3-D APT)

In operando EIS



Summary & Future Work

We have

- Demonstrated the feasibility of EPD barrier layer on YSZ
- Demonstrated the beneficial effect of sintering aids to reduce sintering temperature
- Started the investigation on ORR kinetics at Cathode/Barrier layer interface
- Initiated the characterization of cation diffusion profile in barrier layer

We are going to

- Optimize the EPD process
- Quantify the cation diffusion & zirconate formation kinetics as function of operation parameters and barrier layer thickness
- Test in industrial setting

Acknowledgement

- **NETL-SOFC Team**: Shailesh Vora, Heather Quedenfeld, Briggs White, Steven Markovich, Joe Stoffa,Travis Shultz (formal)...

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- **My Postdoc and Students**: Greg Collins, Shanshan Hu, Nan Zhang