SCALABLE AND COST EFFECTIVE BARRIER LAYER COATING TO IMPROVE STABILITY AND PERFORMANCE OF SOFC CATHODE

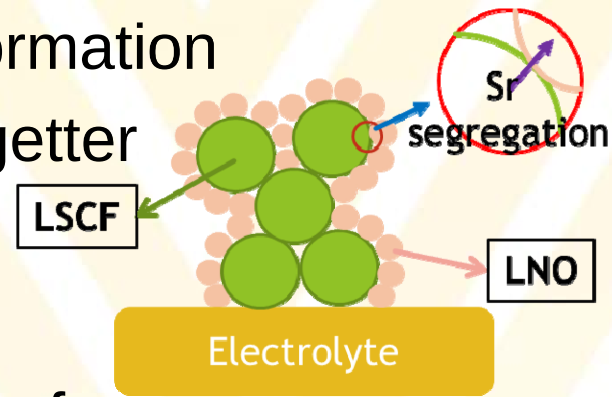
Xingbo Liu
West Virginia University

Scott Barnett
Northwestern University

SOFC Cathodes – Performance & Stability

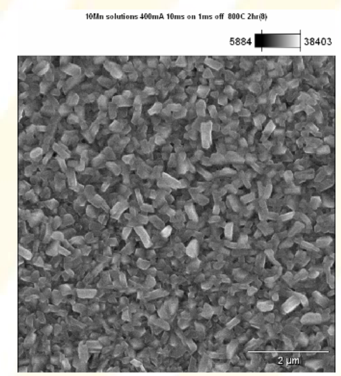
Sr – Segregation & Detrimental phase formation

- Infiltration of R-P phase (LNO) as Sr getter
- Barrier layer



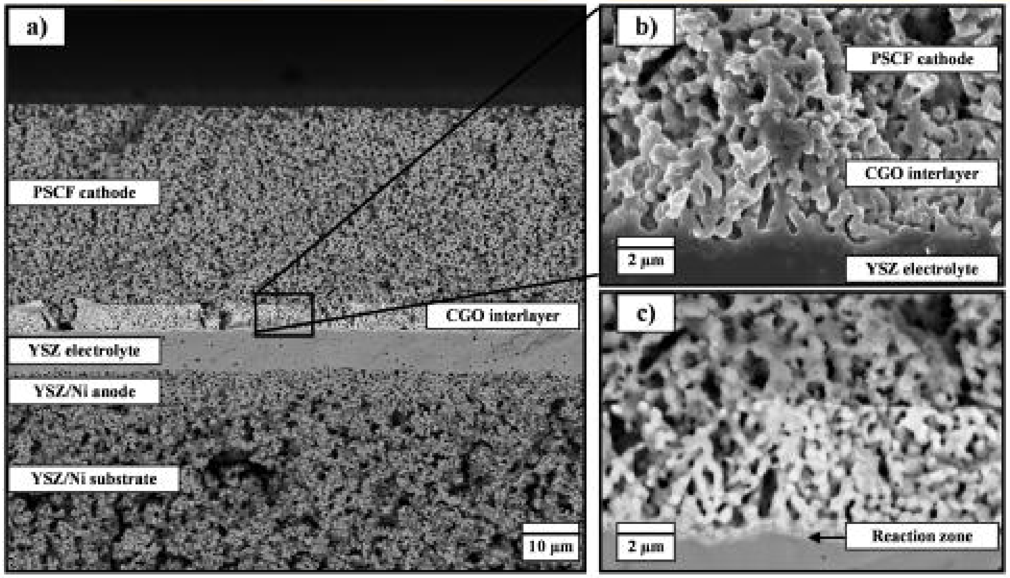
Cr – Poisoning & Cathode/electrolyte interface

- Electroplating and EPD (Mn,Co) spinels for interconnect
- Coating and new alloys for BOP



SOFC Cathode Barrier Layers

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



Effect of Barrier Layers on ORR

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→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

⬆

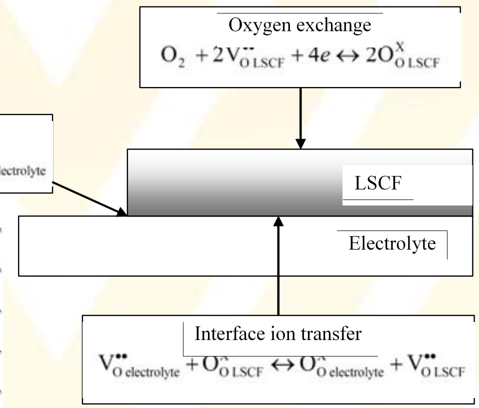
O- stops reducing and bigger gradient built at the interface

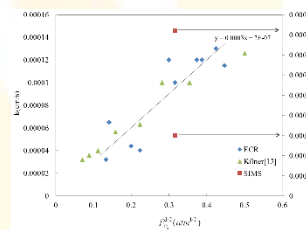
⬆

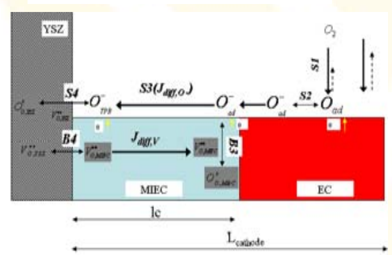
Current is steady but bigger at last

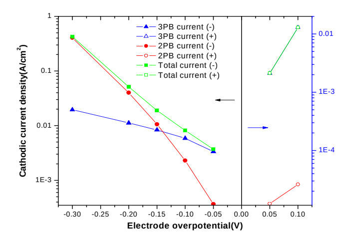
➡

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









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Y. Li, K. Gerdes, T. Horita, **X. Liu*** *Journal of The Electrochemical Society 160 (2013) F343-F350*

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Research Objectives

- Aim 1 - Develop a scalable and cost-effective electrophoretic deposition(EPD) coating process to form a dense barrier layer between a YSZ electrolyte and the cathode in a SOFC.

- Aim 2 - Characterize the Sr diffusion/distribution across barrier layer with the aim to determine optimum barrier layer thickness

EPD vs. Other Possible Coatings

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 – EPD Technical Challenges

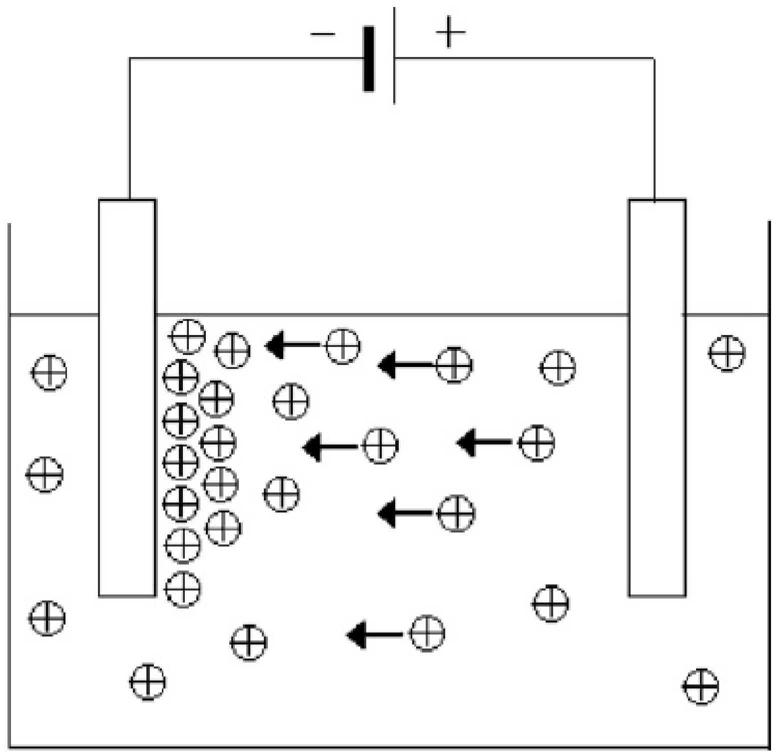
- Prepare stable suspension

  (solvent, additives, pH, concentration, temperature)
- Make substrate (YSZ) conductive

  (conductive polymer, carbon/graphite)
- Optimize layer composition and thickness

  (sintering aid, concentration)

Movement of Particles during EPD



Driving force:
The interaction of the surface charge with the electric field (accelerate particle)

Drag forces:
1 Viscous drag from the liquid
2 The force exerted by the electric field on the counter-ions in the double layer
3 When a particle moves, the distortion in the double layer caused by a displacement between the center of the negative and positive charge

- $CH_3CH_2OH + I_2 \rightarrow CH_3CHO + 2HI \rightarrow CH_3CHO + 2H^+ + 2I^-$

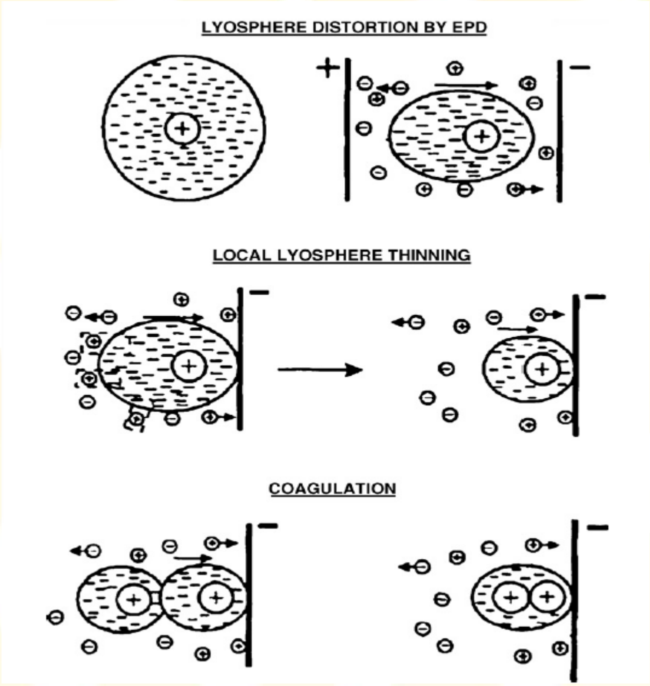
Mechanism of EPD Coating

1 **Flocculation by particle accumulation:** the pressure exerted by the electric field enables the particles close to the deposit to prevail the inter-particle repulsion.

2 **Particle charge neutralization mechanism:** the charged particles are neutralized when they touch the electrode.

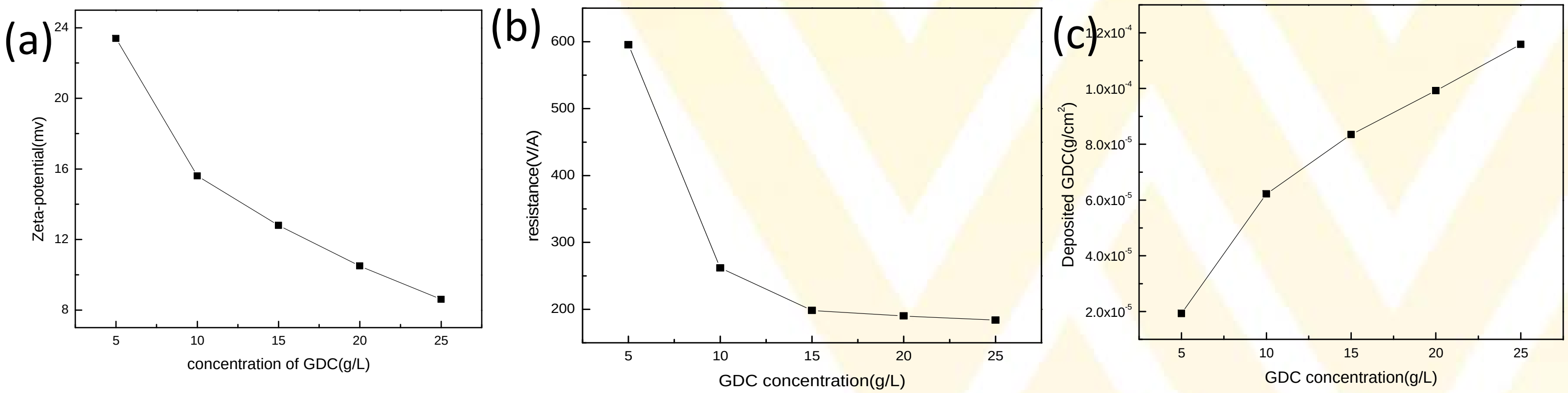
3 **Electrochemical particle coagulation mechanism:** an increase of electrolyte concentration produces a decrease of the repulsion between particles close to the electrode.

Ex: Cathode $2H_2O + 2e \rightarrow H_2 \uparrow + 2OH^-$



Schematic representation of electrical double layer distortion and thinning mechanism

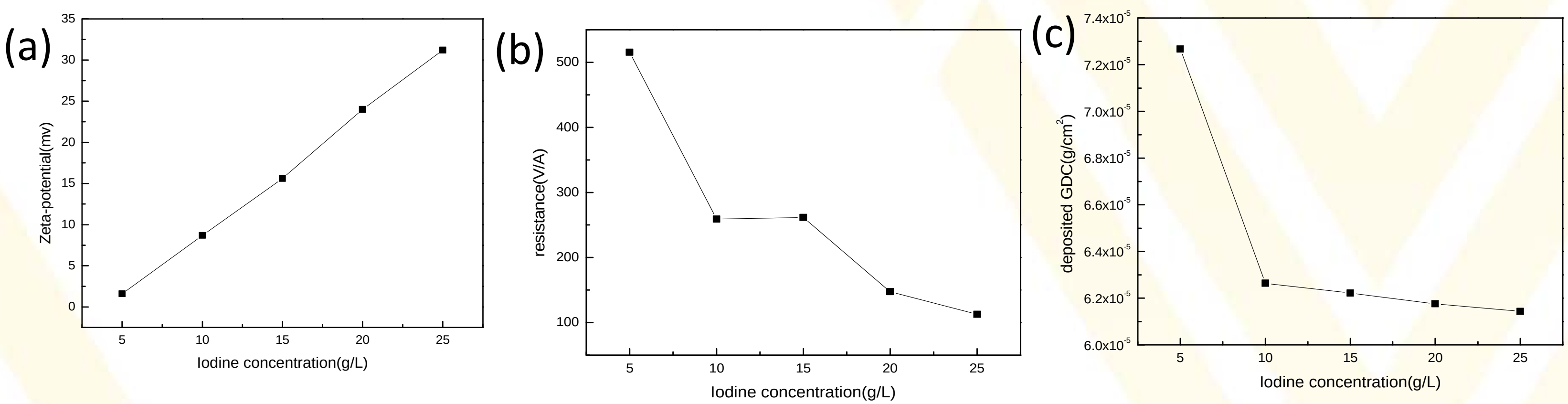
Developing Stable Suspension



Effect of GDC concentration on (a) Zeta-potential, (b) suspension resistance and (c) the amount of deposited GDC

Iodine concentration : 15g/L

Distance: 1cm
Voltage: 50V
Time: 2min



Effect of iodine concentration on (a) Zeta-potential, (b) suspension resistance and (c) the amount of deposited GDC

GDC concentration : 10g/L

EPD coating of GDC on Conducting Substrates

- Suspension: 100ml ethanol+1g GDC+ 1.5g Iodine
- Substrates: Stainless steel

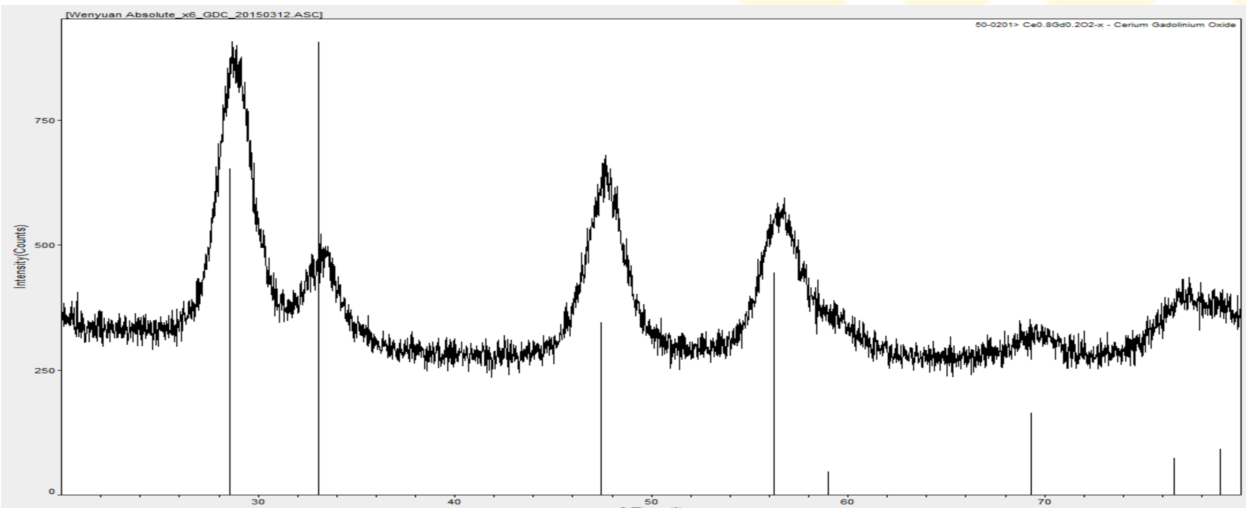


Fig.4 (left) XRD pattern and (right) macroscopy of deposited GDC on stainless steel

Dense GDC layer formed on cathodic substrate; GDC particles are positively charged

Developing Conductive Substrate

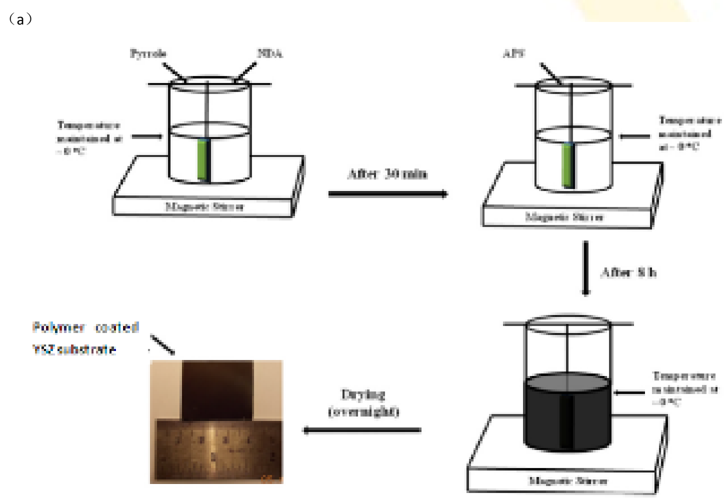
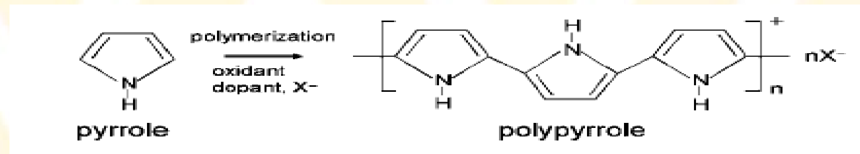


Fig.5 . Schematic of polypyrrole synthesis process



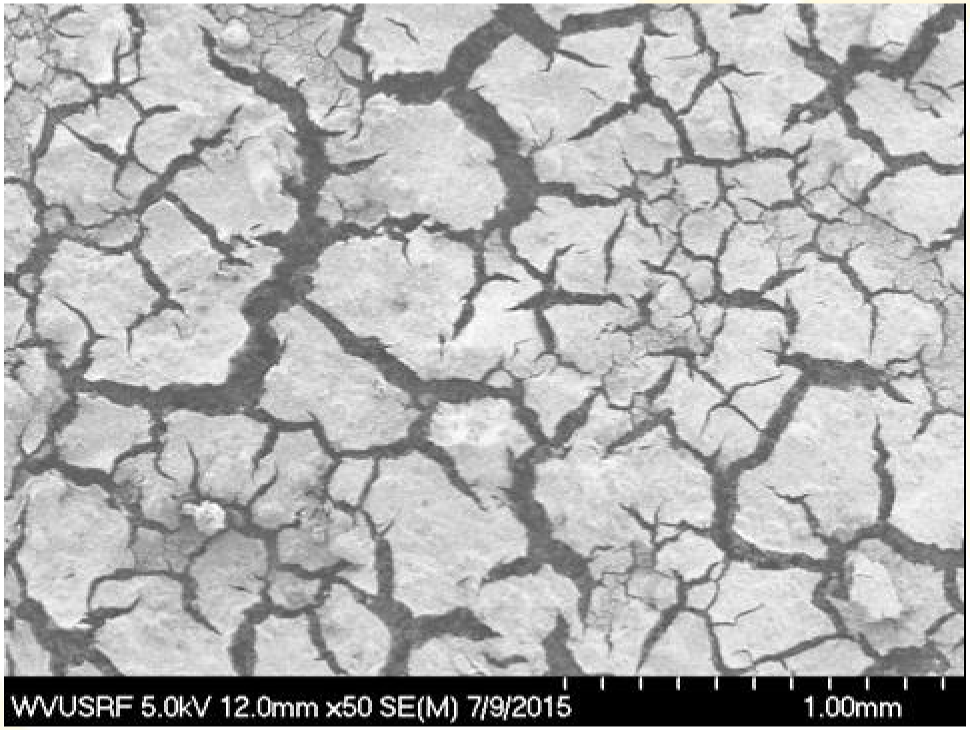
NDA: 2-6-naphthalene-difulfonic acid disodium salt

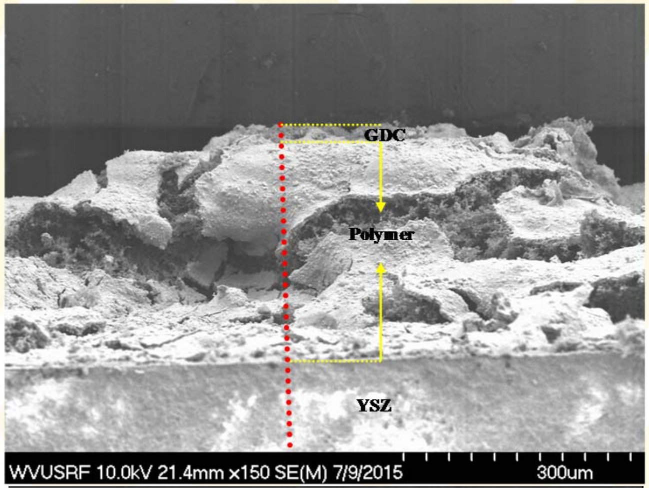
APS: ammonium peroxydisulfate

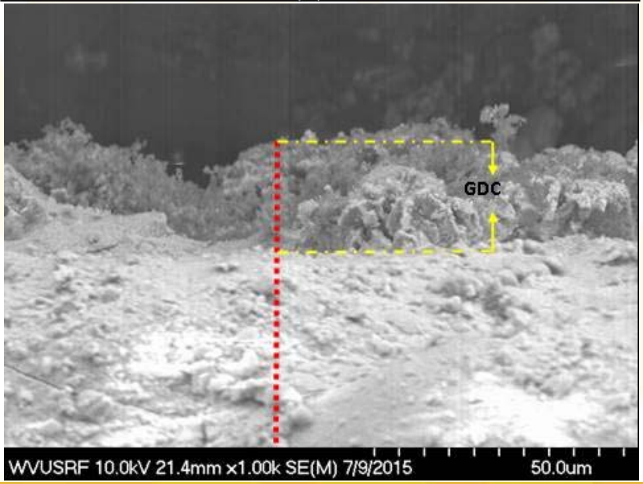
Cost-effective polymerization process.

Preliminary Results in 2015

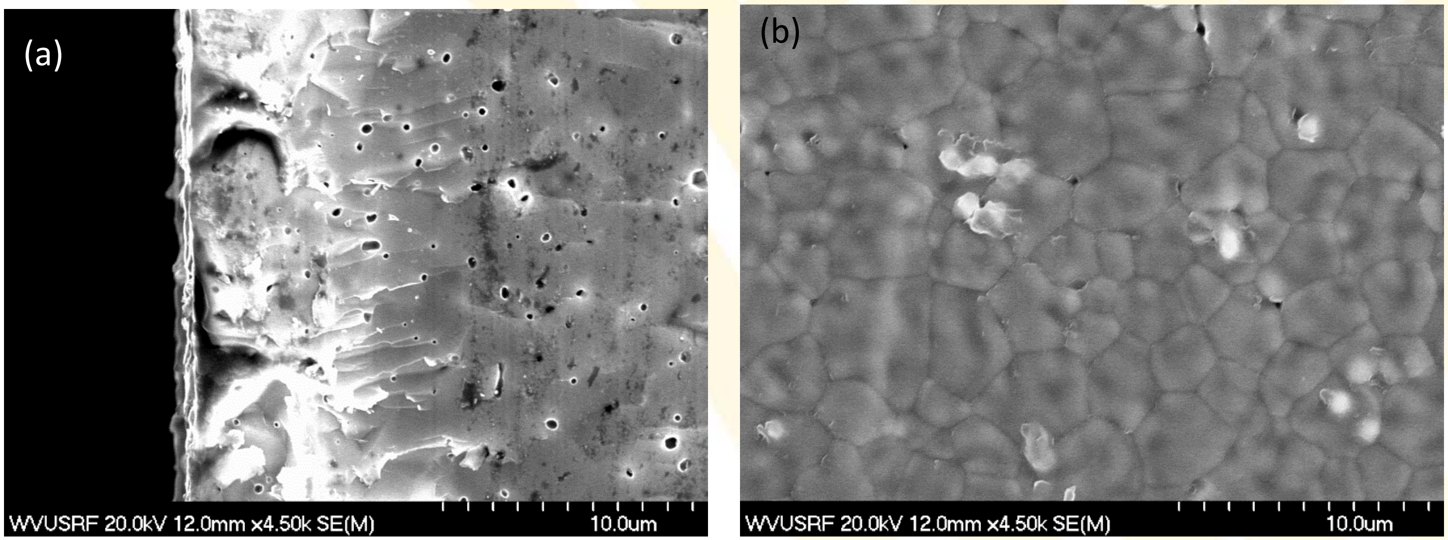
Possible Solutions: In-situ forming a conducting Polymer Layer







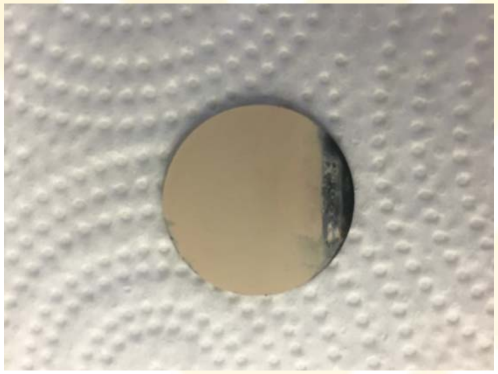
Conductive Polymer – Recent Results



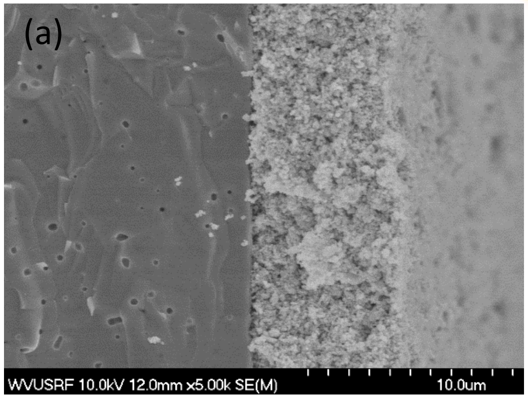
(a) cross - section and (b) microstructure of polypyrrole coated on YSZ before sintering

A uniform Ppy can be coated on YSZ pellet and the thickness is less than 1um.

Deposited GDC by EPD



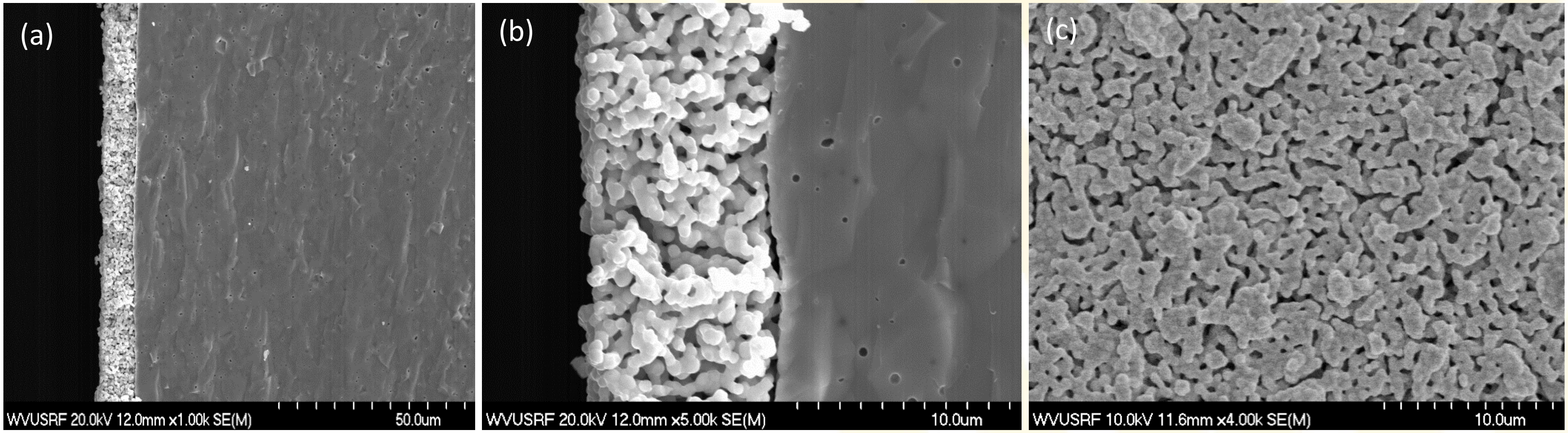
Macrostructure of deposited GDC before sintering



(a)cross-section and (b) surface morphology of GDC layer before sintering

Uniform and dense GDC can be formed by EPD

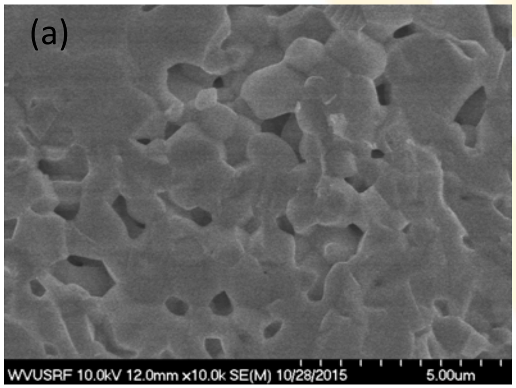
Deposited GDC by EPD

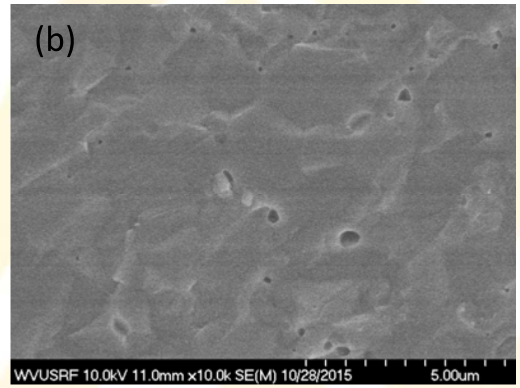


Morphology of GDC deposited on the polypyrrole coated YSZ pellet after sintering at 1300C

A uniform layer of GDC can be formed by EPD, the thickness is 5-8um.

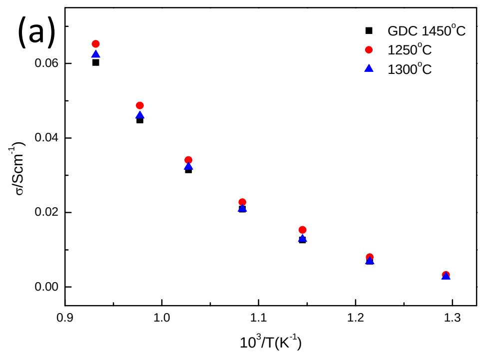
Effect of Sintering Aid



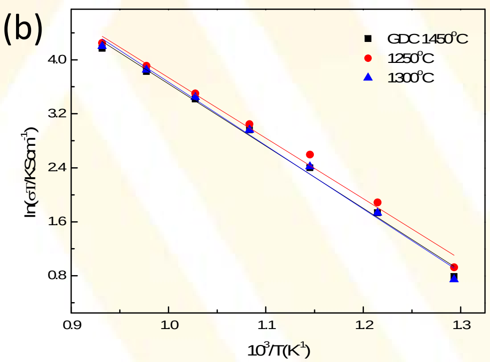


Microstructure of GDC pellets (a) sintering at 1450 without sintering aid and (b) sintering at 1300 with 2mol% iron oxide

(a)



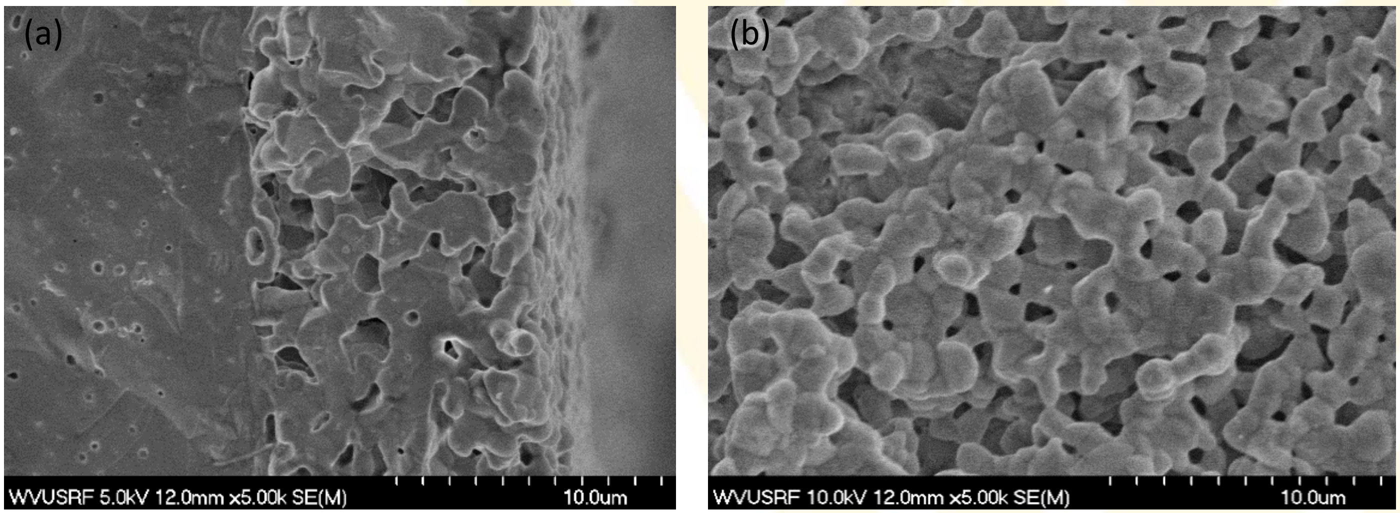
(b)



(a) temperature dependence and (b) Arrhenius plots of the ion conductivity for GDC with and without 2mol% iron oxide after sintering at 1300℃ for 4h

2mol% iron oxide can be used as sintering aid to effectively improve the density with impacting the ion conductivity of GDC

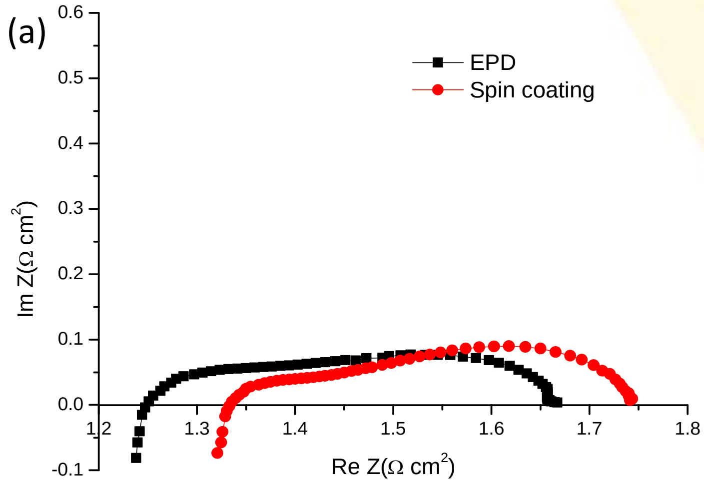
Effect of Sintering Aid

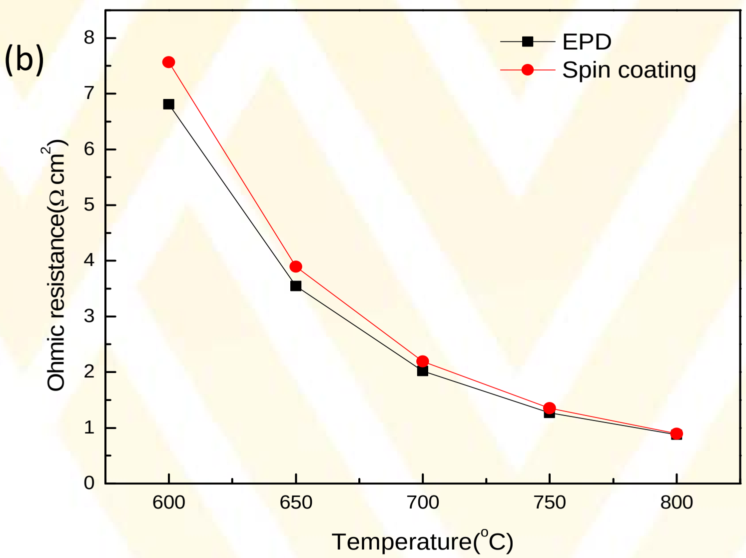


Morphology of GDC with sintering aid deposited on the polypyrrole coated YSZ pellet after sintering at 1300℃

Iron oxide can be used to improve the density of GDC

Performance of Symmetric Cell





(a) EIS at 750℃ and (b) temperature dependence of Ohmic resistance of symmetric cell with GDC layer with sintering aid formed by spin coating and EPD

AIM 1 – Summary & Conclusions

- A uniform layer of GDC can be formed by EPD, and the thickness is about 5-8um.
- The density of GDC formed by EPD is reliable and the adhesion between GDC and YSZ is good.
- Iron oxide can be used as sintering aid to effectively enhance the density of GDC without impacting the ion conductivity.
- Compared with spin coating, the total Ohmic resistance of symmetric cell with GDC formed by EPD is smaller.

AIM 2 - Sr Distribution/Diffusion Across GDC Barriers

- Cell preparation and performance
- Cross-sectional SEM-EDS
- Angle-lapped SEM-EDS
- Atom-probe tomography

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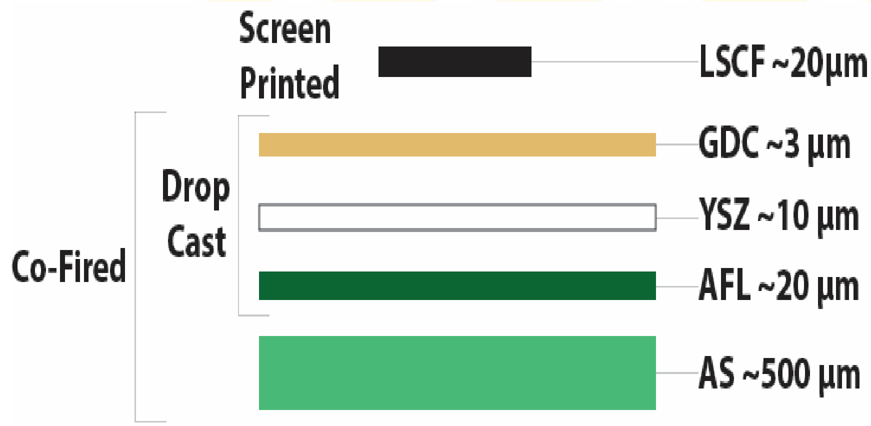
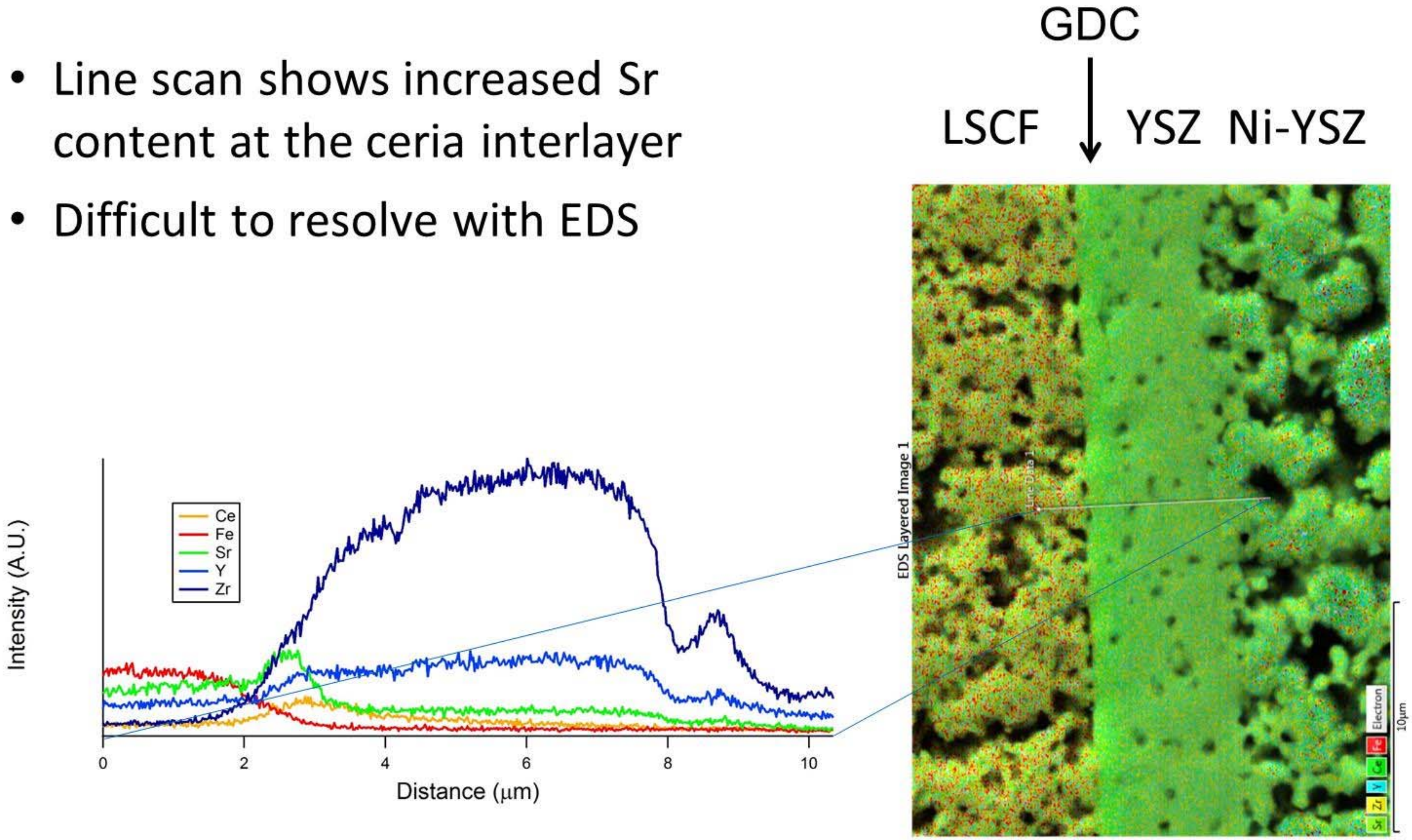
Cell Preparation

- Anode supported cells
  - Co-fired GDC/YSZ/Ni-YSZ
  - LSCF cathode fired at 1100 °C for 1 h
- Reduced co-firing temperature: 1250°C
  - Fe_3O_4 sintering aid yields reasonably dense GDC layer
  - Reduced GDC/YSZ interdiffusion
  - Optimized cells with LSCF-GDC cathodes yield power density 1.8 Wcm^{-2} (800°C, 0.7V) *Gao et al., J. Mater. Chem. A (2015)*



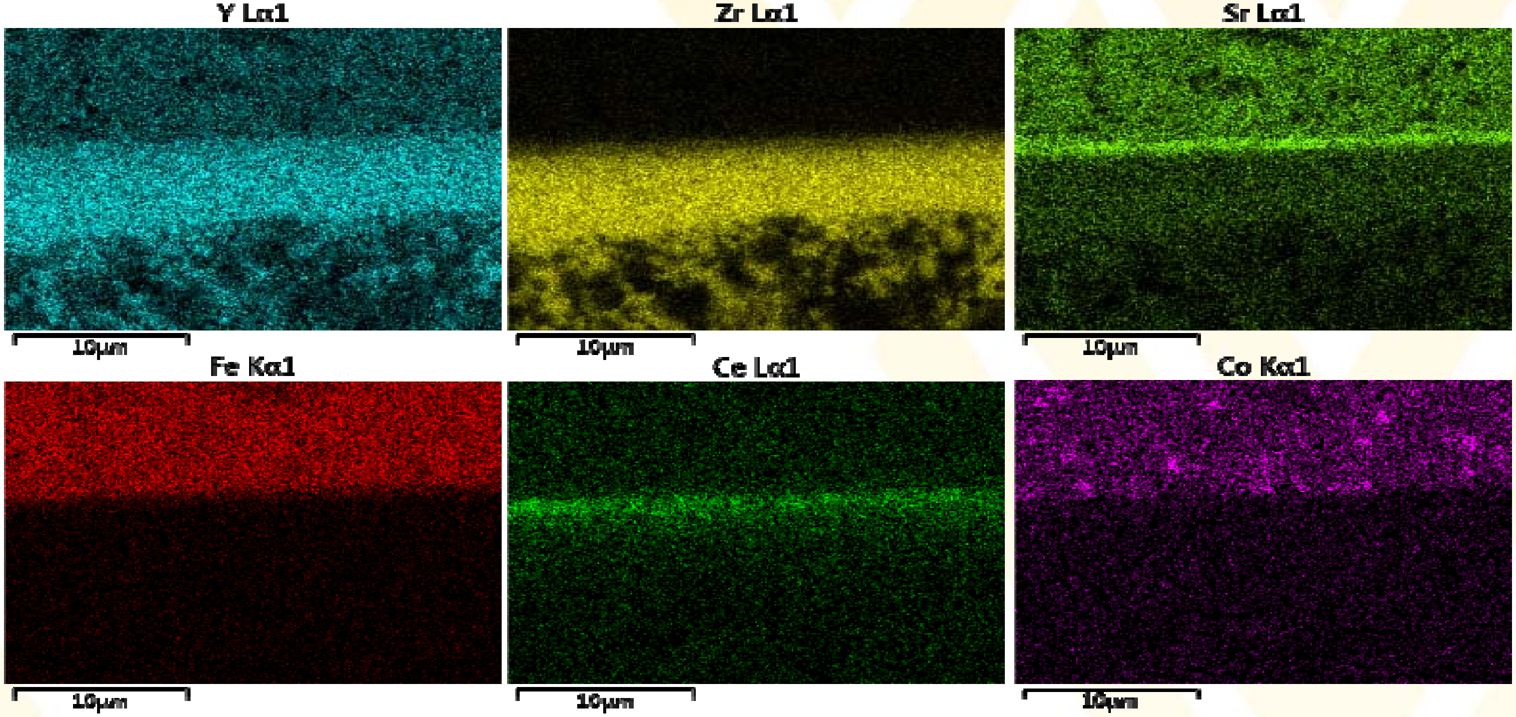
Cross-Sectional EDS

- Line scan shows increased Sr content at the ceria interlayer
- Difficult to resolve with EDS



SEM-EDS Chemical Maps

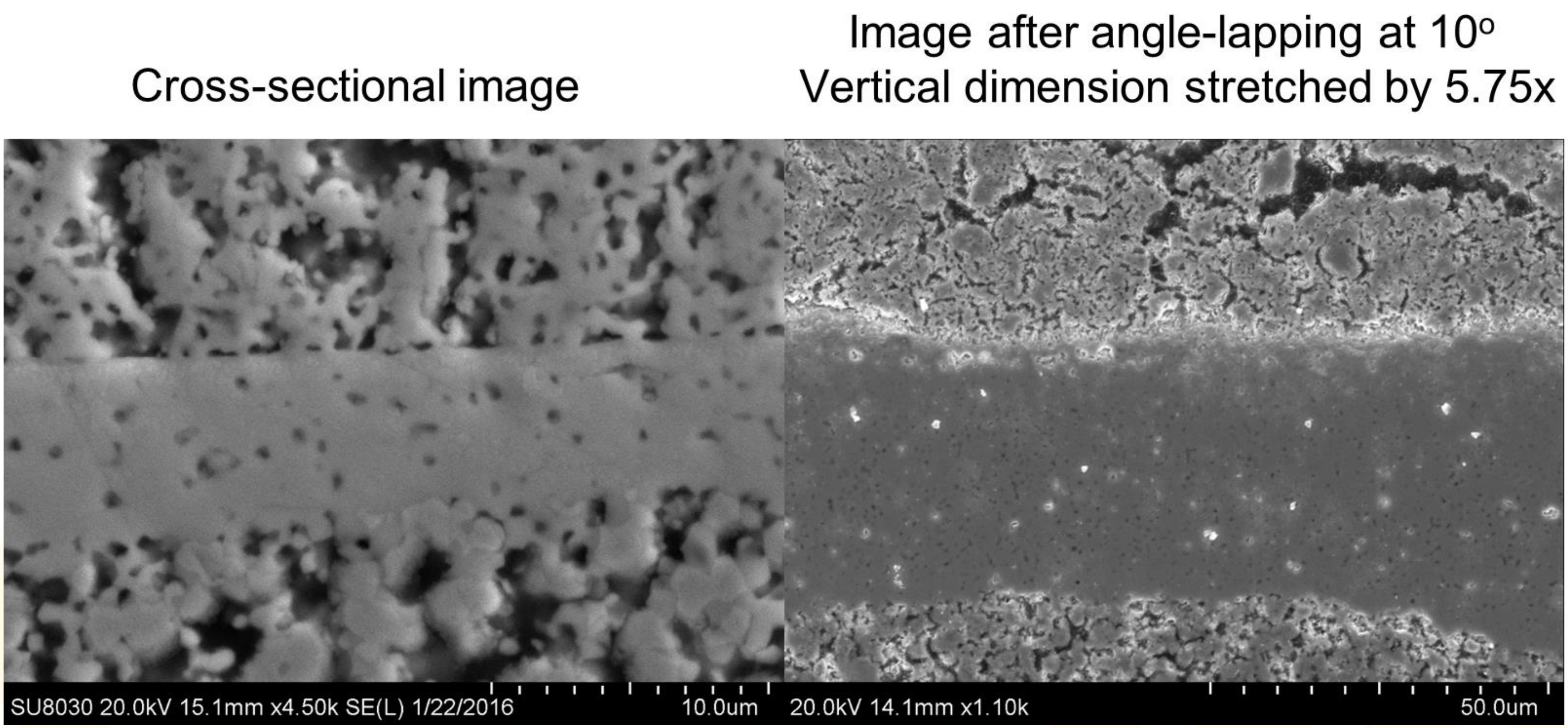
- Excess Sr observed in GDC layer
- Difficult to resolve with SEM-EDS



Angle-Lapped SEM

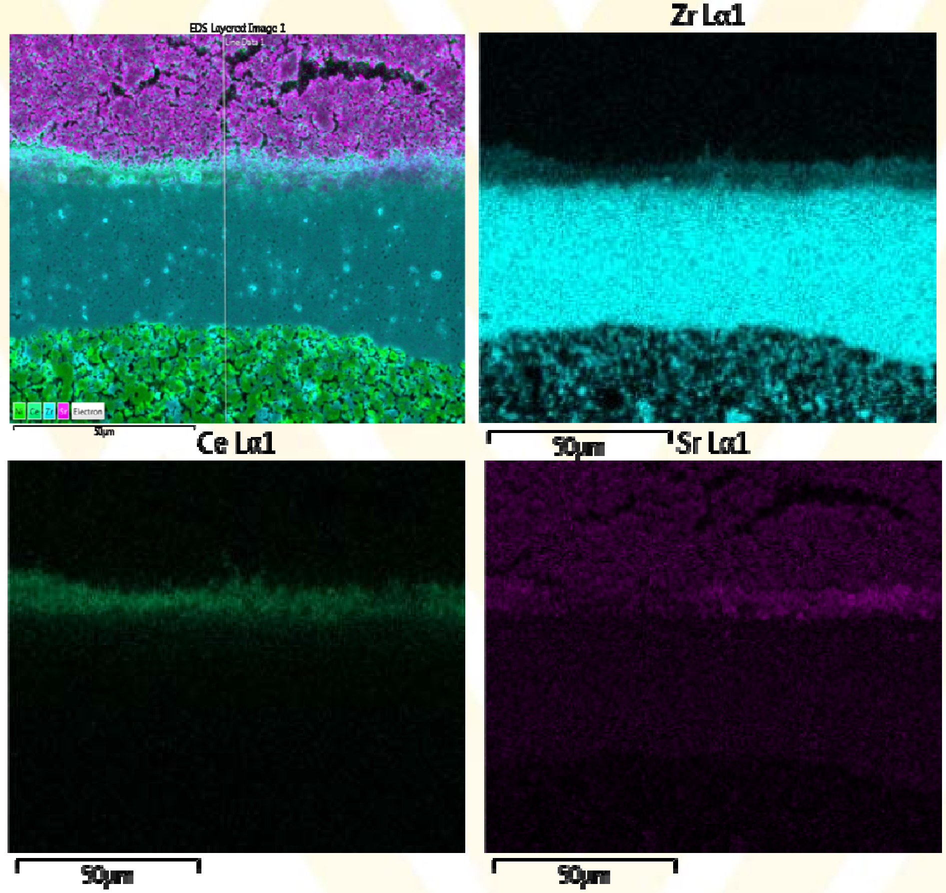
Angle lapping used to improve SEM-EDS resolution perpendicular to layer

Note that GDC layer is at top side of electrolyte



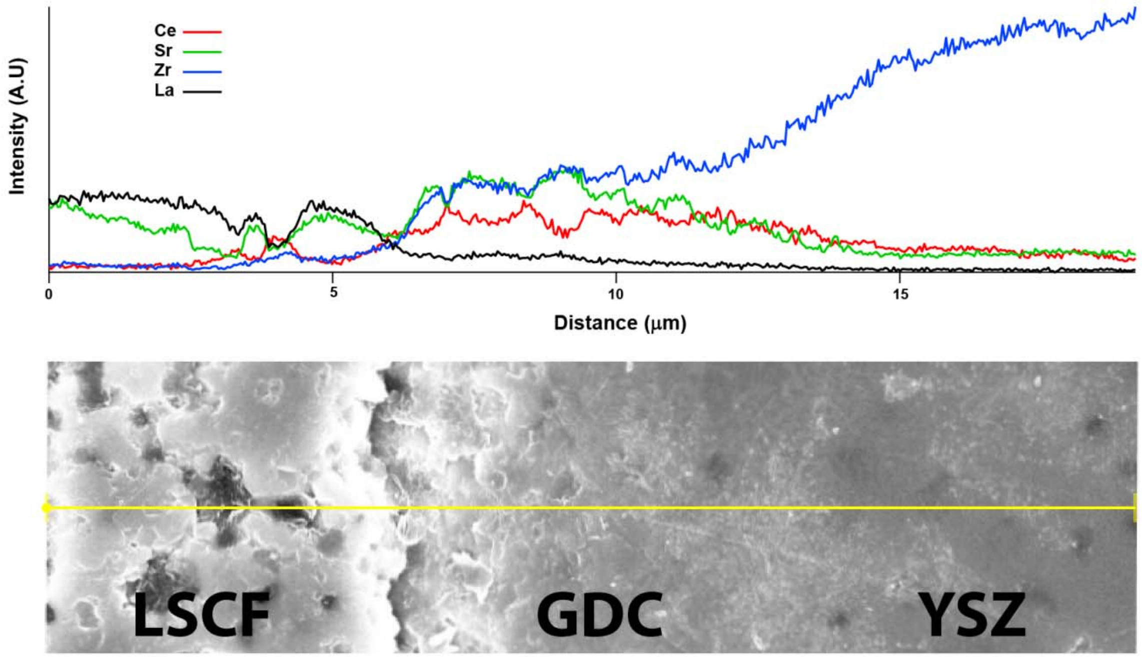
Angle-Lapped SEM-EDS Maps

- Sr accumulated at GDC layer



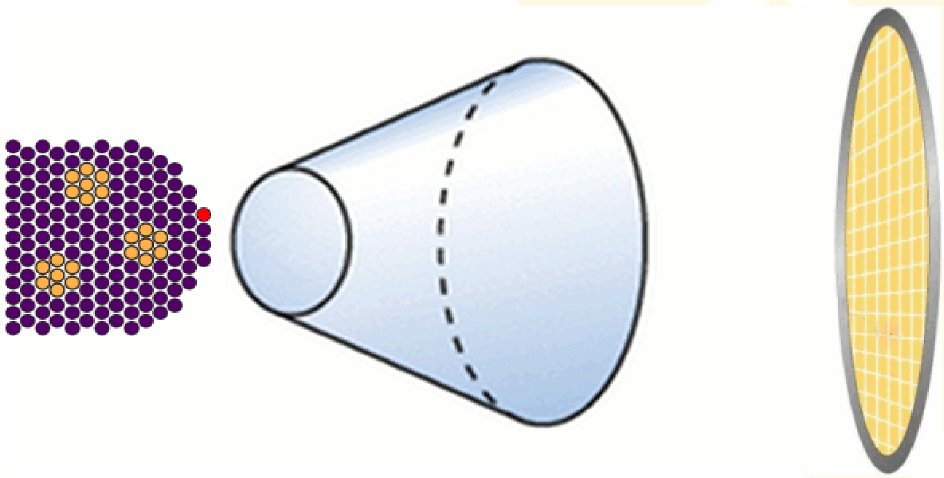
Angle-Lapped EDS Line Scan

- Sr present throughout GDC layer
- Clear evidence of GDC/YSZ interdiffusion
- GDC layer thickness: ~ 8 µm /5.75 ~ 1.4 µm



3D Atom Probe Tomography
3D-APT

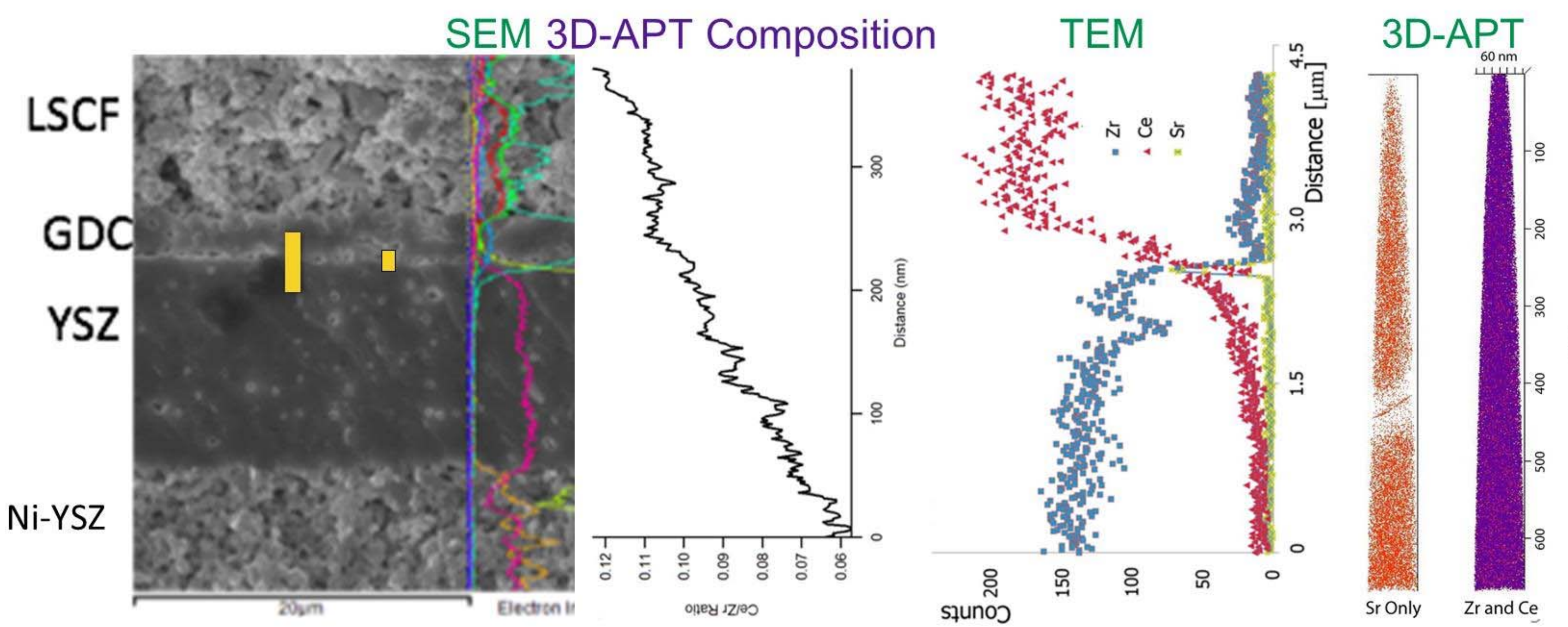
- Atomic resolution 3D imaging with high chemical sensitivity
- Applied here to interface between GDC barrier layer and YSZ electrolyte (LSCF cathode)
  - Probe for impurity diffusion and reaction from LSCF to YSZ



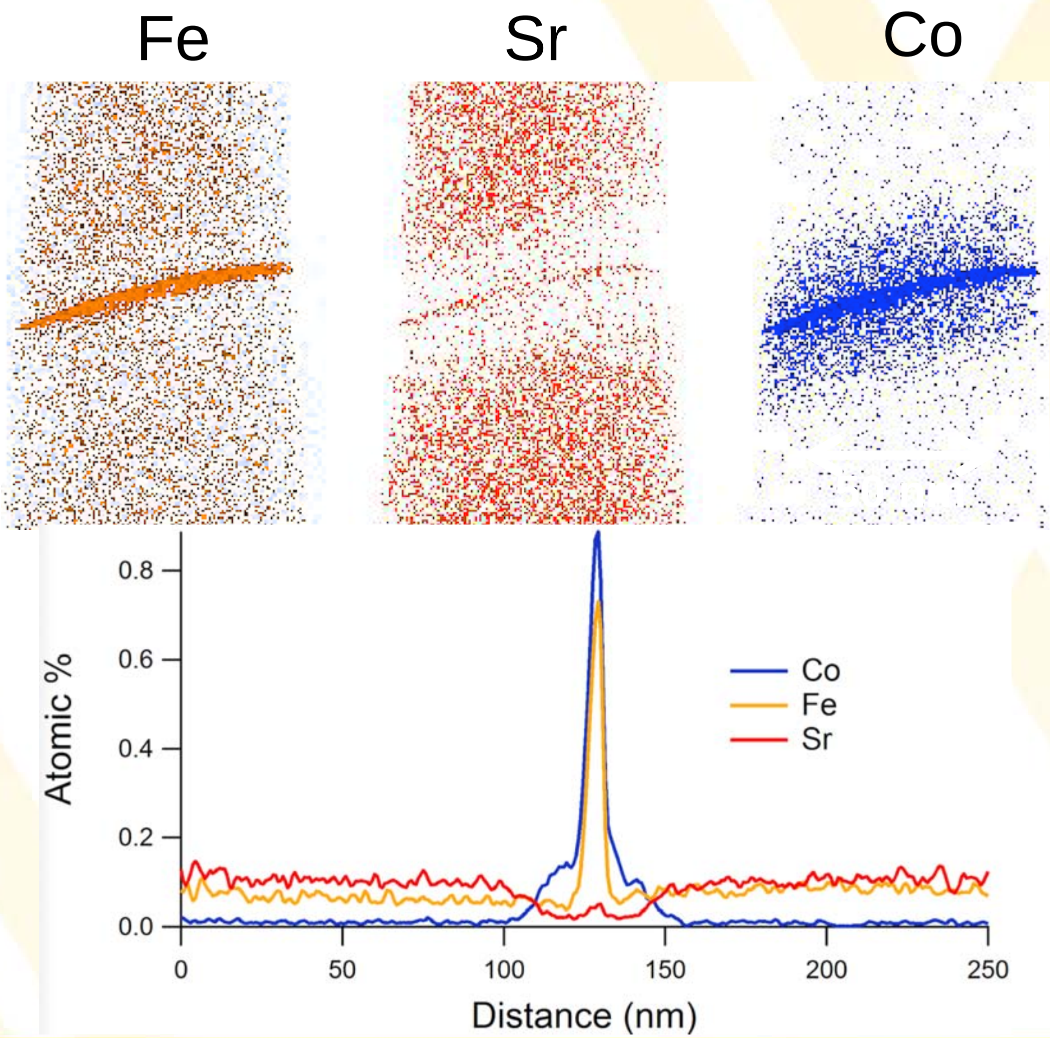
- Northwestern University Atom Probe Tomography Center

Scale of 3D-APT Measurements

- Measures very small volume (~100 x 500 nm, ~ $30x10^6$ atoms)
- Atomic resolution
- High chemical sensitivity (well below 0.1%)
- Ideal for observing interfaces



Impurities Near Grain Boundary



- Sr:
  - Present at ~ 0.2% in YSZ/GDC
  - Depleted around boundary, but slight spike at boundary
- Co
  - Strongly segregated at and near boundary
- Fe:
  - Used as sintering aid at 0.2%
  - Strongly segregated at boundary

AIM 2 - Summary and Conclusions

- Reduced-temperature co-firing yields reasonably dense GDC barrier with minimal GDC/YSZ interdiffusion
- Angle-lapped SEM-EDS provides good resolution of chemical distribution across GDC and surrounding layers
- Sr present throughout GDC barrier, but no apparent accumulation in broadened GDC/YSZ interface region
- 3D-APT provides high sensitivity 3D chemical imaging
  - Confirms presence of Sr in GDC/YSZ interface region
  - Accumulation of impurities at grain boundary near interface

Future Work

(Now - September 2017)

AIM 1 – EPD Coating (WVU)

- Investigate and Optimize sintering aids to achieve fully densified GDC sintering at below 1300C
- Explore other conducting agent (carbon/graphite etc.)
- Investigate the interaction between GDC barrier layer and LSCF cathode and the effects on ORR kinetics, electrochemical performance, and long-term stability

AIM 2 – Compositional Profiling (Northwestern U)

- Carry out compositional profiling of the cells with EPD GDC layers from WVU;
- Observe compositional profiles versus GDC layer thickness and LSCF firing temperature
- Carry out additional APT measurements to get more complete atomic-resolution information on Sr distributions

Acknowledgement

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  - NWU - Justin Railsback

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