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

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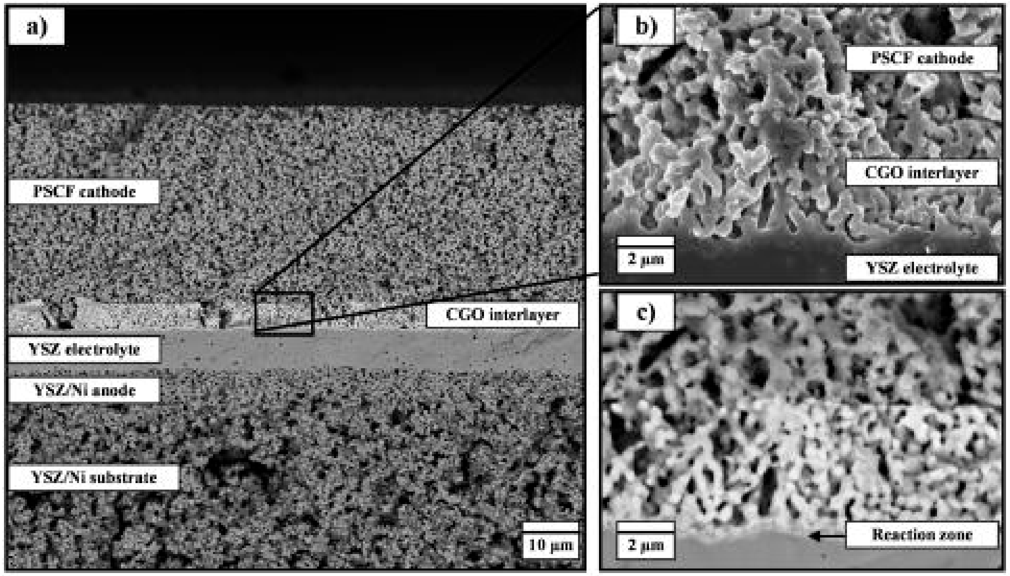
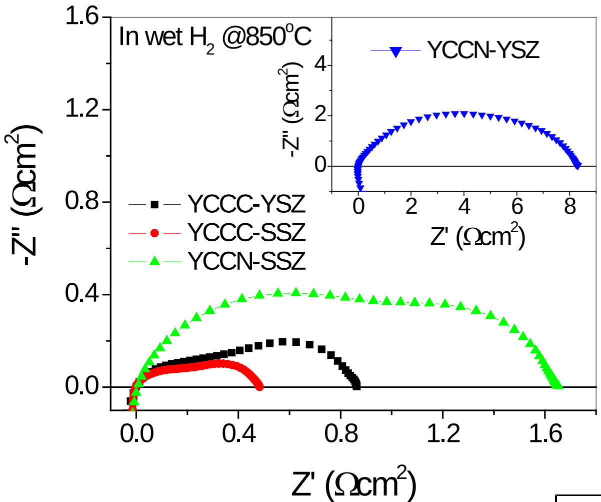
SOFC Cathode Barrier Layers

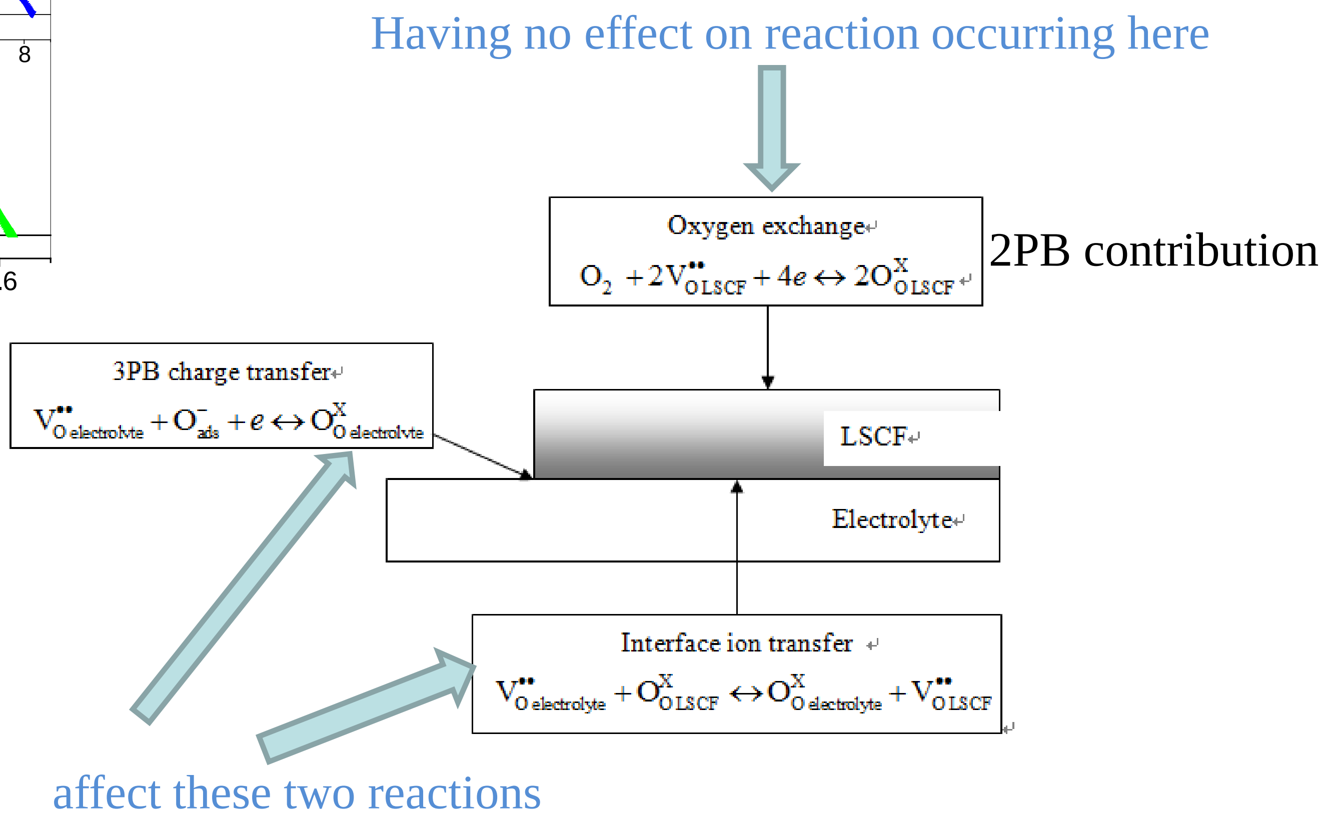
- **Chemical Compositions (GDC, SDC, etc.)**
- **Coating Methods (Screen Printing + Sintering)**
- **Functions**
  - Avoid Zirconate Formation
  - Improve ORR
- **Current Issues**
  - Porosity
  - Thickness



Electrolyte/Barrier Layer Effect on ORR Kinetics



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



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

Research Objectives

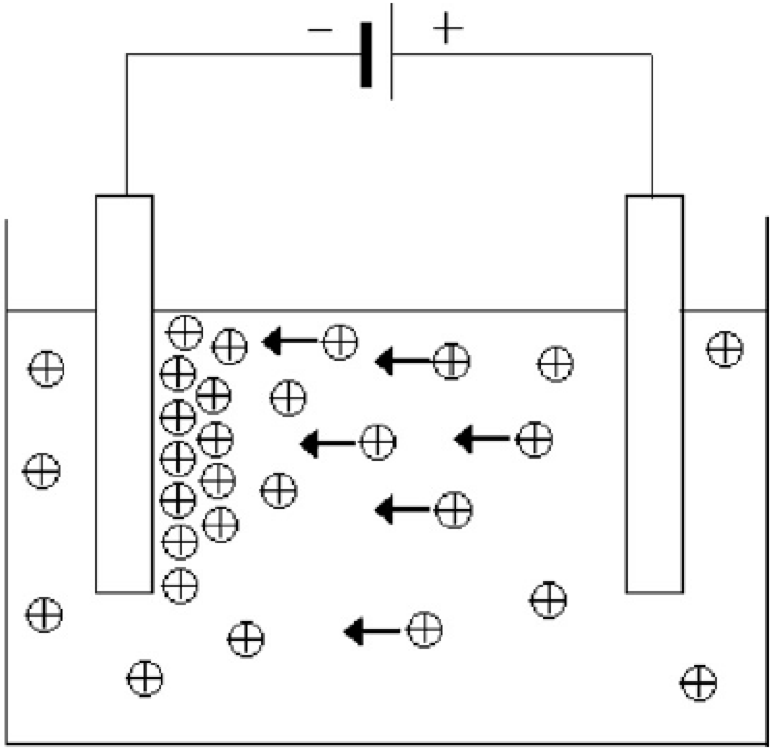
- Aim 1 - Develop a scalable and cost-effective electrophoretic deposition(EPD) coating process to form a dense barrier layer between a YSZ electrolyte and the cathode in a SOFC.

- 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]

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

Preparing Stable Suspension

- Suspension: 100ml ethanol+1.5g GDC+ 1g Iodine
- Zeta-potential: 18 mV
- Substrates: Stainless steel
- Voltage: 50V
- Time: 2min
- Distance:1cm

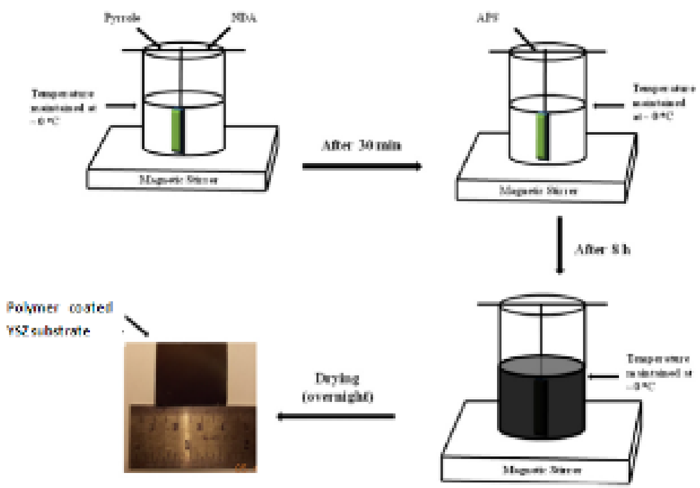
- GDC Particles are positively charged (absorbed H+)

$$2CH_3CH_2OH+I_2 \rightarrow 2CH_3CHOH+2HI \rightarrow 2CH_3CHOH+2H^++2I^-$$

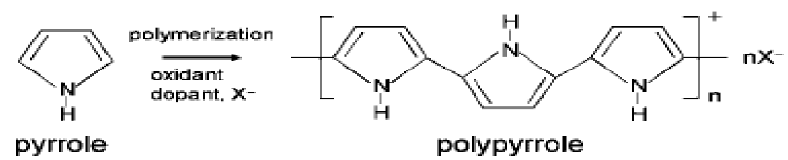
Conductive Substrate

- In-situ synthesis of polypyrrole
- Easy and industrial viable

(a)



Schematic of polypyrrole synthesis process

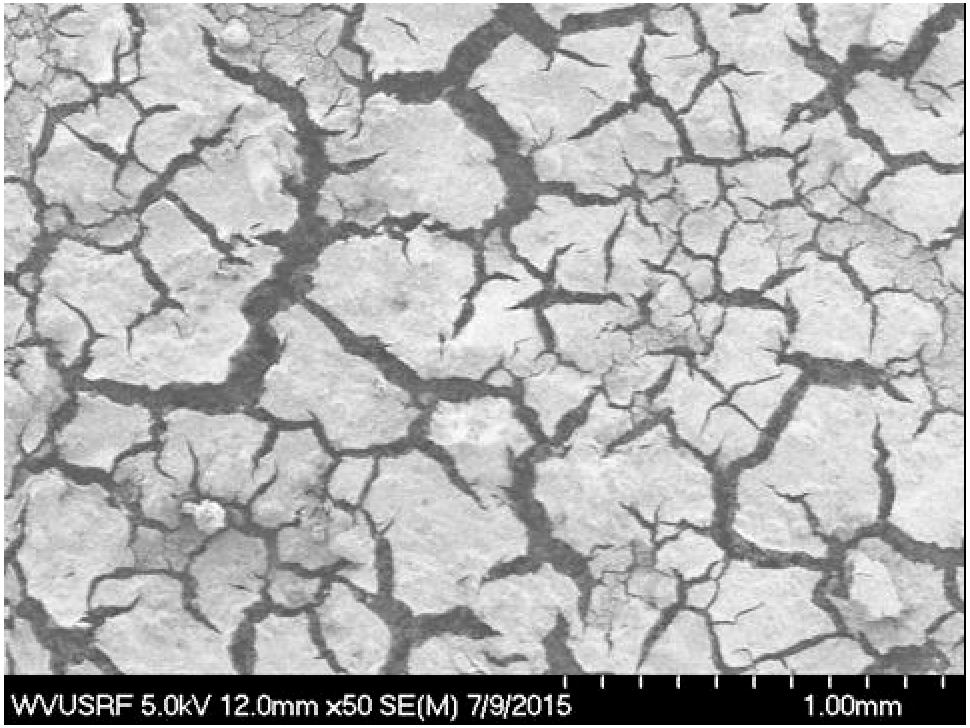


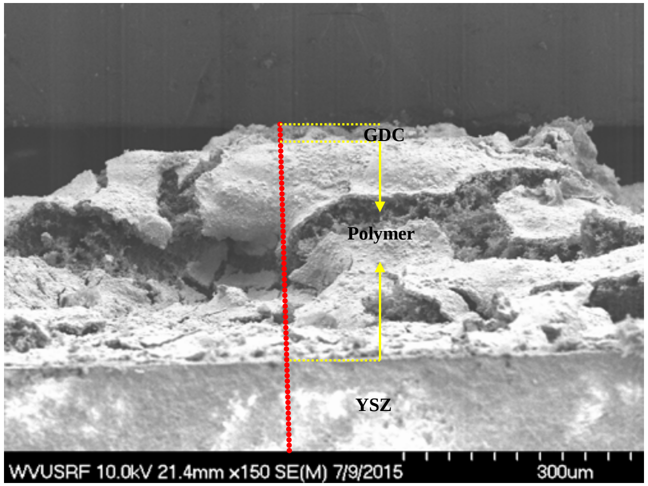
NDA: 2-6-naphthalene-difulfonic acid disodium salt

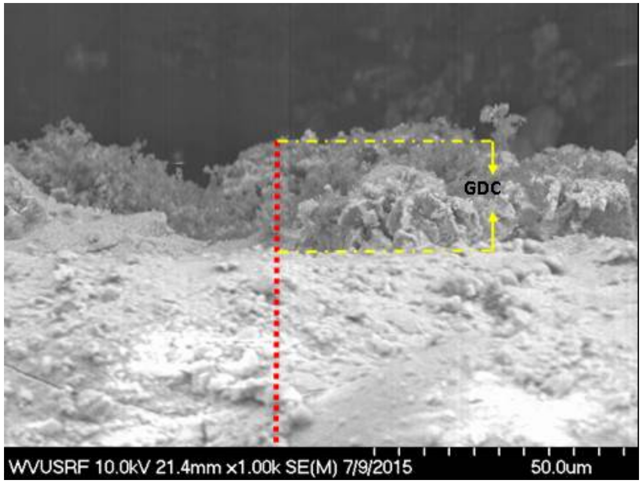
APS: ammonium peroxydisulfate

Preliminary Results – 2015

Possible Solutions: In-situ forming a conducting Polymer Layer

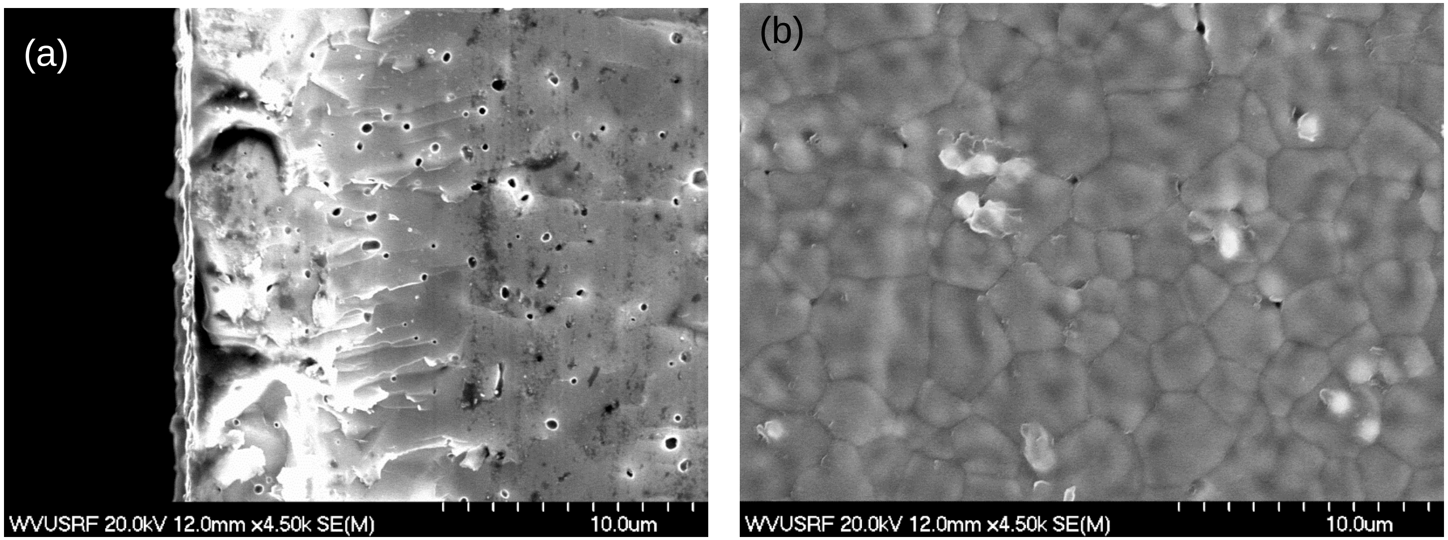






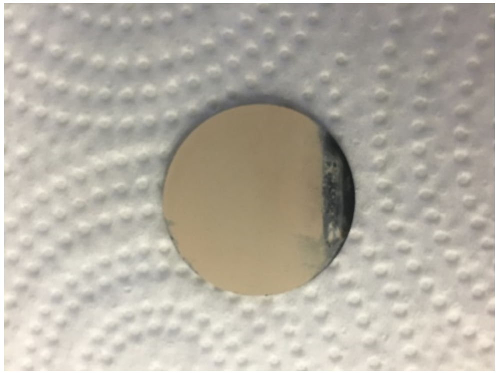
Results in 2016 – Conductive Polymer

- Uniform layer of Ppy
- Thickness less than 1um
- Conductivity is about 9 S/cm

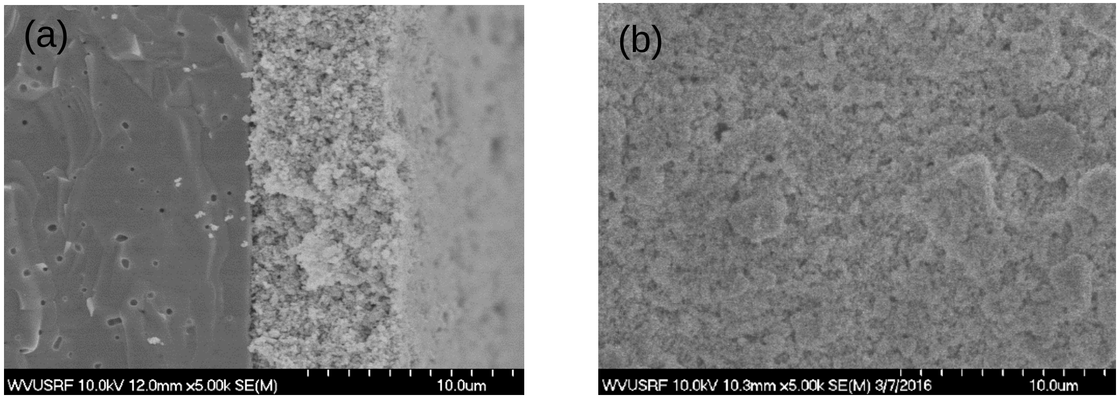


(a) Cross - section and (b) microstructure of polypyrrole coated on YSZ before sintering

Results in 2016 - Deposited GDC by EPD



Microstructure of deposited GDC before sintering



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

Effect of Voltage

The hydrogen gas bubble will impair the density of GDC layer

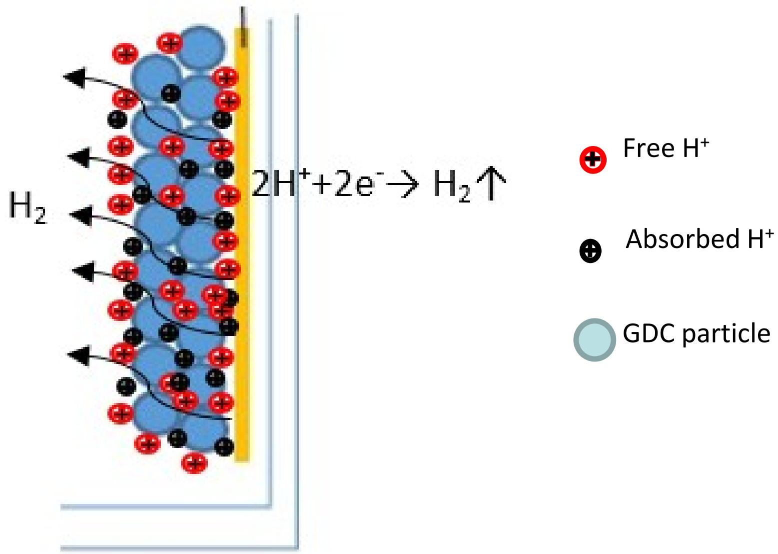


Fig.4 Shematic of reaction near cathode

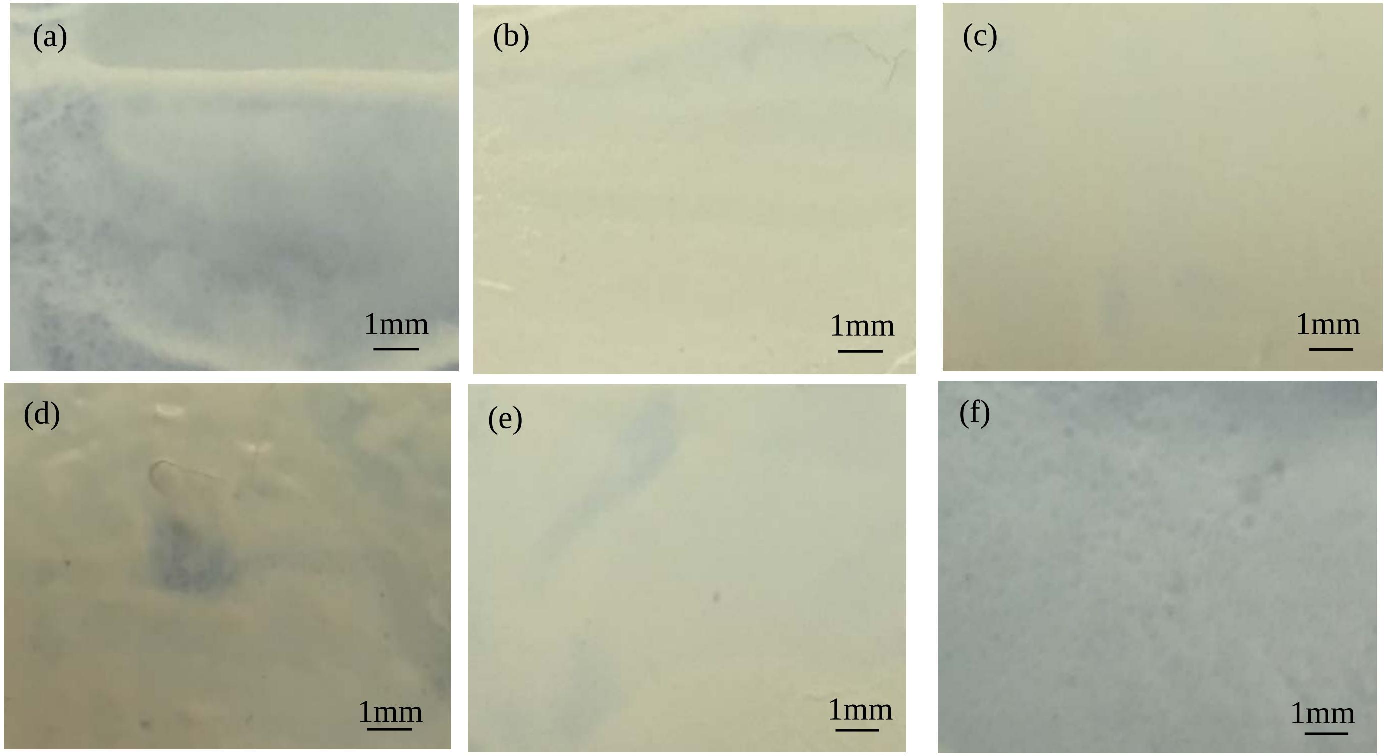
Two type of H^+ : free H^+; absorbed H^+

H^+ can pass through GDC deposit to cathode and reduced under DC electric field

Note: hydrogen gas pass through the GDC deposit and impair the density and adhesion between GDC and YSZ

Optimal Voltage

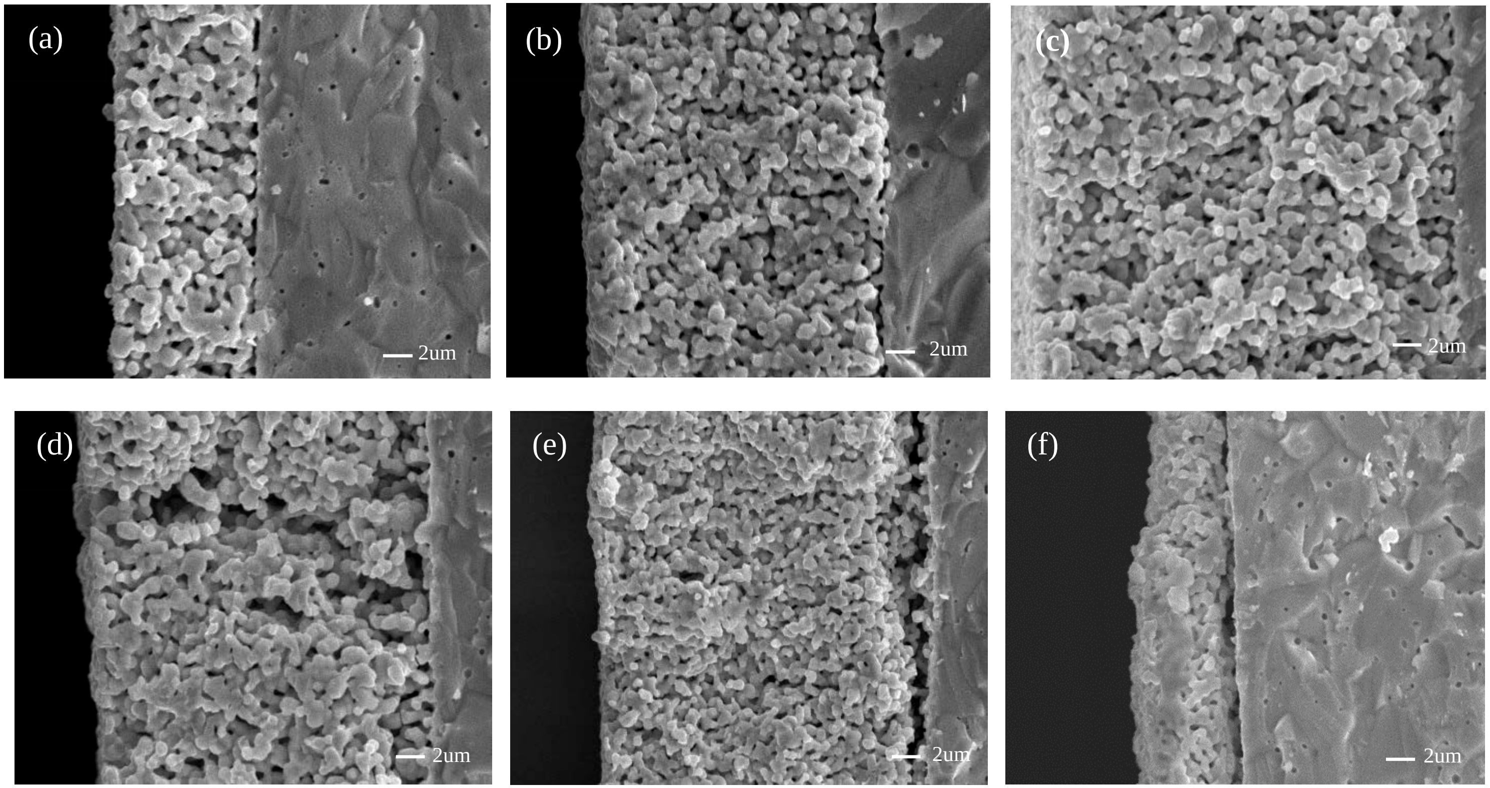
- Uniformness and thickness of deposit depends on applied voltage



The deposit for 10 mins as a function of applied voltage (a) 60V, (b) 80V, (c) 100V, (d) 120V, (e) 140V and (f) 160V

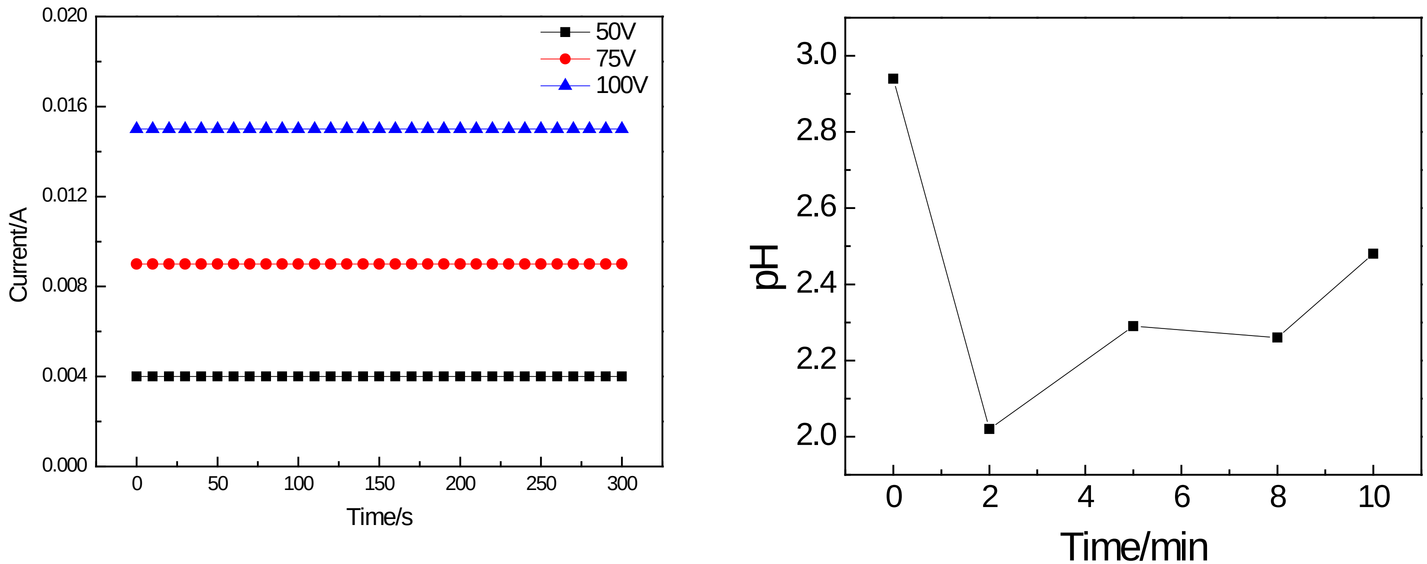
Optimal Voltage

- Good adhesion between GDC and YSZ after sintering when voltage is not larger than 100V



Cross-sectional morphology of the deposit for 10 mins as a function of applied voltage (a) 60V, (b) 80V, (c) 100V, (d) 120V, (e) 140V and (f) 160V

Rate-Determining Step

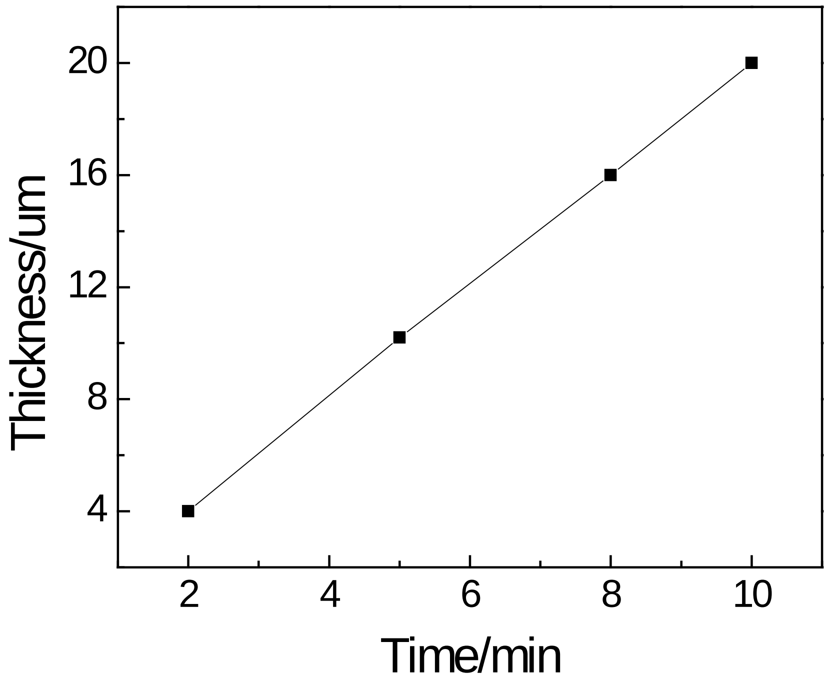


(a) current and (b) pH near the cathode as a function of time under constant voltage

- Constant current under constant voltage → constant deposition rate
- H+ accumulation zone near cathode
- The reduction of H+ is the rate-determining step

Thickness of Deposit

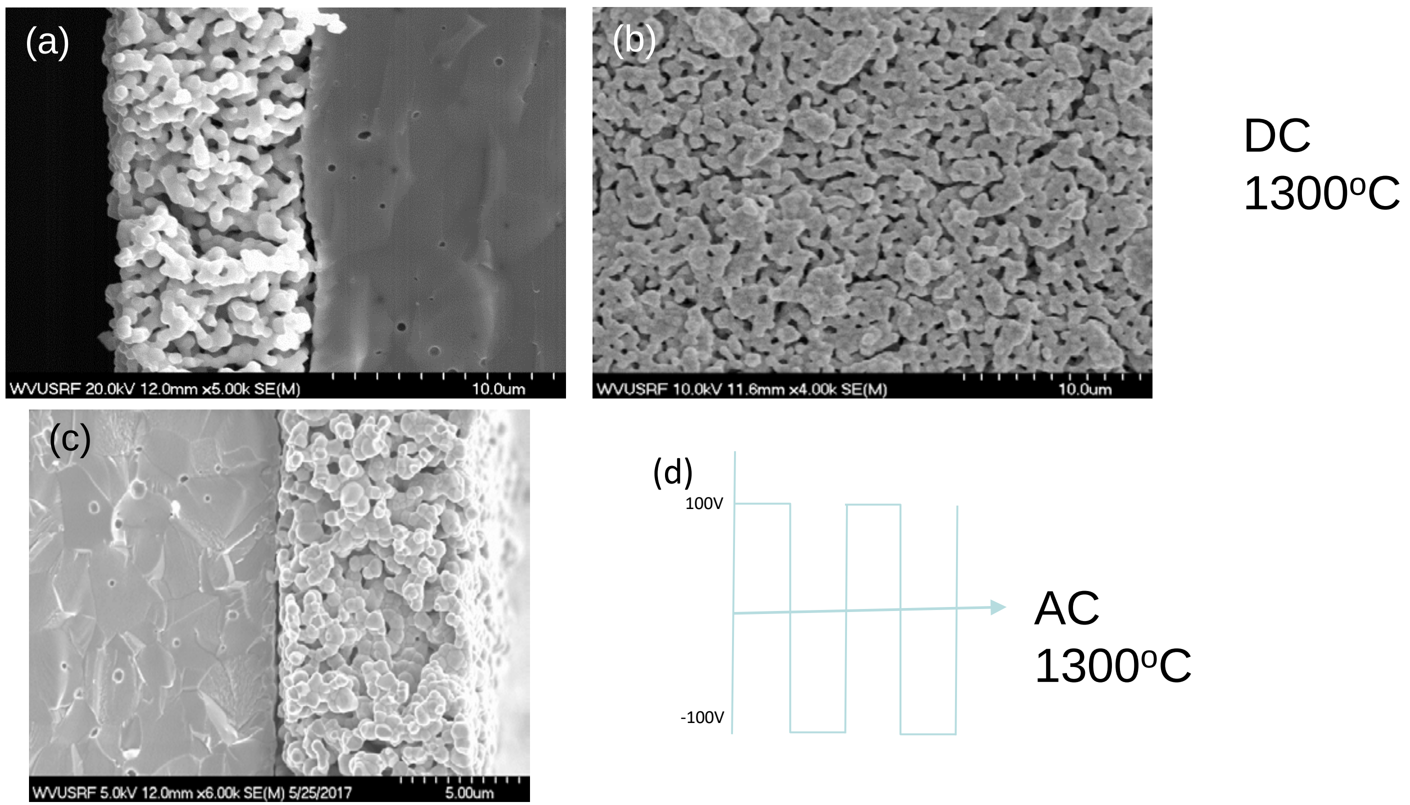
- The thickness of deposit is proportional to time



Thickness as a function of time for a GDC/ethanol suspension, under constant-voltage conditions (100V) when using polypyrrole coated YSZ as the cathodic electrode

AC EPD of GDC

- A uniform layer of GDC can be formed by EPD
- AC-EPD can improve the density



Microstructure of pure GDC layer formed by (a, b) DC and (c) AC-EPDafter sintering at 1300ºC; (d) schematic of symmetric AC signal

Effect of Sintering Aid

- Iron oxide can be used as sintering aid to improve the density of GDC
- Dense GDC layer can be obtained at 1300ºC by DC-EPD
- AC-EPD can decrease the densification temperature to 1250ºC

DC
1300ºC

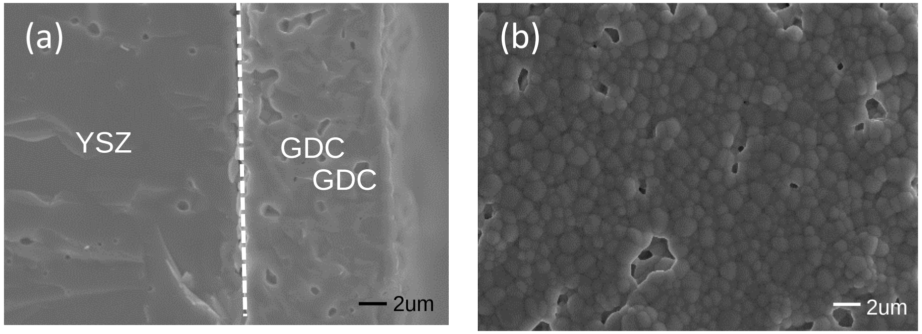


Fig.12 (a)cross-section and (b) surface morphology of GDC layer with 2mol% $FeO_{1.5}$ after sintering at 1300ºC

DC and AC
1250ºC

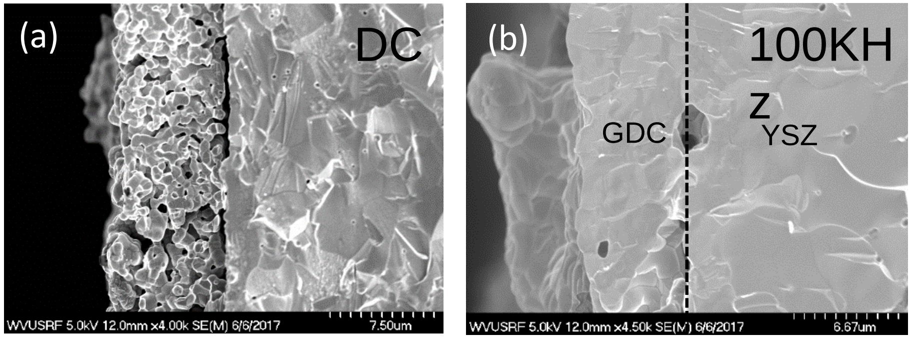


Fig.13 cross-section of GDC layer with 2mol% $FeO_{1.5}$ formed by (a)DC and (b) 100kHz AC EPD after sintering at 1250ºC

LSCF fired at 1000ºC

- No Sr diffusion to YSZ

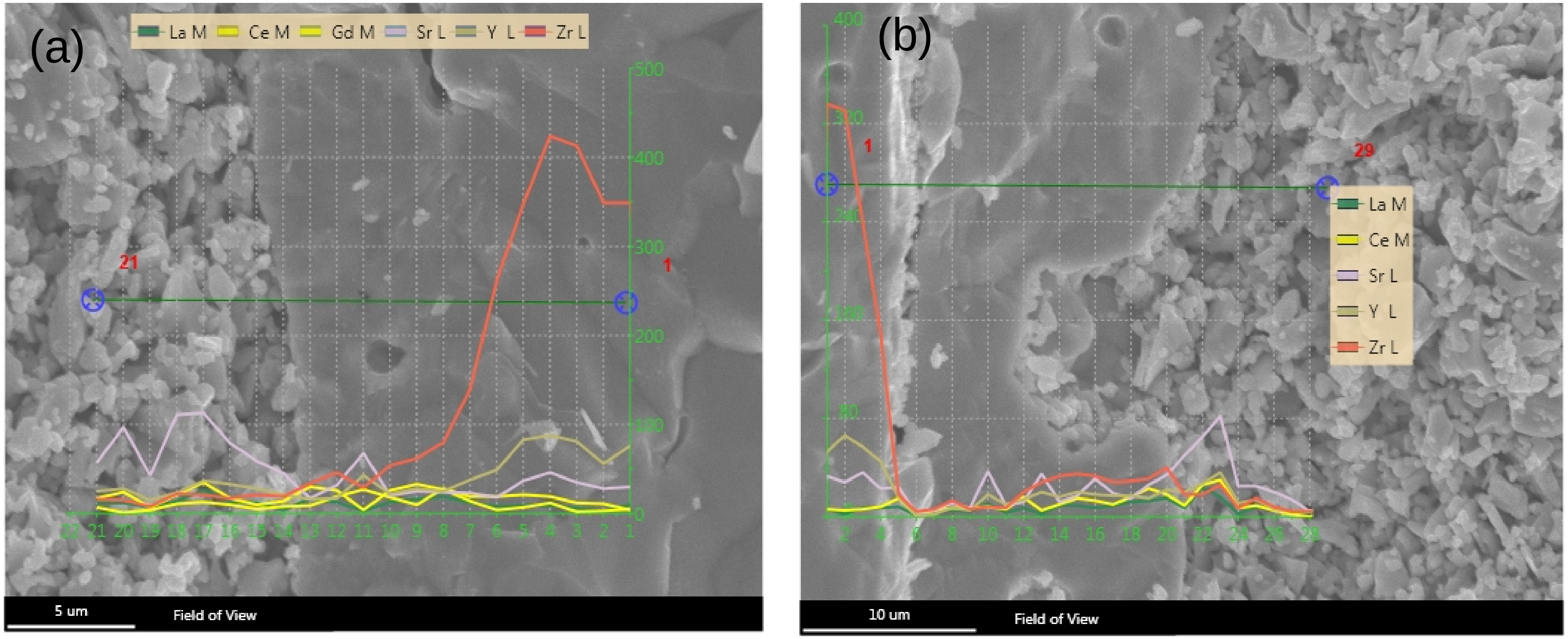
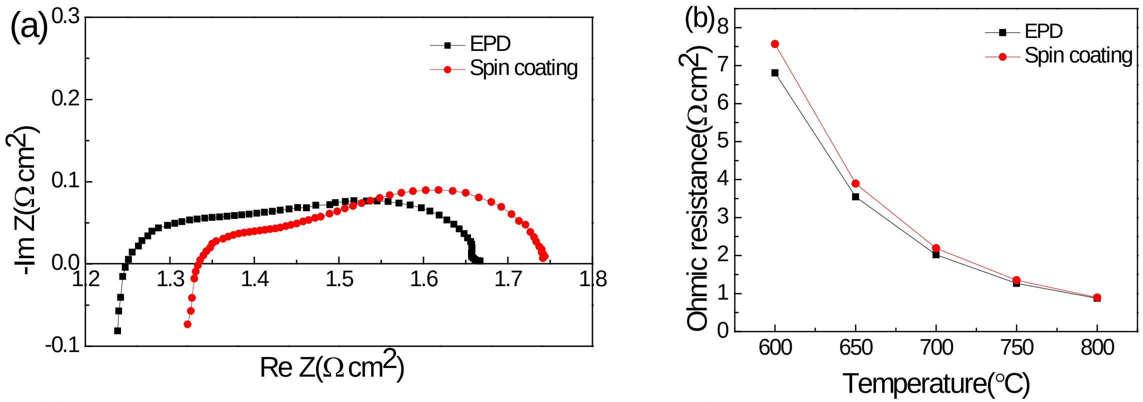


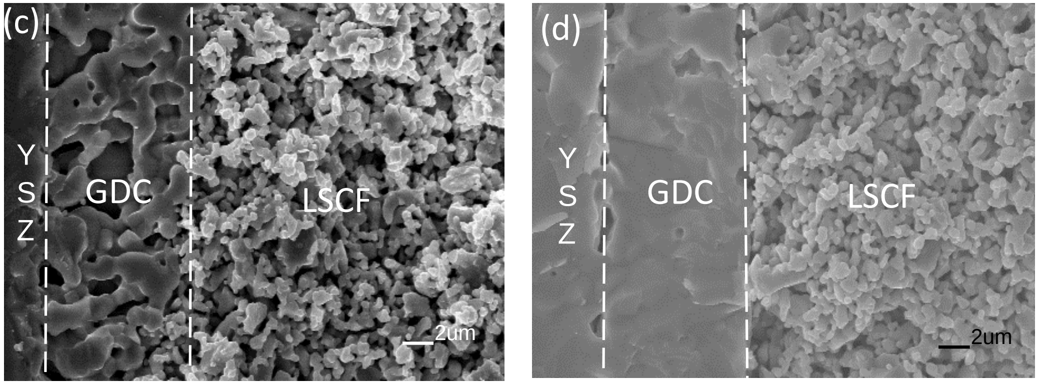
Fig.17 EDAX analysis of LSCF/GDC/YSZ before after long-time stability test

Performance of Symmetric cell

- Compared with spin coating, the total Ohmic resistance of symmetric cell with GDC formed by EPD is smaller



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



Cross-section micrograph of symmetric cell formed by (a) spin coating and (b) EPD

Aim 1 - Summary

1. 100V is the optimal voltage for the suspension. The rate-determining step is the reduction of H^+.

2. A uniform layer of GDC can be formed by EPD with a constant deposition rate under 100V.

3. Dense GDC layer can be obtained at 1300^{o}C by DC-EPD, densification temperature can be decreased to 1250^{o}C by AC-EPD

4. Compared with spin coating, the total Ohmic resistance of symmetric cell with GDC formed by EPD is smaller.

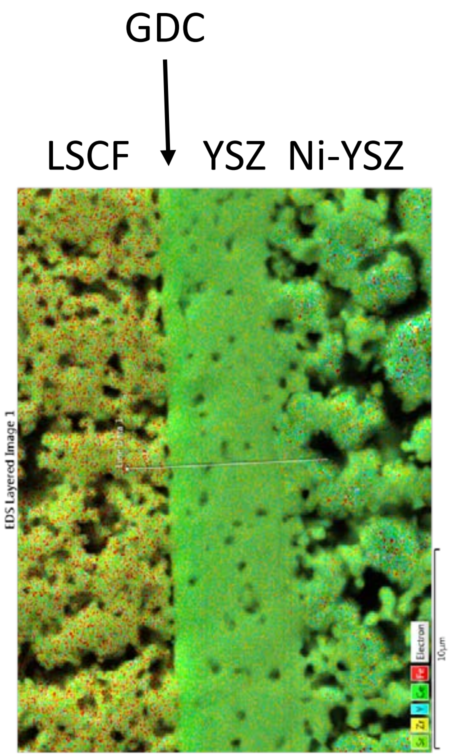
Aim 2: Characterization of GDC Barrier Layers

- Co-fired GDC/YSZ bi-layer electrolytes
  - Cross-sectional SEM-EDS, TEM-EDS
  - Atom-probe tomography

- GDC barriers made by WVU
  - Cross-sectional SEM-EDS

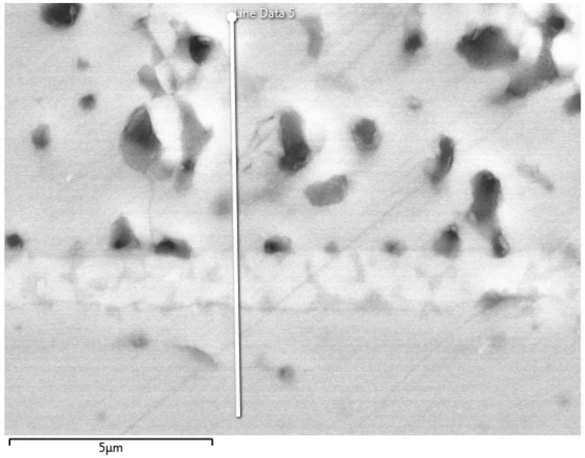
Co-Fired GDC/YSZ Electrolyte Cells

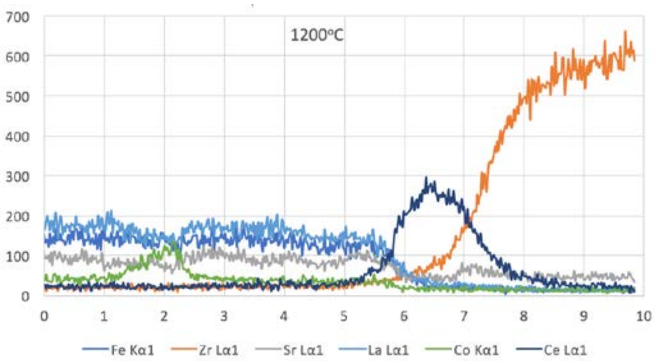
- Reduced firing temperature yields fairly dense thin GDC layers with little GDC/YSZ interdiffusion
  - GDC thicknesses varied from 1.5 to 6.0 microns
- LSCF layer applied
  - Fired at 1000, 1100, or 1200 ^oC
- Aim: explore interdiffusion effect over range of conditions

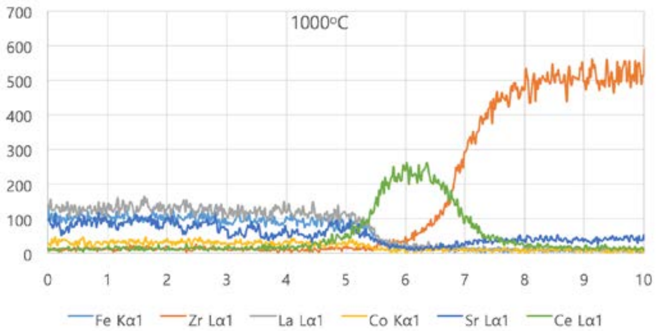


Effect of LSCF Firing Temperature

- 1.5 micron thick GDC
- Sr segregation to YSZ/GDC interface detected for 1200, not 1000 or 1100 C
- Little Sr at typical LSCF firing temperature of 1100 C
- Apparent Sr in YSZ layer due to Sr/Y peak overlap

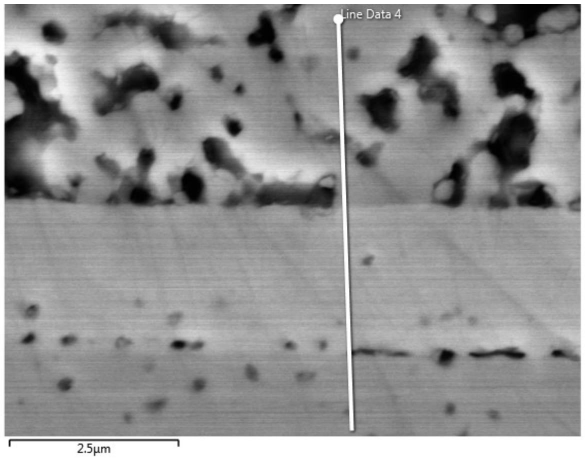




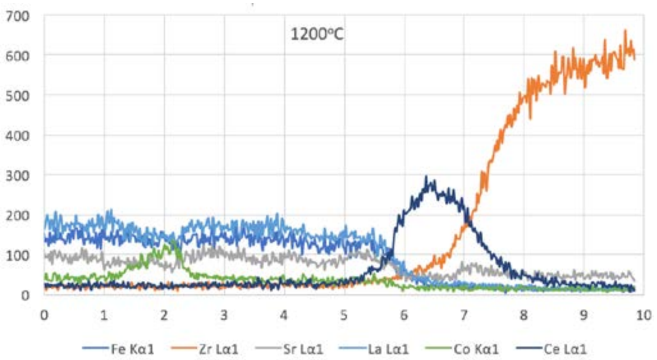


Effect of GDC Thickness

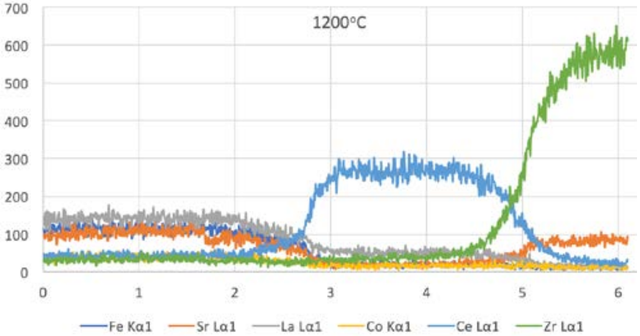
- Thicker GDC layer appears to prevent Sr diffusion even at 1200 C



1.5 micron thick

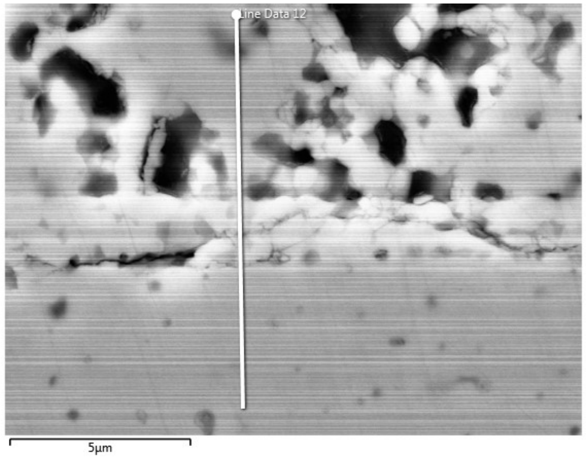


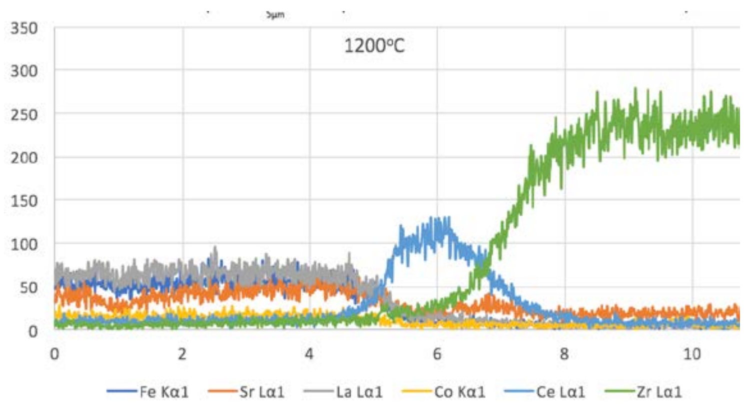
6 microns thick



Effect of GDC Pores

- Defects in GDC layer allow Sr diffusion to GDC/YSZ interface
- Example shown is a 3 micron thick GDC layer

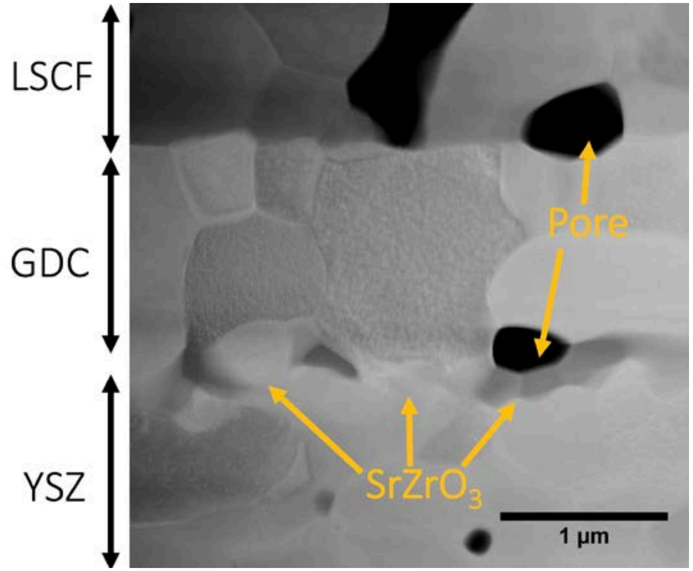




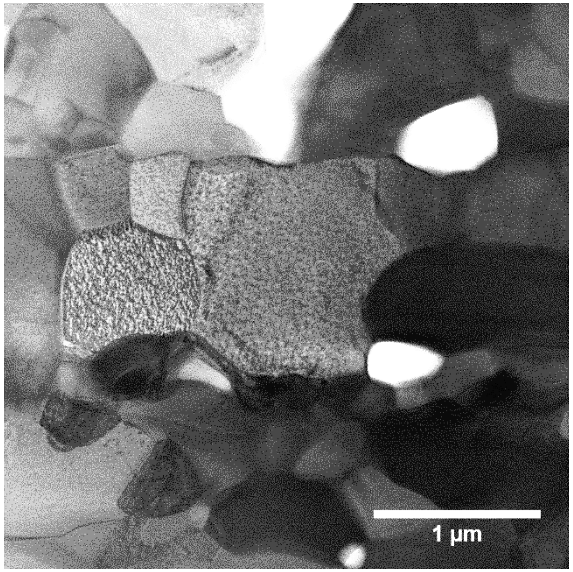
Transmission Electron Microscopy

- Above results show limited Sr at GDC/YSZ interface for 1.5 micron, 1200 C case
- TEM with energy dispersive x-ray spectroscopy (EDS) used to explore at higher resolution

HAADF – Z contrast

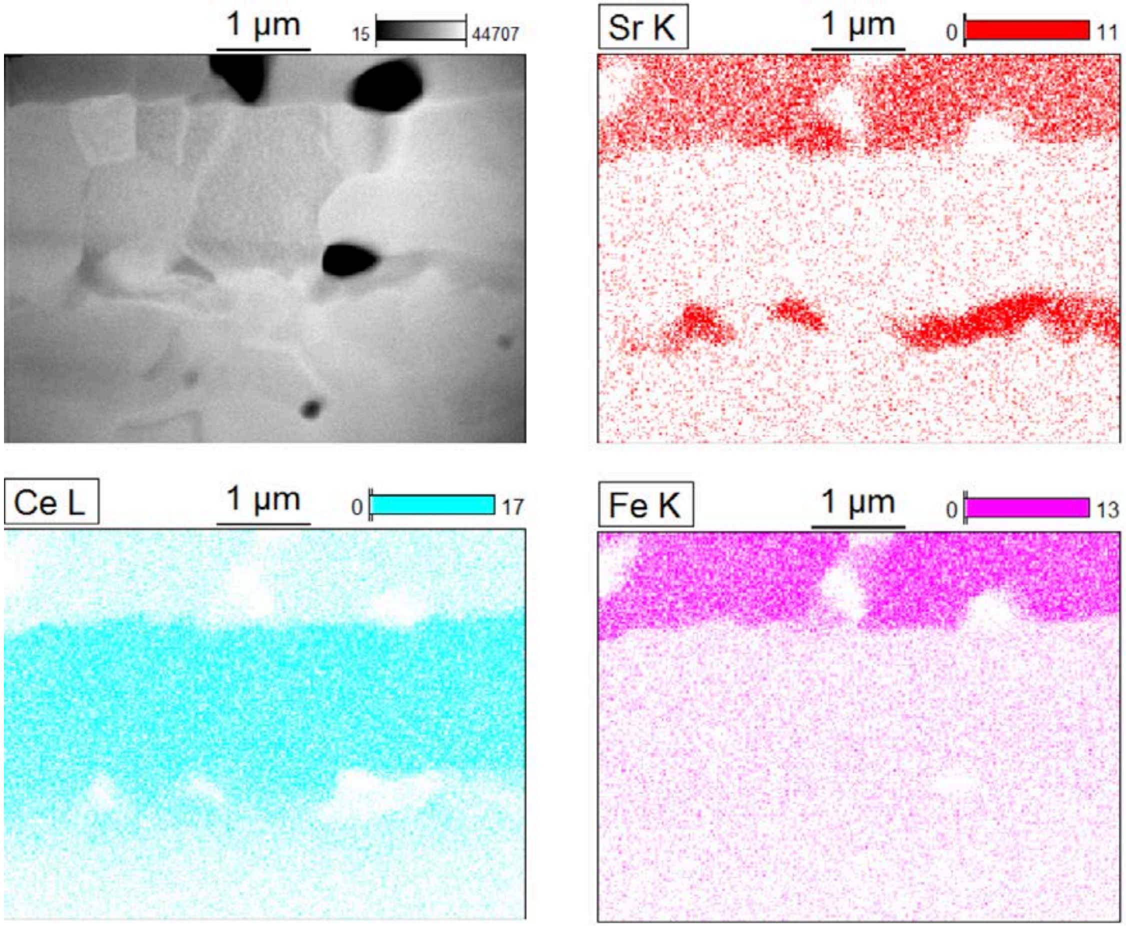


Bright field

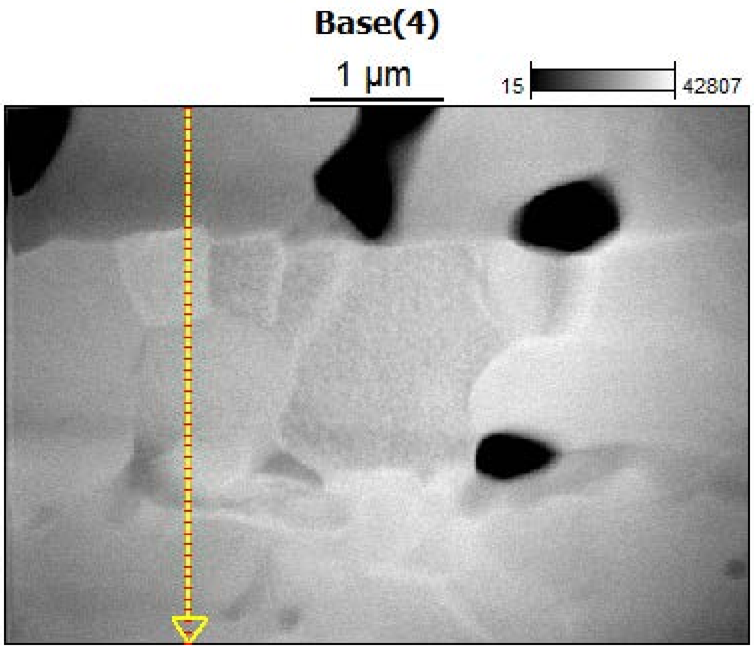


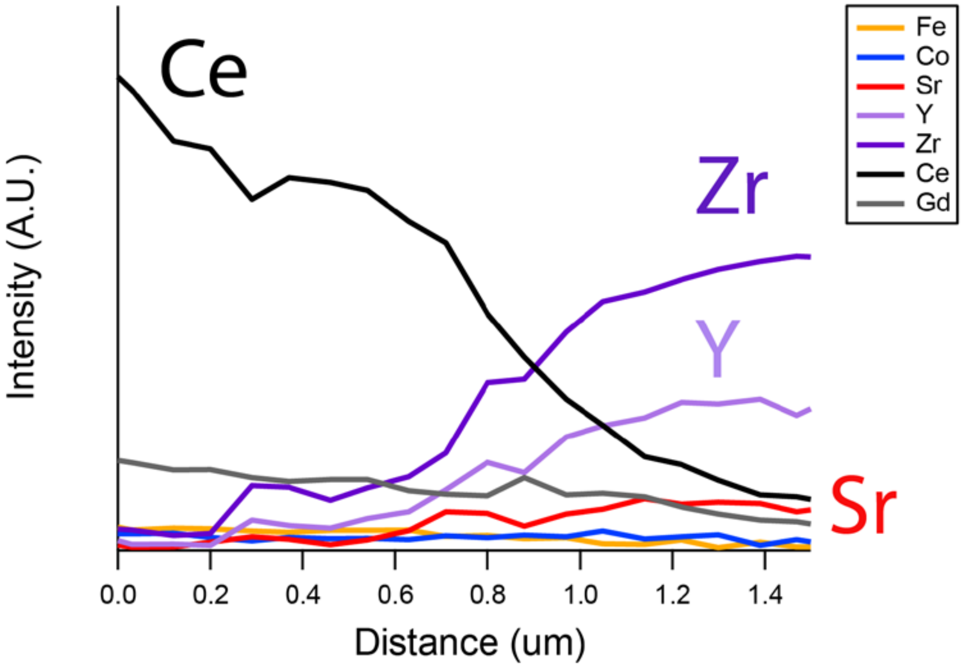
TEM-EDS

- $SrZrO_3$ detected in selected areas



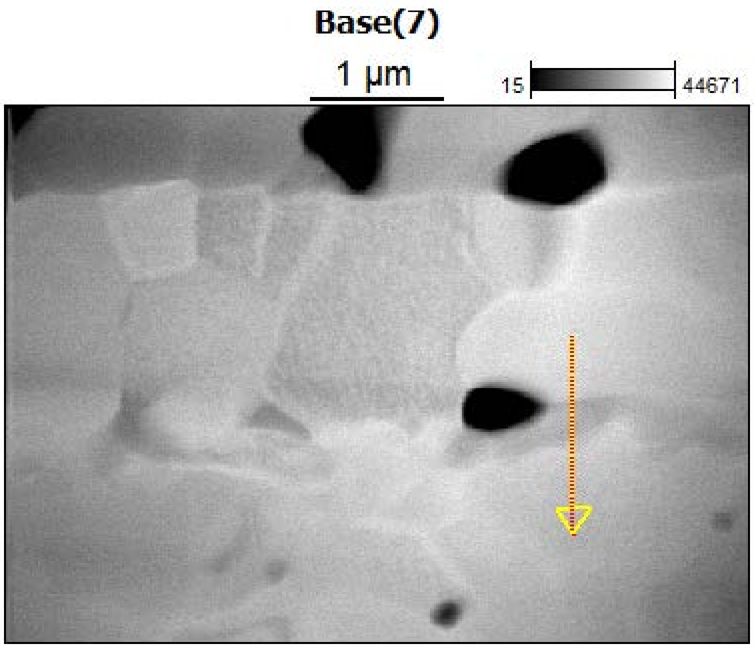
EDS Line Scan #1

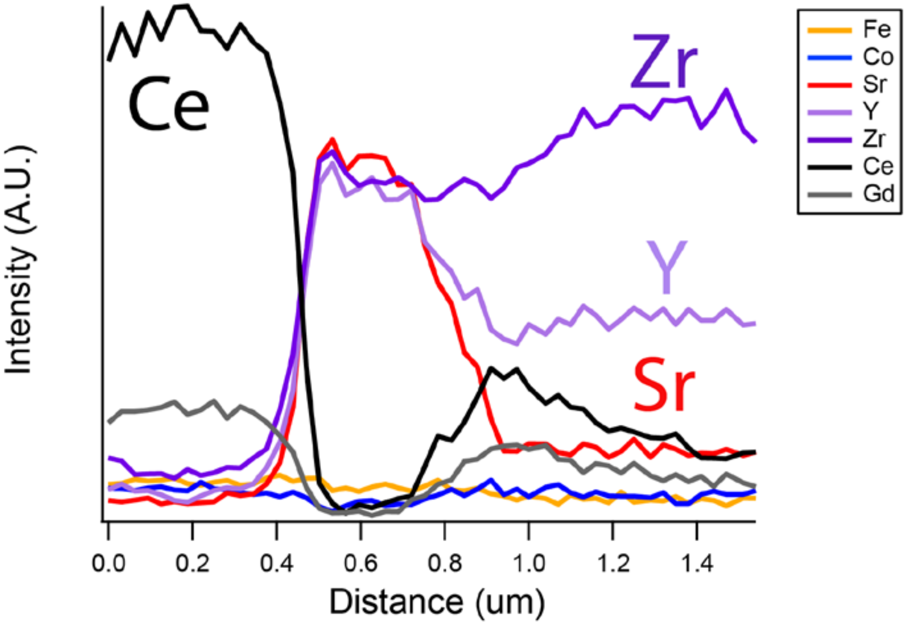




- No SrZrO3 detected at void-free location

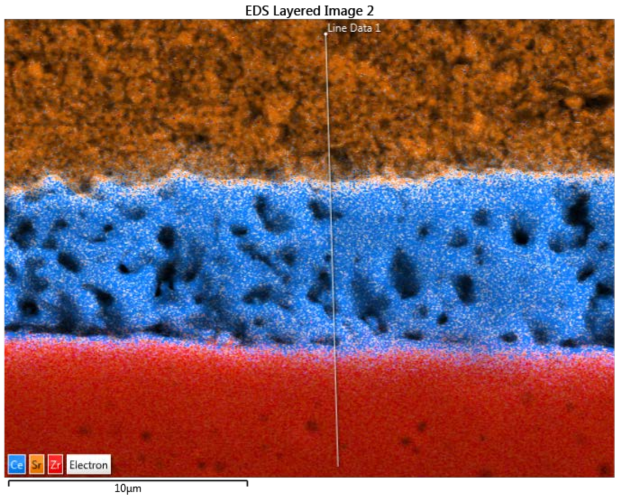
EDS Line Scan – Cont'd



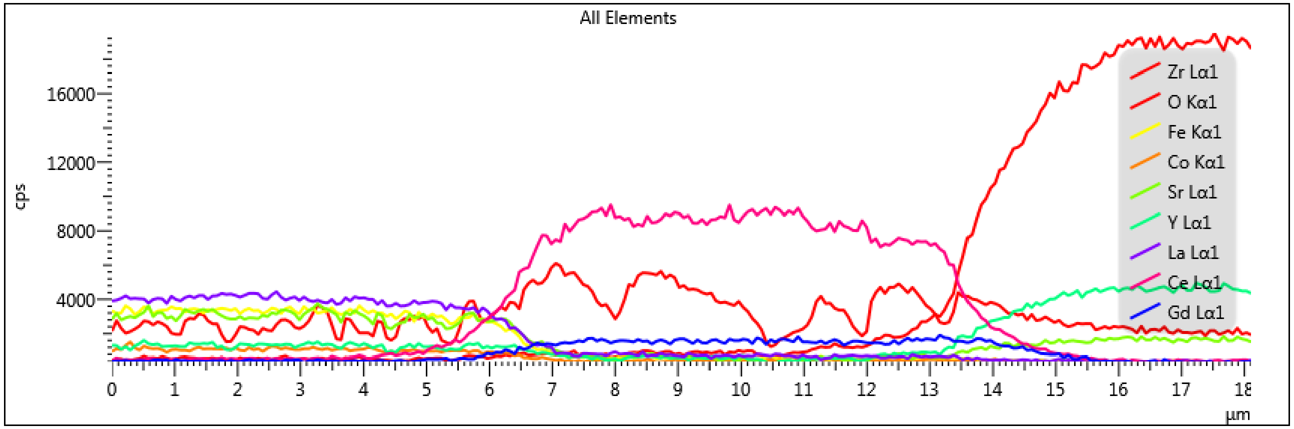


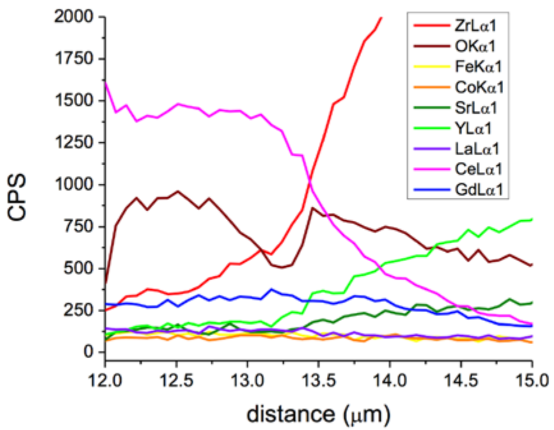
- Thick $SrZrO_3$ layer detected near GDC void

Barrier Layers by WVU EPD LSCF Fired at 1000 C: SEM-EDS

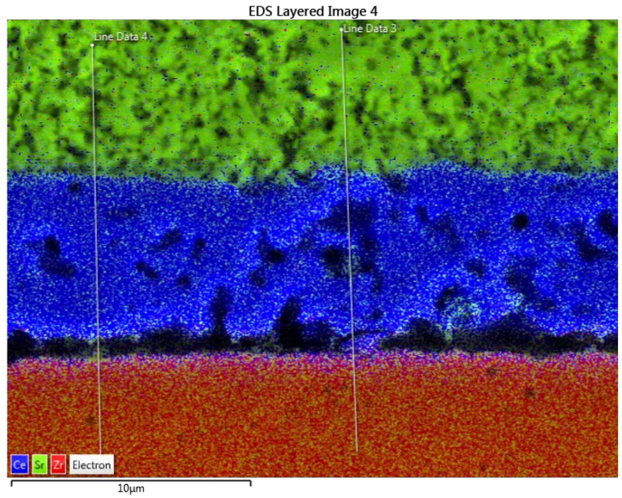


- Barrier layer shows limited porosity
- No evidence of Sr accumulation at GDC/YSZ interface
  - Apparent Sr in YSZ layer is an artifact of peak overlap (with Y)

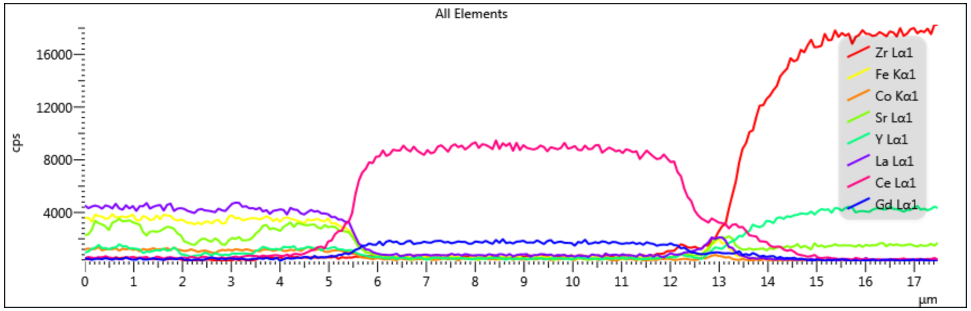


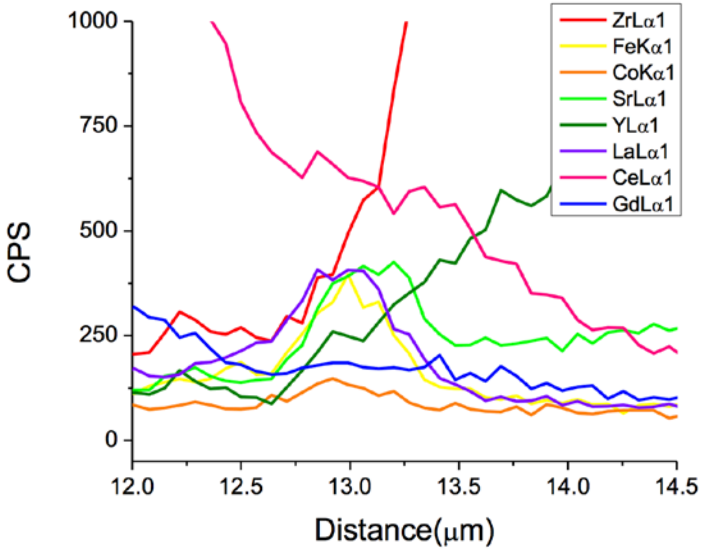


LSCF Fired at 1100 C: SEM-EDS

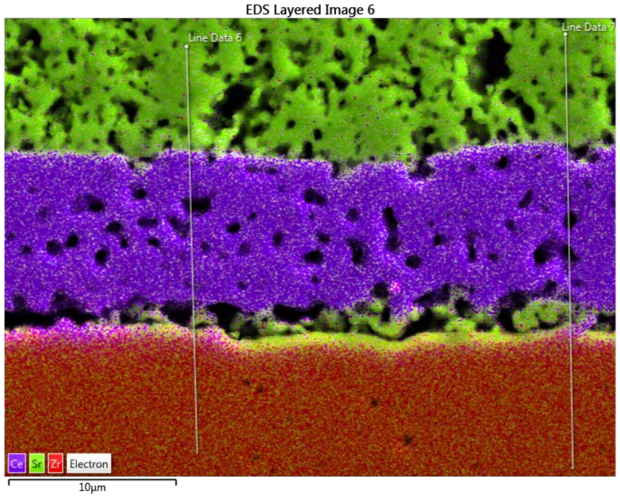


- Clear evidence of Sr segregation to GDC/YSZ interface
- La, Fe, and Co also appear to be present

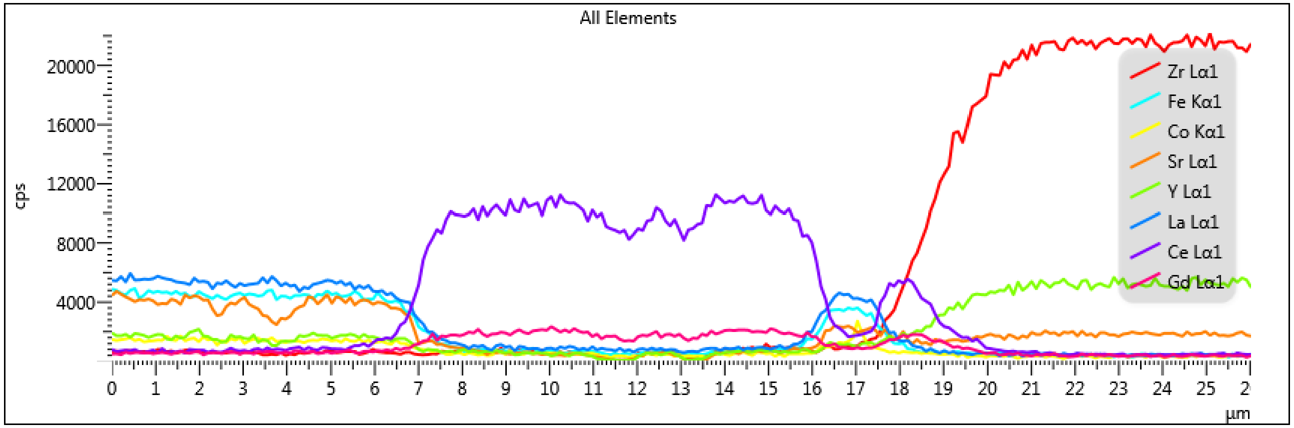


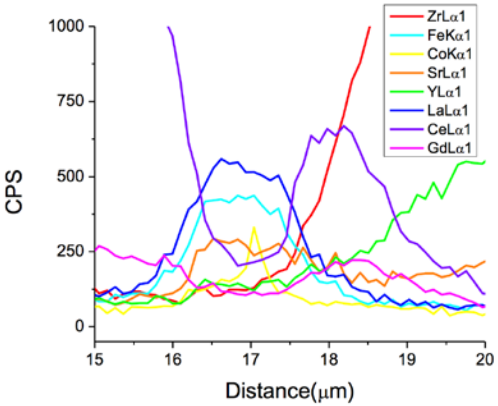


LSCF Fired at 1200 C



- More pronounced Sr segregation, along with La, Fe, and Co





Aim 2: Summary and Conclusions

- Reduced-temperature co-firing yields reasonably dense GDC barrier with minimal GDC/YSZ interdiffusion
  - Even a 1.5 micron co-fired barrier provides good protection for 1100C firing
  - 1200C causes considerable zirconate formation, unless a thicker GDC layer is used
  - Zirconate forms at defects/pores in the GDC layer
- WVU GDC layer shows greater porosity but is thicker
  - Effective as a barrier layer at 1000 C, but some zirconate formation at 1100 & 1200 C

Acknowledgement

- **NETL-SOFC Team**: Shailesh Vora, Heather Guedenfeld, Steve Markovich etc.

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Electrochemical Systems Research Center Forum
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US DOE NETL
Minfang Han,
Tsinghua University
Teruhisa Horita,
Japan AIST
Stefan Megel,
Fraunhofer-IKTS
James Swistock,
Penn Cara Energy
WestVirginiaUniversity.

SOFC Cathode Degradation

- Microstructural changes (loss effective TPB area)
  - Grain growth
  - Coarsening of the particles
  - Surface re-construction
- Strontium segregation related issues

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

- Chemical reaction with YSZ electrolyte.

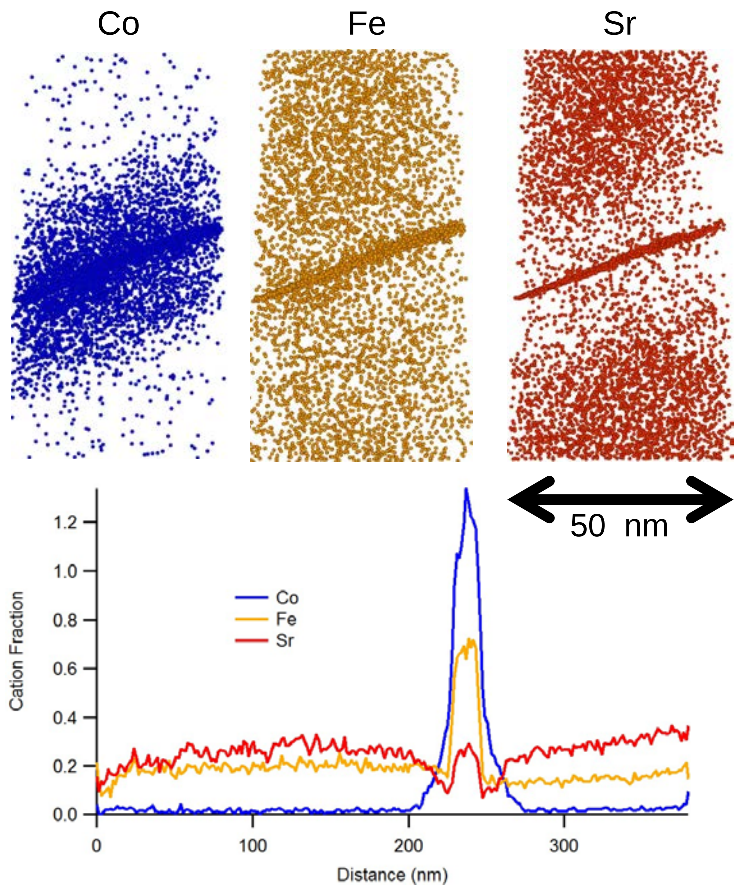
$$La_2O_3(s) + 2ZrO_2(s) \rightarrow La_2Zr_7O_3(s) \qquad SrO(s) + ZrO_2(s) \rightarrow SrZrO_3(s)$$

- Poisoning of the cathode (e.g. by CO_2, chromium species etc.)

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

$$2Cr_2O_3(s) + 3O_2(g) + 4H_2O(g) \rightarrow 4CrO_2(OH)_2(g)$$

Atom Probe Tomography



- §Sr:
  - Present at ~ 0.2% in YSZ/GDC
  - Higher concentration at boundary
  - Depleted around boundary
- §Co
  - present only near boundary
- § Fe:
  - Used as sintering aid at 0.2%
  - Strongly segregated at boundary