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

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Background - 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**

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

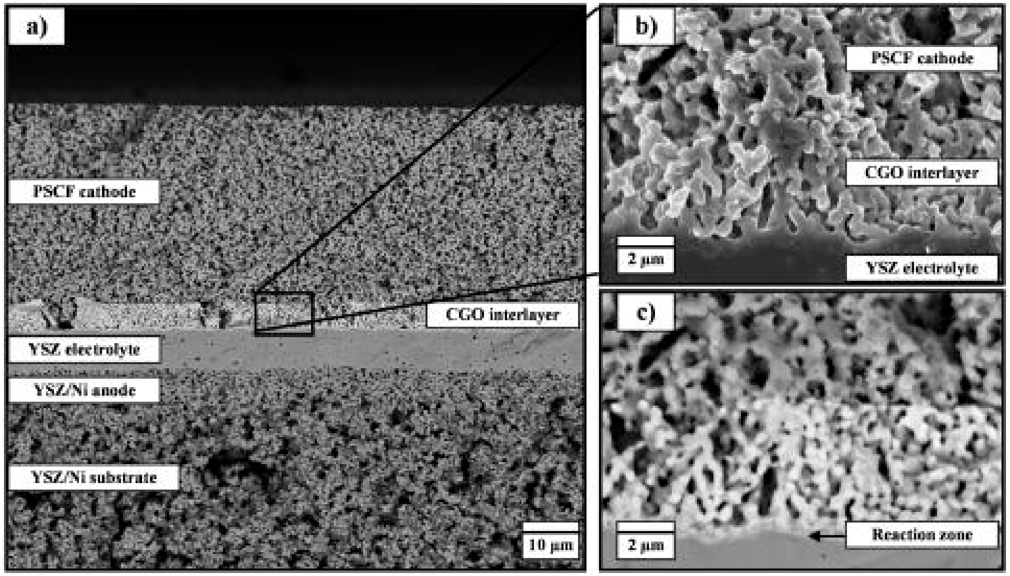
- Poisoning of the cathode (e.g. by CO_2, chromium species etc.)

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

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

SOFC Cathode Barrier Layers

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



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

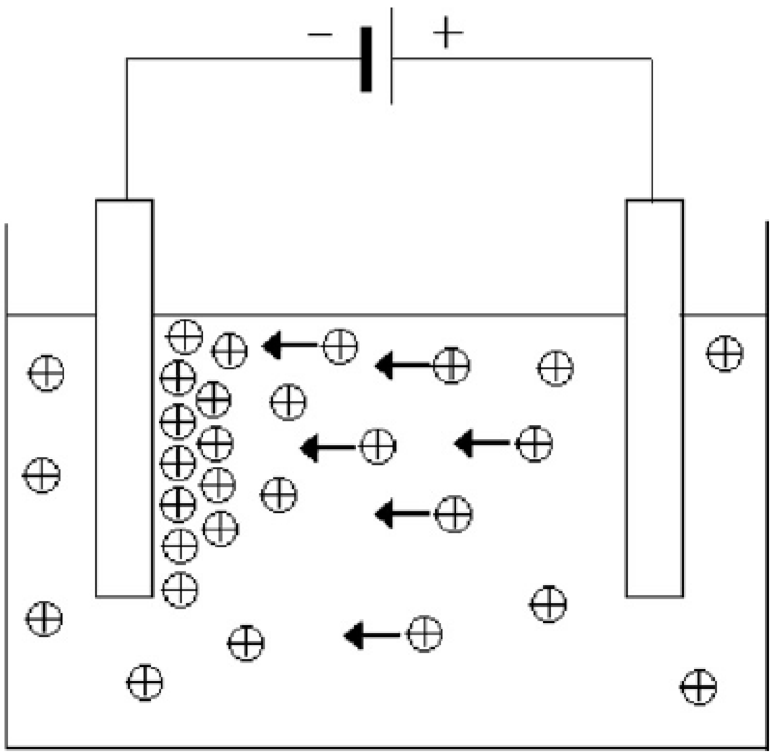
Major Technical Challenges

- Suspension stability
- Non-conductive YSZ substrate
- Non-shrinking pre-sintered YSZ substrate

AIM 1 – EPD Coating of GDC on Non-shrinking YSZ

- Prepare stable suspensions
- Develop conductive substrates
- DC EPD
  - Deposition kinetics
  - Deposition mechanisms
  - Substrate conductivity effects
- AC EPD
  - Deposition mechanisms
  - Effect of duty cycles
  - Effect of voltages

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

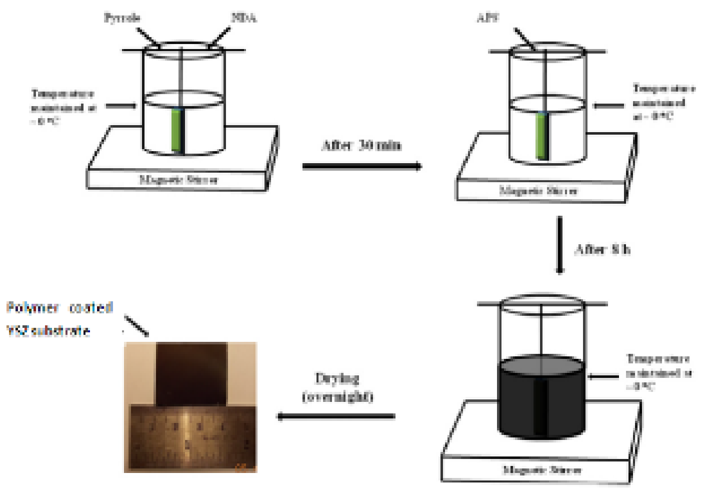
- GDC Particles are positively charged (absorbed H+)

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

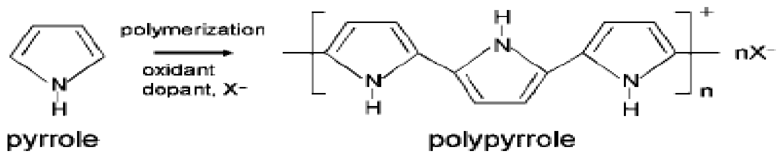
In-situ formation of conductive substrate

- In-situ synthesis of polypyrrole
- Easy and commercial

(a)



Schematic of polypyrrole synthesis process

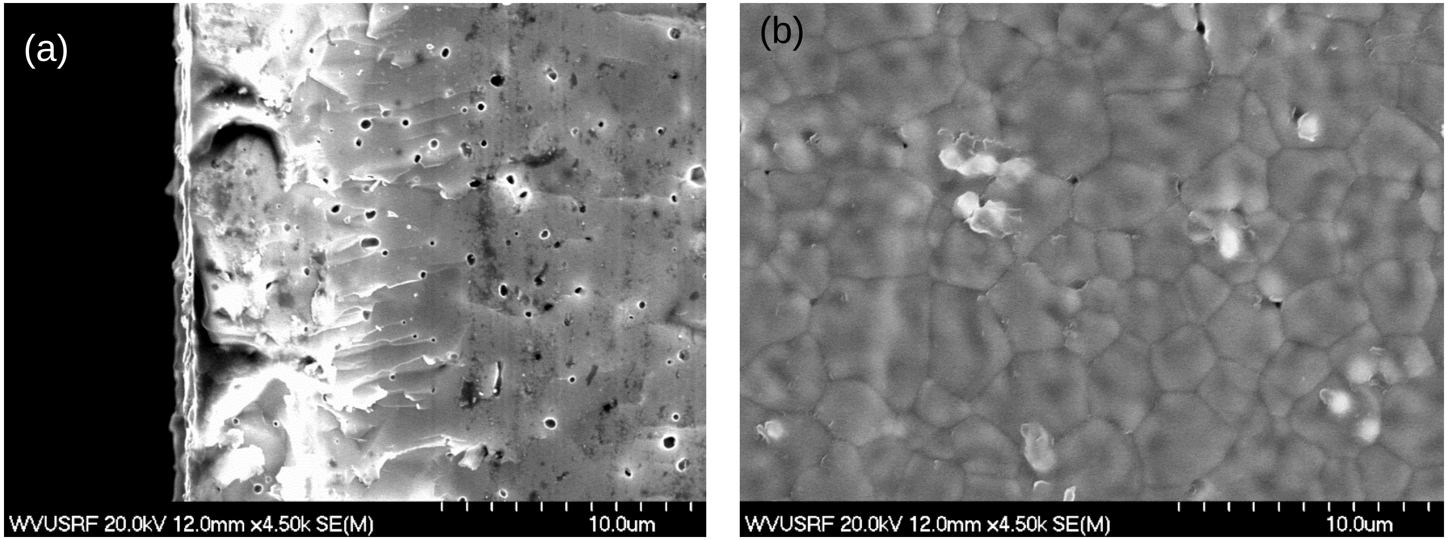


NDA: 2-6-naphthalene-difulfonic acid disodium salt

APS: ammonium peroxydisulfate

In-situ formation of conductive substrate

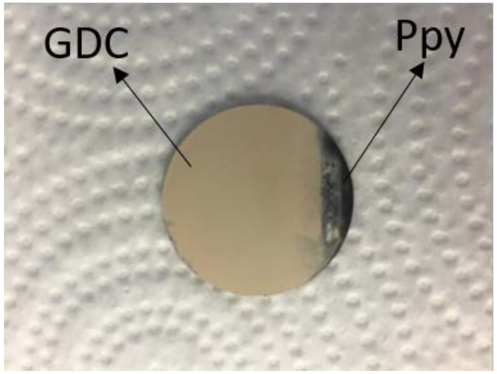
- Uniform layer of Ppy
- Thickness less than 1um
- Conductivity is about 9 S/cm



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

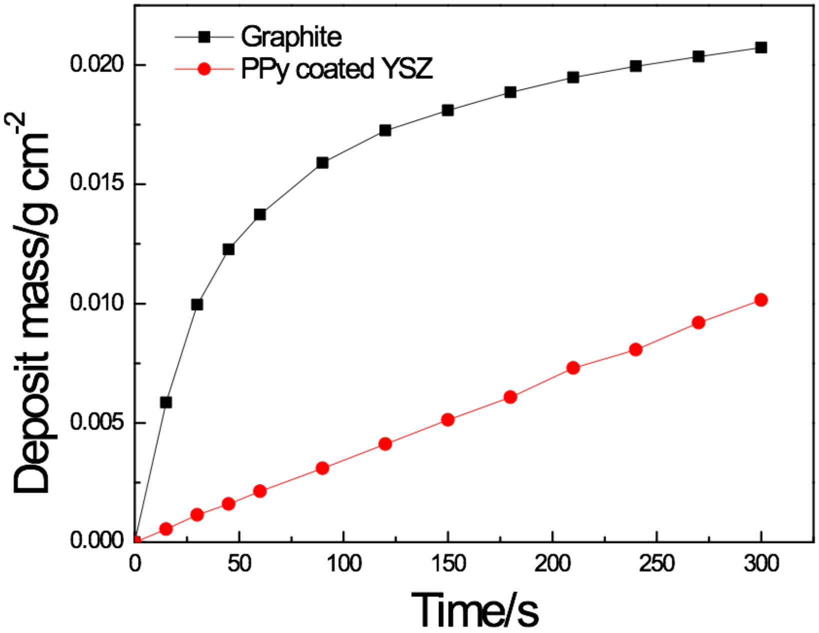
DC deposition kinetics

- The conductivity of PPy is sufficient to carry out EPD experiment
- Deposition rate on PPy is slower than that on graphite



Distance: 1cm

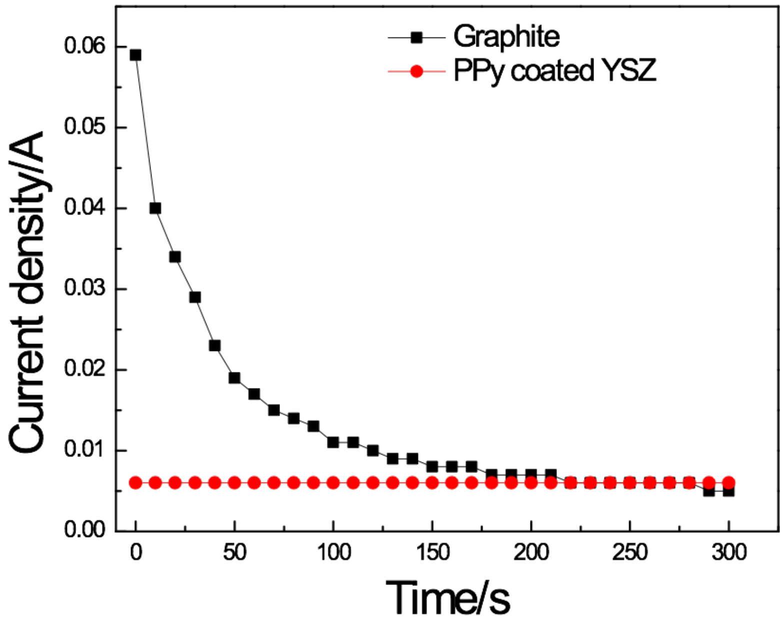
Voltage: 60V



Deposit mass per unit area as a function of time under constant voltage (60 V) by using different cathode

DC deposition kinetics

- The rate determining step of the deposition on PPy is the charge transfer step
- An H^+ ion accumulation zone exists near PPy coated YSZ with a decrease of pH



Current as a function of time under constant voltage (60 V) using different cathode

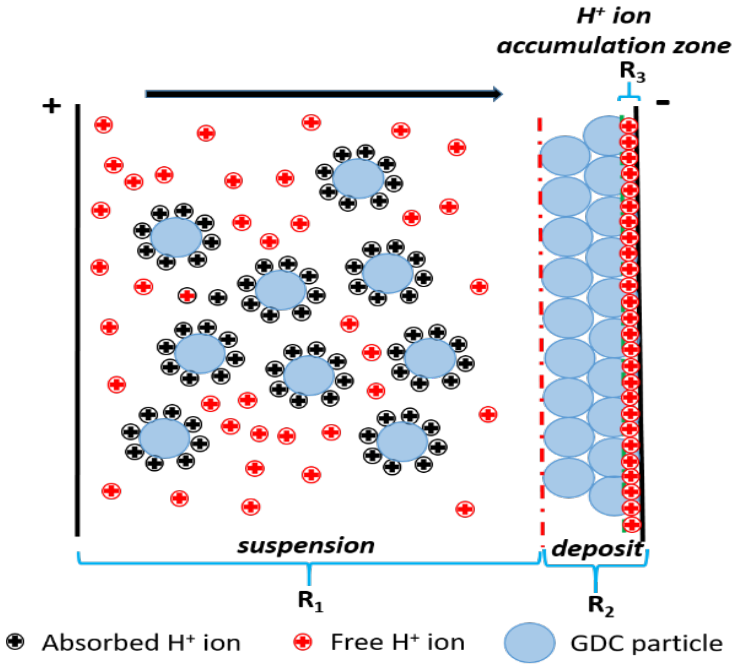
The reduction of H^+ at the cathode:

$$H^+_{x=\infty} \xrightarrow{transport\ process} H^+_{x=0} \xrightarrow{charge\ transfer} \frac{1}{2} H_2$$

Initial pH: 3.87

pH near cathode after 10s: 2.09 < 3.87

Increasing resistance



Resistance distribution in the EPD cell using PPy coated YSZ as the cathode

$$R = U/I = R_1 + R_2 + R_3 = \rho_s (L - \delta_1)/S + \rho_d \delta_1 / S + a\delta_2$$

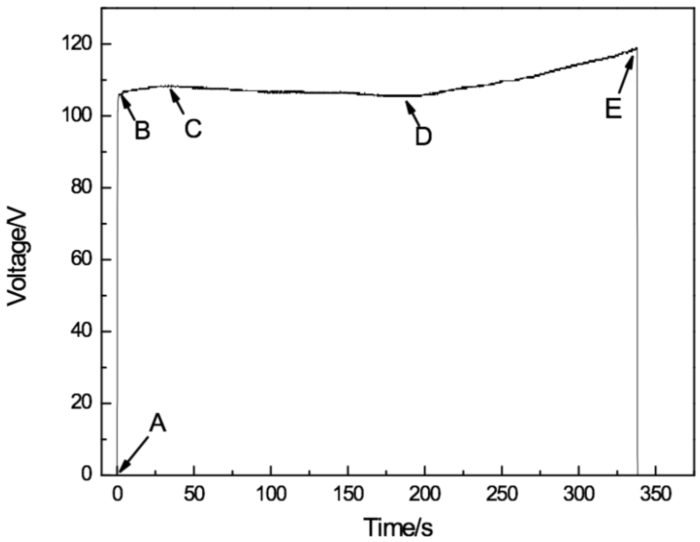
$$= \rho_s L/S + \delta_1 (\boldsymbol{\rho_d} - \boldsymbol{\rho_s}) / \mathbf{S} + k\delta_2 = \mathbf{C_1 + C_2\delta_1 + k\delta_2}$$

R is the total resistance, Ω; ρ_s, ρ_d are the resistivity of suspension and the deposit, respectively, Ω cm, $\rho_s < \rho_d$; L is the distance between two electrodes, cm; δ_1 and δ_2 are the thickness of deposit and the ion accumulation zone near cathode, respectively, cm; S is the area of the electrode, cm^2; k, a constant, means k Ω for 1 cm ion depletion zone

δ_1 increases with time

Increasing resistance

- The thickness of the ion accumulation zone increases at the beginning, then decreases, finally the ion accumulation zone is replaced by an ion depletion zone
- The main resistance is from the ion depletion/accumulation zone



Variation of voltage as a function of time under **constant current** (0.016 A) using PPy coated YSZ as the cathode

A-B: Charging of the double layer

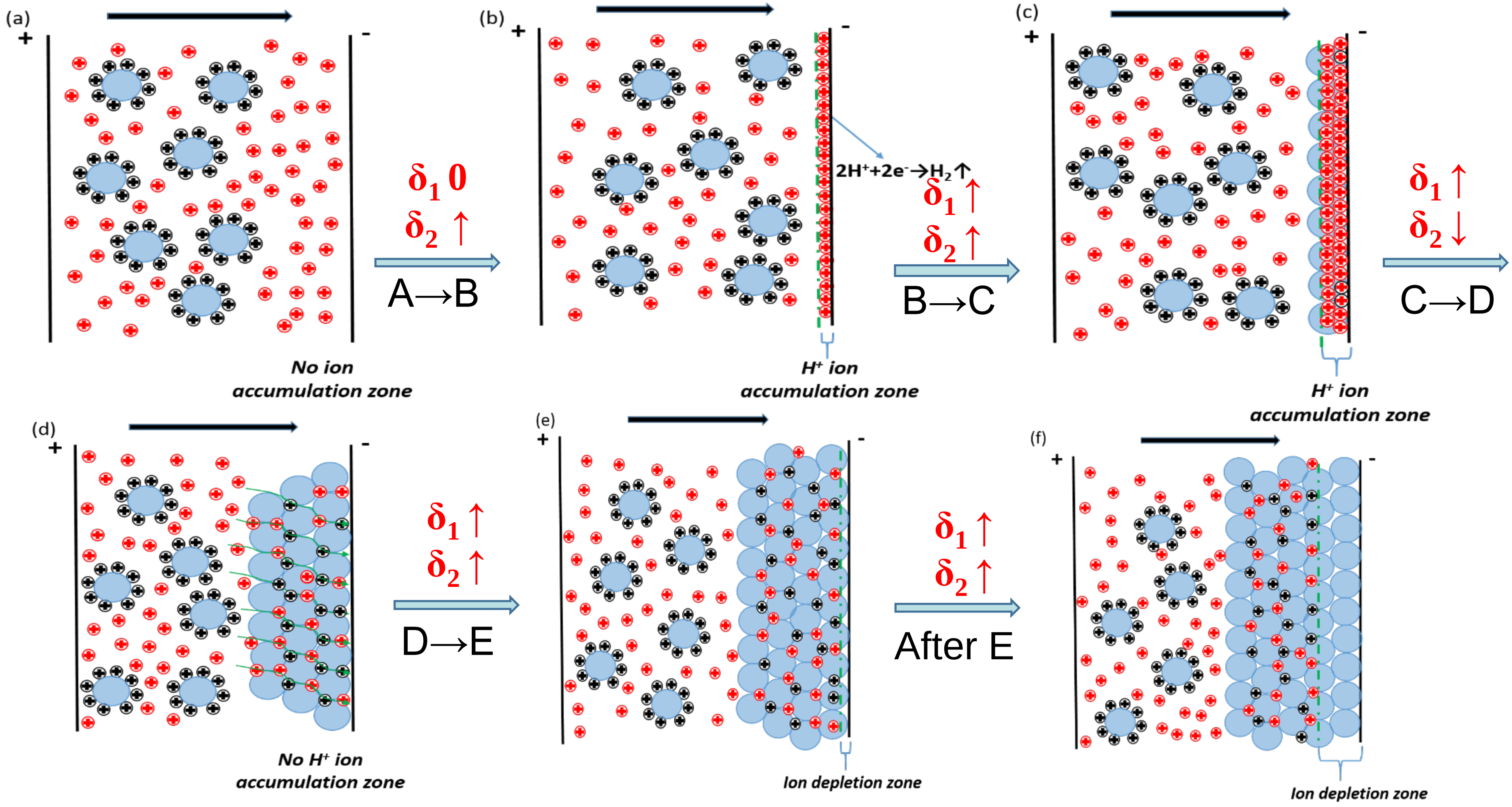
B-C: Ion accumulation zone (thickness increases)

C-D: Ion accumulation zone (thickness decreases)

Point D: minimum value (transition point)

D-E: Ion depletion zone

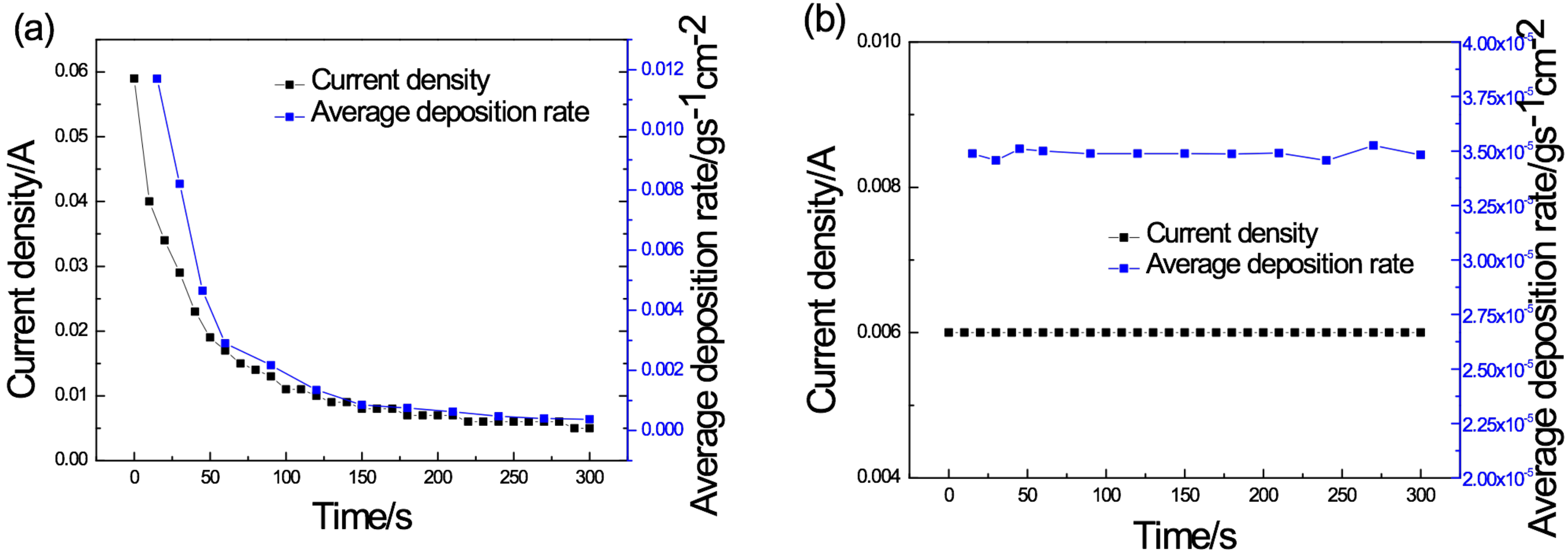
Increasing resistance



Schematic of EPD process on PPy coated YSZ

DC EPD efficiency

- Deposition rate increases the current density regardless of the conductivity of cathode



Average deposition rate and current as a function of time under constant voltage (60 V) when using (a) graphite and (b) PPy coated YSZ as the cathode

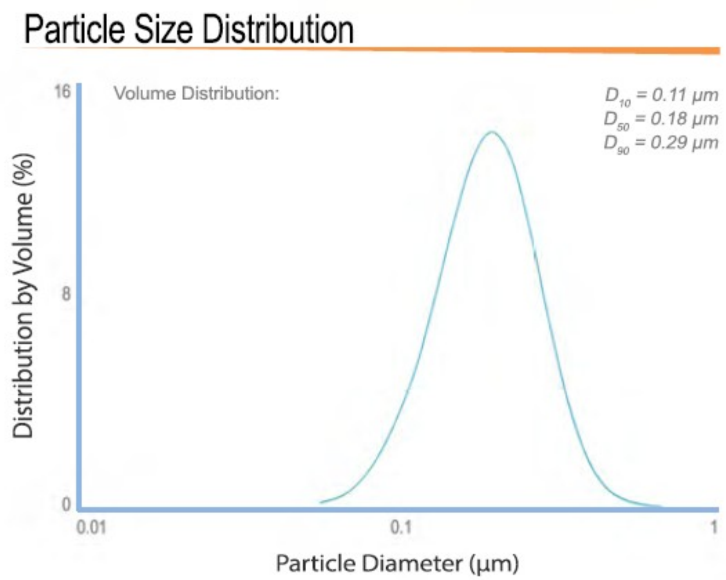
DC EPD efficiency

$$\frac{m}{m_0} Ze = Q_{ab} \qquad Q = \int I dt$$

Anode: $2H_2O - 4e^- \rightarrow 4H^+ + O_2$

Cathode: $2H^+ + 2e^- \rightarrow H_2$
or $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

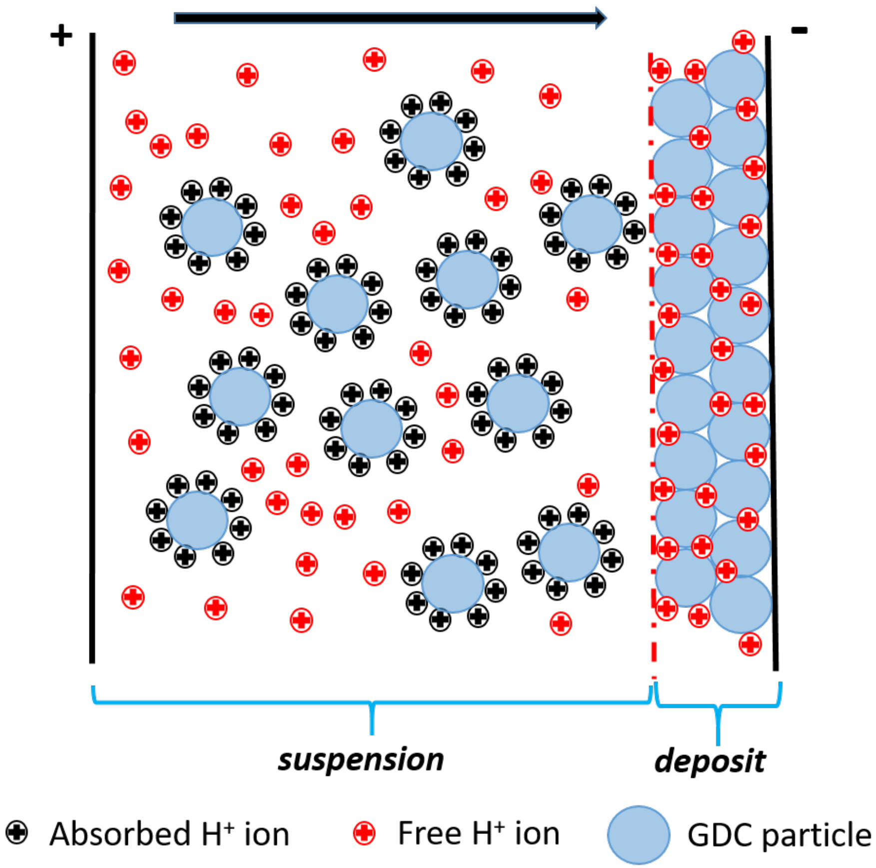
$$\frac{m}{m_0} Ze = Q_{ab} = f Q_T$$



m is the deposit mass, g; m_0 is the average mass of a single particle, g; Z is the valence of a charged particle which is proportional to the zeta potential; e is the electronic charge, C; Q_{ab} is the charge quantity transferred resulted from the reduction of H^+ ions which desorbed from the particles, named as "absorbed H^+ ions"; Q_T is the total charge amount transferred during EPD process, C; **f, EPD efficiency**, is the percentage of total charge transferred resulted from the reduction of absorbed H^+ ions, with a range from 0 to 1.

DC EPD efficiency

- f is in the range from 0 to 0.5



Schematic of EPD process

(1) The primary charge carriers are free ions.

(2) Free H^+ ions moves faster than absorbed H^+ ions.

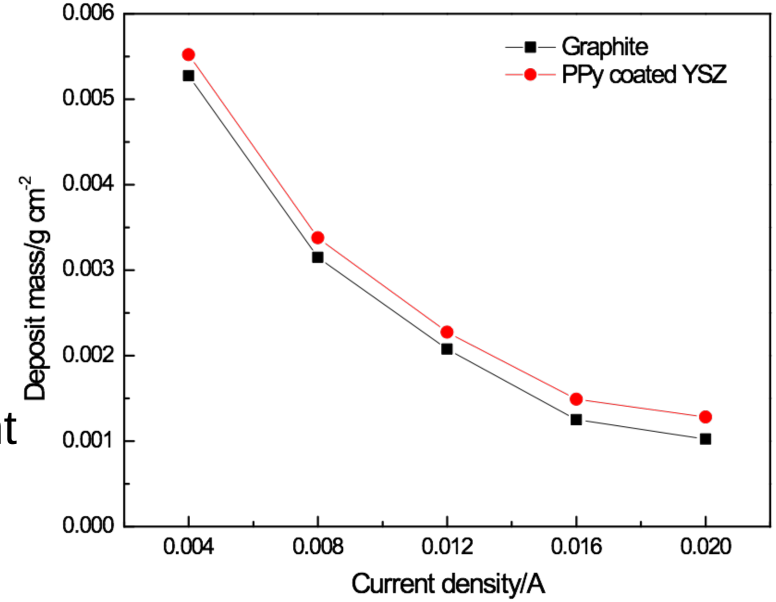
DC EPD efficiency

- f decreases with the increase of voltage or current density
- f decreases with the increase of the conductivity of cathode due to hydrogen evolution

Same Q_T

Different I

Constant current



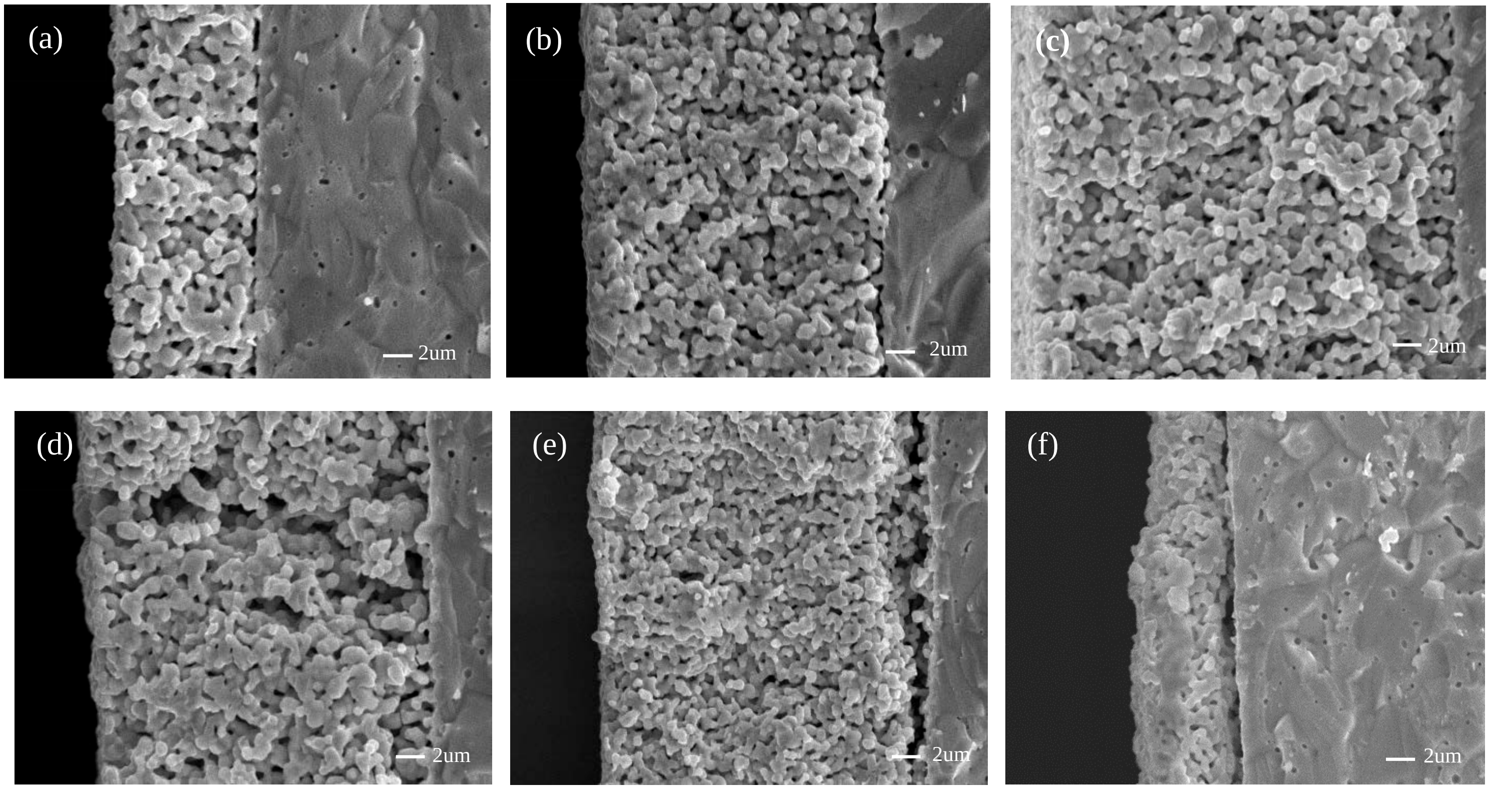
Cathode: $2H^+ + 2e^- \rightarrow H_2$

or $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Deposit mass per area as a function of current density under constant current and same total charges by using PPy coated YSZ and graphite as the cathode

Optimal Voltage

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



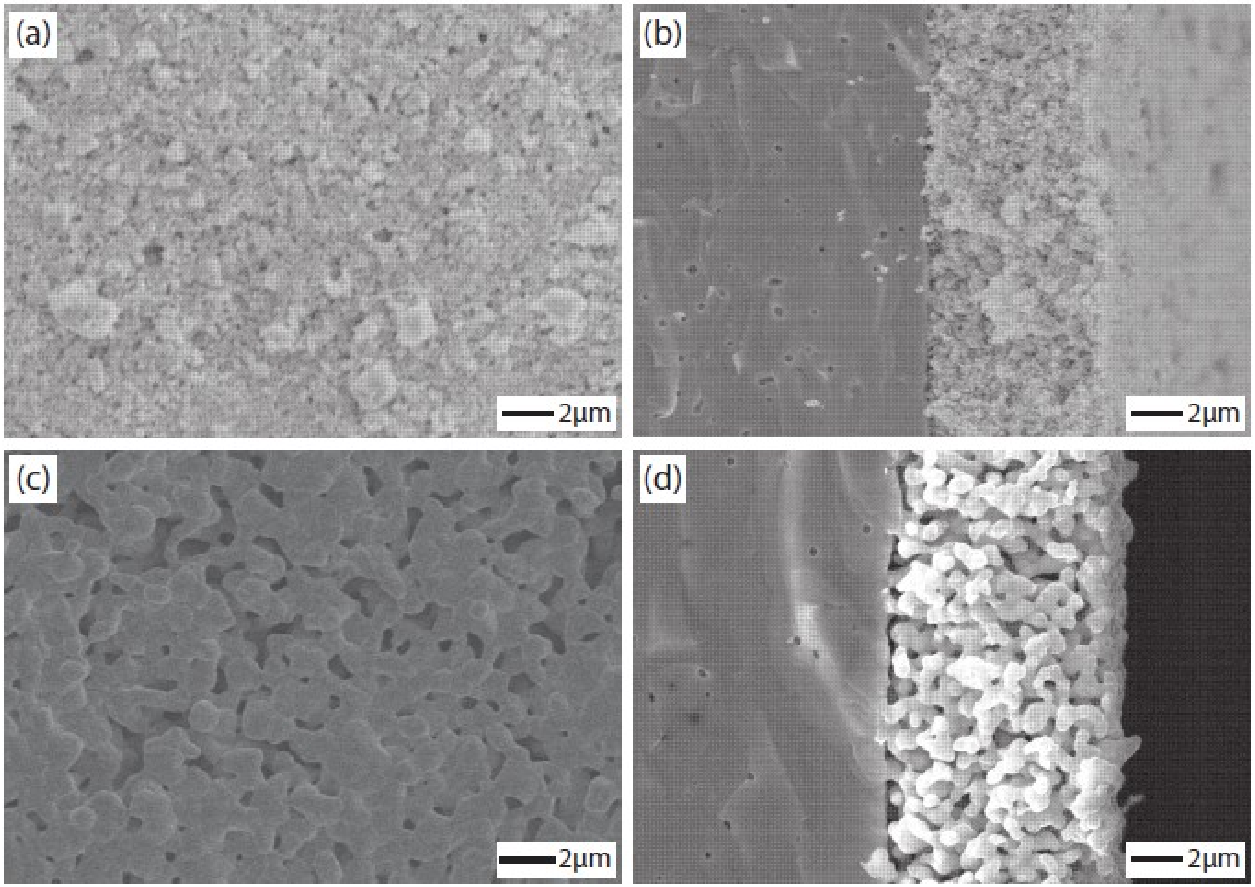
Cross-sectional morphology of the deposit for 10 mins as a function of applied voltage (a) 60V, (b) 80V, (c) 100V, (d) 120V, (e) 140V and (f) 160V

Morphology of GDC layer

- a uniform layer of GDC can be formed by EPD

Before sintering

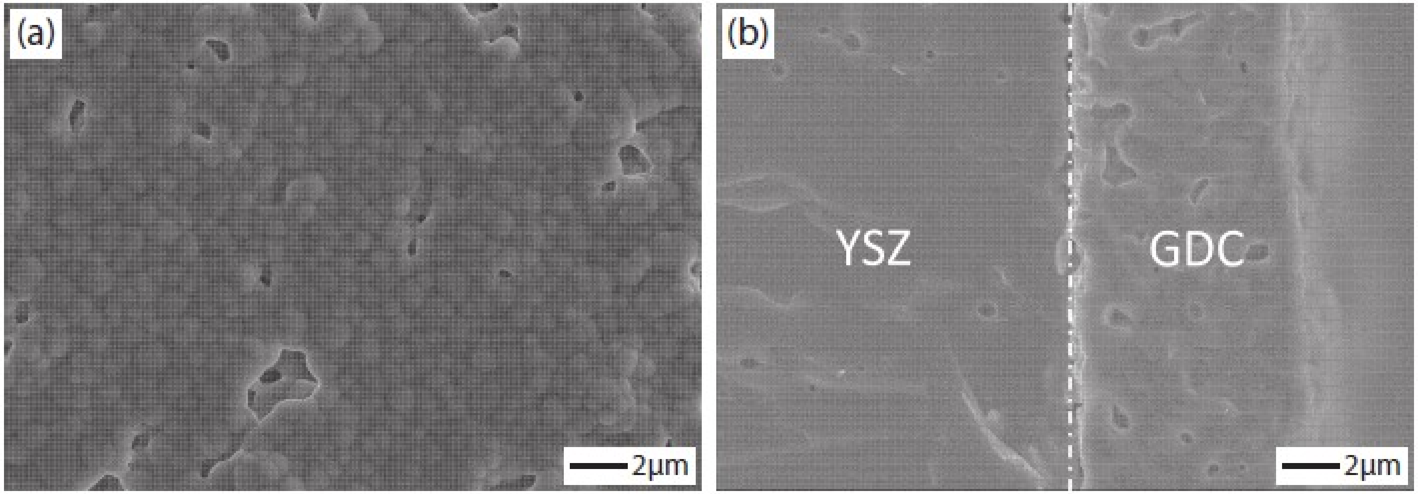
After sintering



SEM top view of (a) green, (b) sintered GDC surface, and cross-sectional view of (c) green, (b) sintered GDC layer.

Morphology of GDC layer

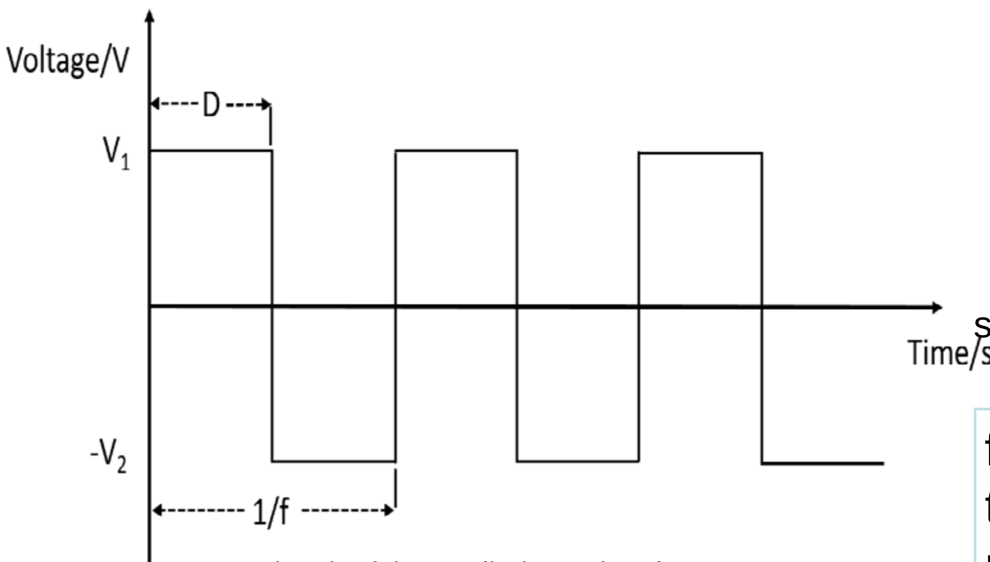
- Iron oxide can be used as sintering aid to improve the density of GDC
- Dense GDC layer can be obtained at 1300^oC by DC-EPD



Morphology of GDC with 2 mol% Fe_2O_3 formed by EPD after sintering at 1300 ^oC

AC-EPD

To minimize the bubble evolution during coating, to decrease the densification temperature, AC signal was used to avoid the electrochemical reaction.

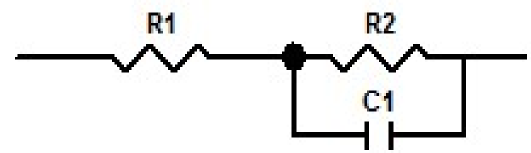


Sketch of the applied AC signal

V1, V2: 0-100V

D(duty cycle): 0-100%

f: 0~400 kHz



Equivalent circuit of electric double layer

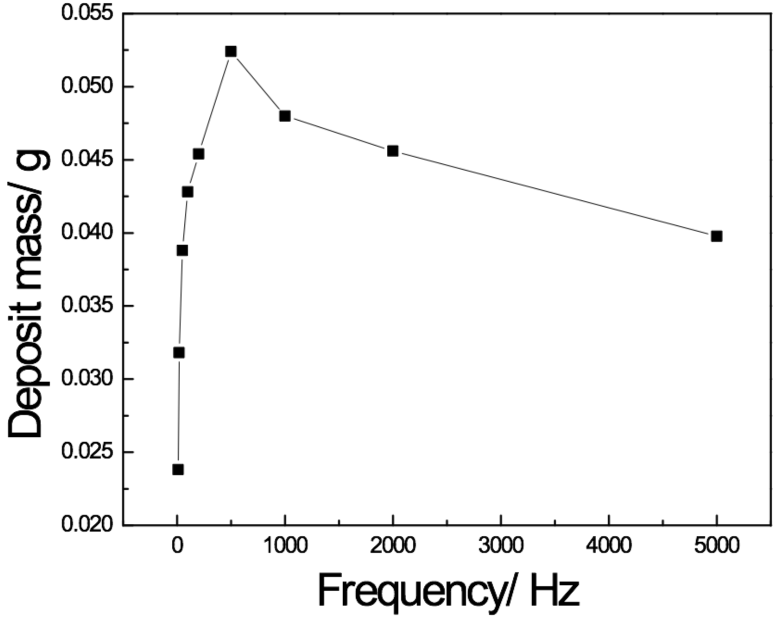
R_1 is the resistance of the suspension; R_2 is the resistance to faradaic current at the electrode surface; C_1 is the differential capacity of the double layer

f sufficiently high → No current flows through R_2 → No electrochemical reaction or bubble evolution

Very low f → No current flows through C_1 → electrochemical reaction occurs

AC frequency effect

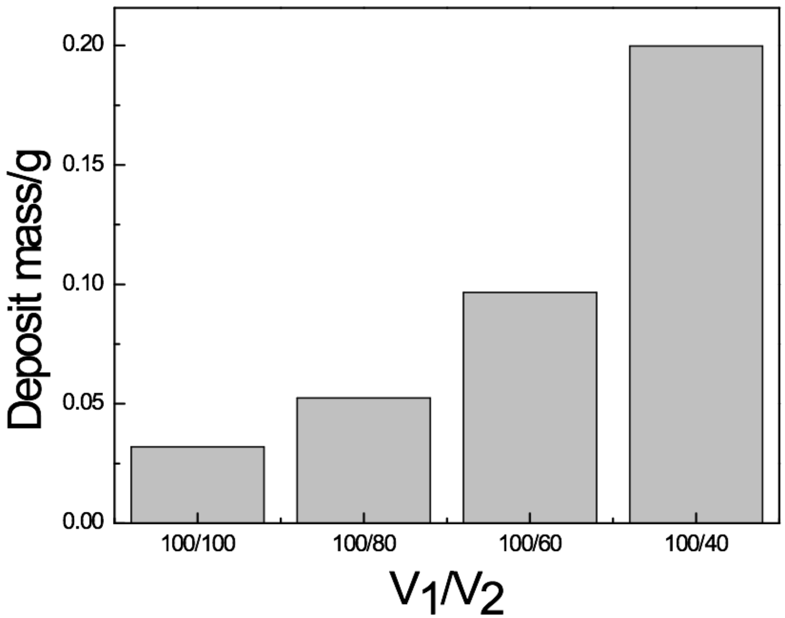
- The deposition rate increases when the frequency increases from 10 Hz to 500 Hz, while decreases when further increases the frequency to 5000 Hz



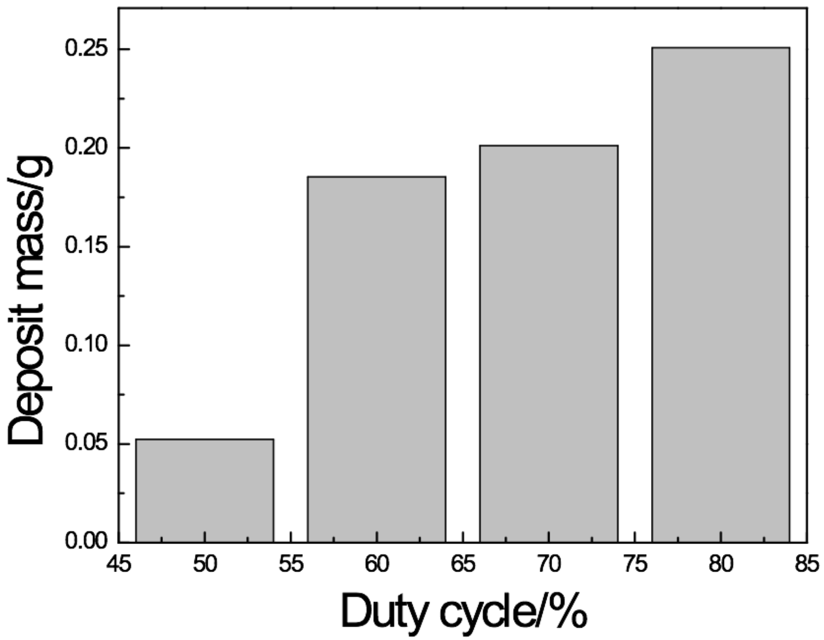
Deposit mass as a function of frequency of the AC power supply with a fixed **V_1/V_2 ratio of 100/80** and a fixed **duty cycle of 50%** when using graphite as the cathode.

AC parameters

- The deposition rate increases with the increase of voltage ratio
- The deposition rate increases with the increase of duty cycle



Deposit mass as a function of voltage ratio of the AC power supply with a fixed **duty cycle of 50%** and a fixed **frequency of 500 Hz**.



Deposit mass as a function of duty cycle of the AC power supply with a fixed V_1/V_2 **voltage ratio of 100/80** and a fixed **frequency of 500 Hz** when using graphite as the cathode.

AC-EPD mechanism--desorption

- The deposit mass decreases a little when reversing the DC direction because of the bubble evolution derived from the electrolysis of water.
- Desorption of absorbed charge carrier is irreversible.

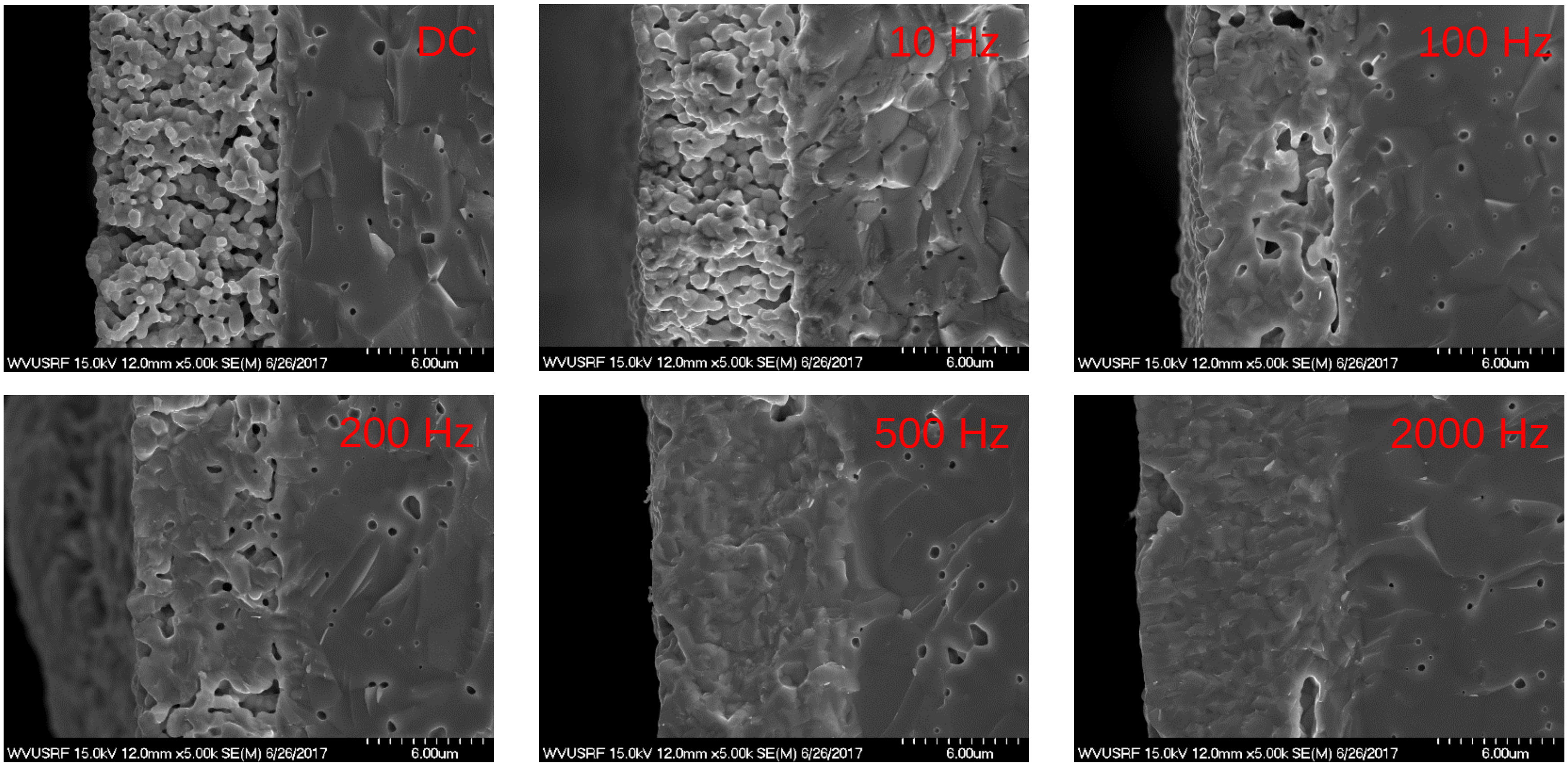
Deposit mass before and after the reversed EPD under different conditions

Reversed EPD parameters	Deposit mass before reversed EPD/g	Deposit mass after reversed EPD/g	Decrease of deposit mass/g	Ratio of decrease/%
80 V, 5 min	0.1395	0.1344	**0.0051**	**3.6559**
80 V, 8 min	0.1385	0.1336	**0.0049**	**3.5379**
80 V, 10 min	0.1489	0.1437	**0.0052**	**3.4923**
80 V, 12.5 min	0.1481	0.1431	**0.005**	**3.3761**
50 V, 8 min	0.1621	0.1577	**0.0044**	**2.7144**
100 V, 8 min	0.1555	0.1505	**0.005**	**3.2154**

Note: the graphite along with preformed deposit and a new graphite plate were used as anode and cathode, respectively. An DC was used to supply electric field.

AC frequency effect

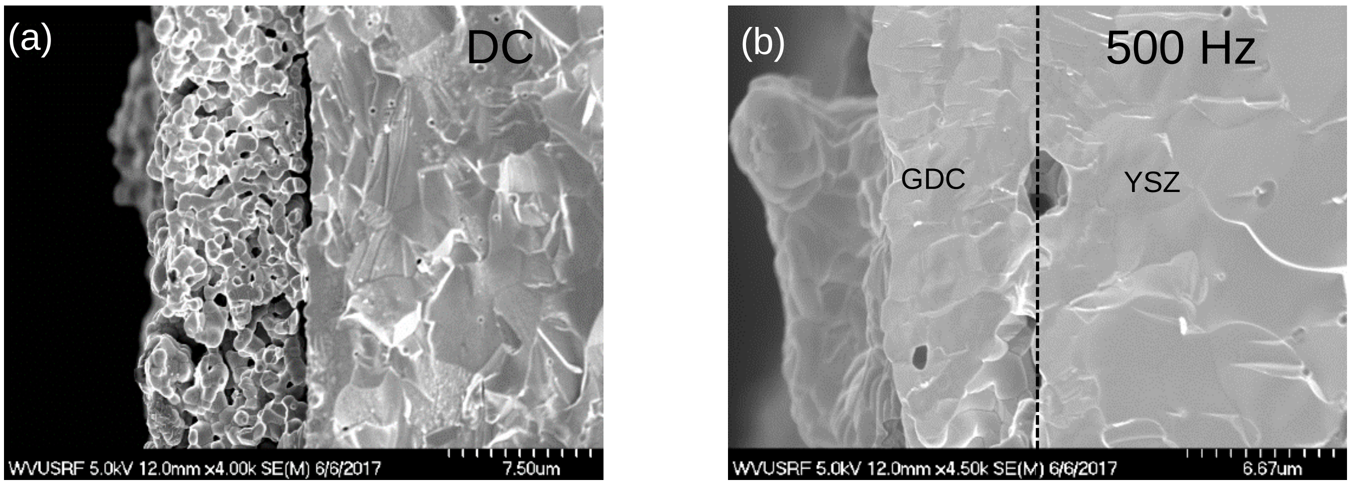
- The density of the GDC layer increases when the frequency increases from 10 Hz to 500 Hz. Further increase of frequency does not increase the density any more



Corresponding cross-sectional morphology of GDC layer formed on PPy coated YSZ after sintering at 1350^{o}C for 4h.

Coating Morphology

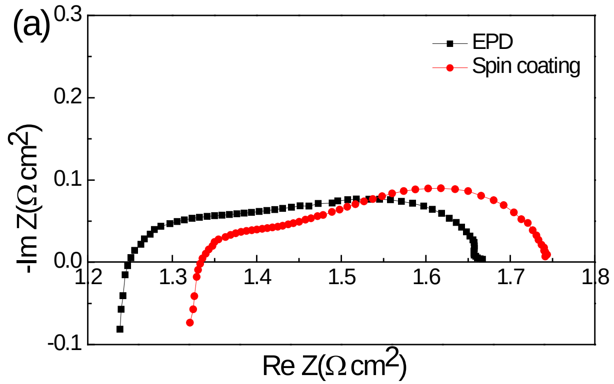
- Dense GDC layer on non-shrinking substrate can be obtained by AC-EPD + sintering @ 1250°C



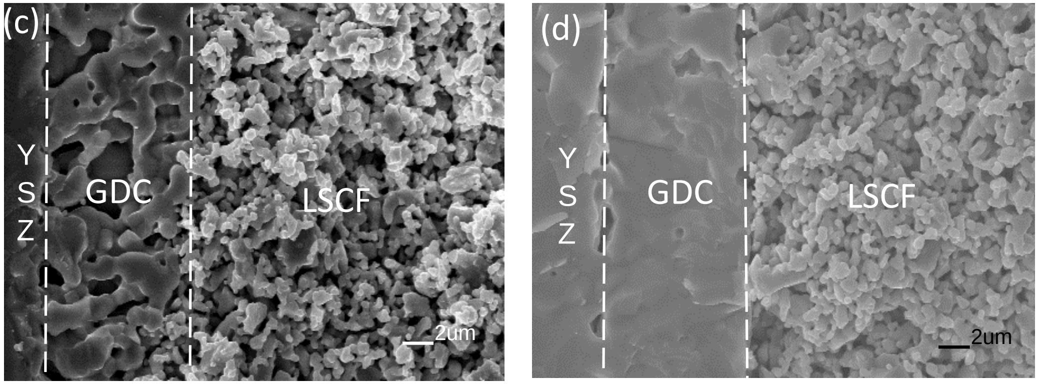
Morphology of GDC layer on Ppy coated YSZ formed by (a) DC-EPD and (b) AC-EPD after sintering at 1250°C

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 2: Characterization of Diffusions in GDC Barrier Layers in SOFCs

§Co-fired GDC/YSZ bi-layer electrolytes

–Cross-sectional SEM-EDS, TEM-EDS

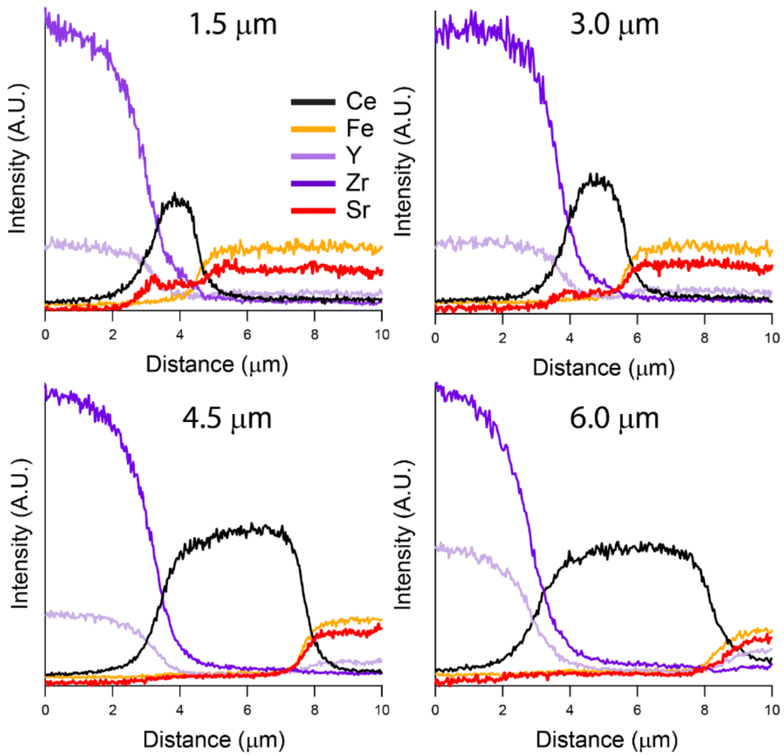
–Atom-probe tomography

§GDC barriers made by WVU

–Cross-sectional SEM-EDS

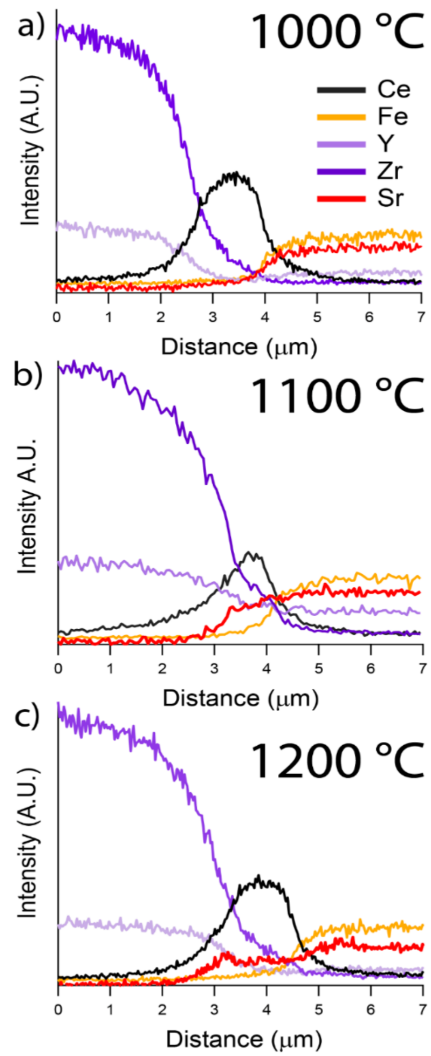
Effect of GDC Barrier Layer Thickness

- Averaged elemental intensities from SEM-EDS maps versus distance perpendicular to the LSCF/GDC/YSZ interfaces.
- The LSCF cathodes were fired at 1200 ° C
- GDC thicknesses were 1.5 μm, 3.0 μm, 4.5 μm, or 6.0 μm
- Increased Sr intensity can be seen at the interface for 1.5 and 3.0 μm



Effect of LSCF Firing Temperature

- 1.5 micron thick GDC
- Sr segregation to YSZ/GDC interface detected for 1200 and 1100 C, not 1000 C



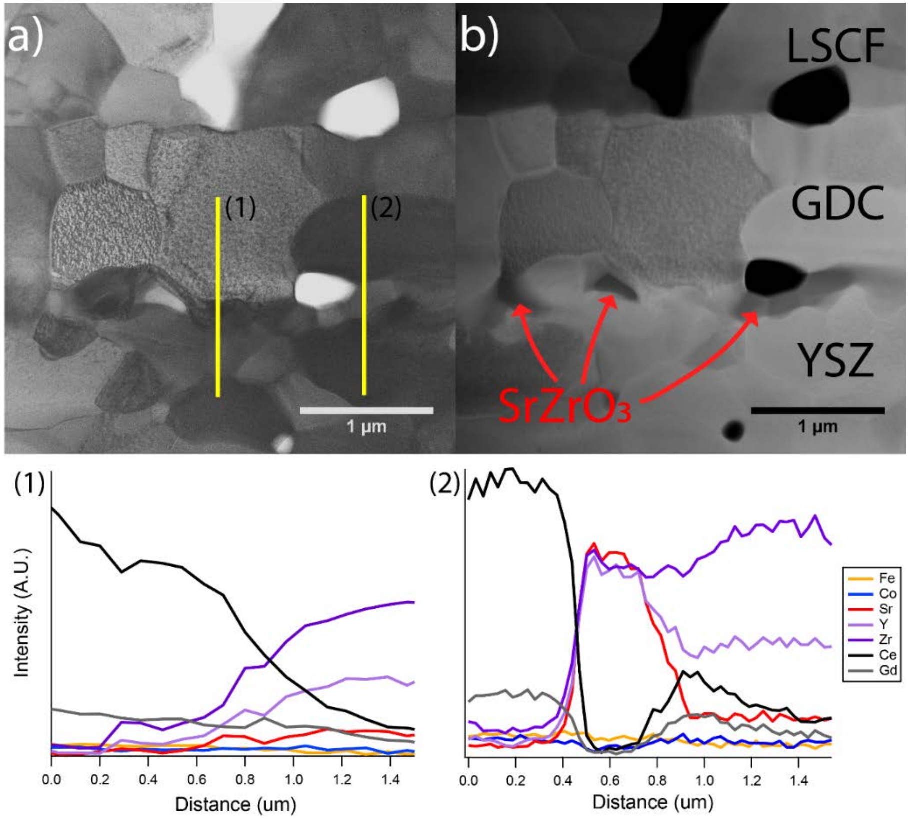
Summary of Sr Interfacial Amounts

- Integrated intensity of interfacial Sr from SEM-EDS data
- Tabulated versus firing temperature and GDC thickness

GDC thickness / Temp	1000 °C	1100 °C	1200 °C
6.0 μm	<0.1	< 0.1	<0.1
4.5 μm	<0.1	<0.1	<0.1
3.0 μm	<0.1	0.15	0.3
1.5 μm	<0.1	0.5	0.5

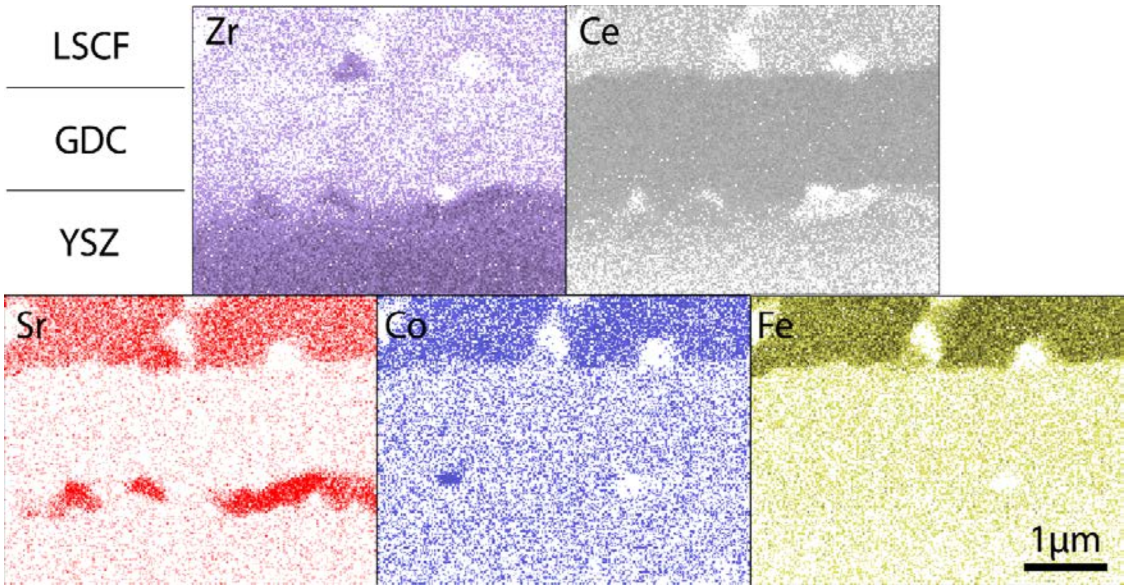
TEM-EDS

- Cross-sectional bright field (a) and HAADF (b) images
- From a 1.5 µm GDC electrolyte layer with LSCF fired at 1200 ^oC
- EDS line scans taken along the lines indicated
- Zirconate forms where Sr can transport across GDC pores and/or grain boundaries

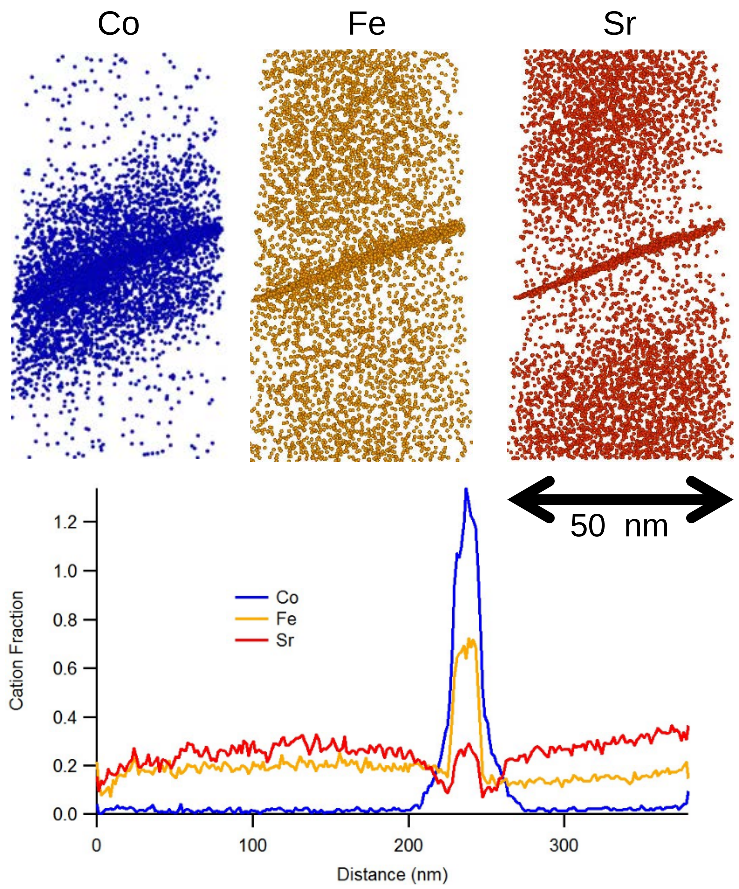


TEM-EDS

§ $SrZrO_3$ detected in selected areas of GDC/YSZ interface

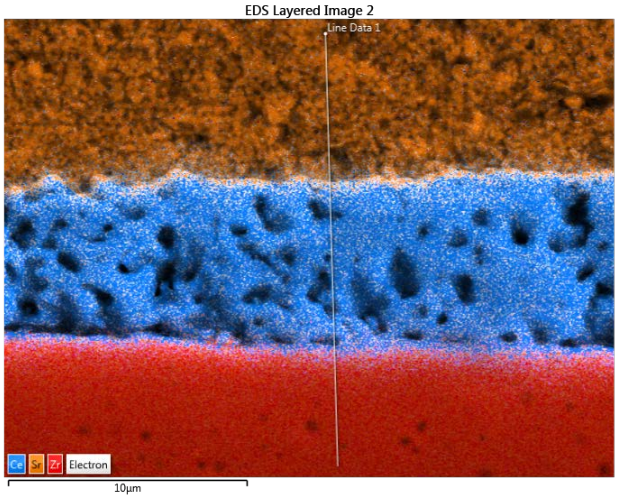


Atom Probe Tomography

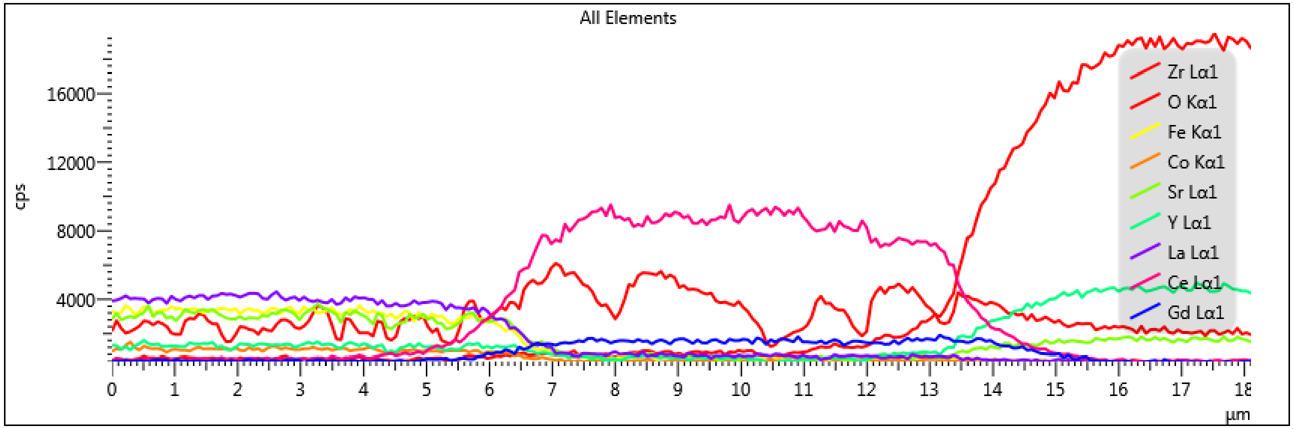


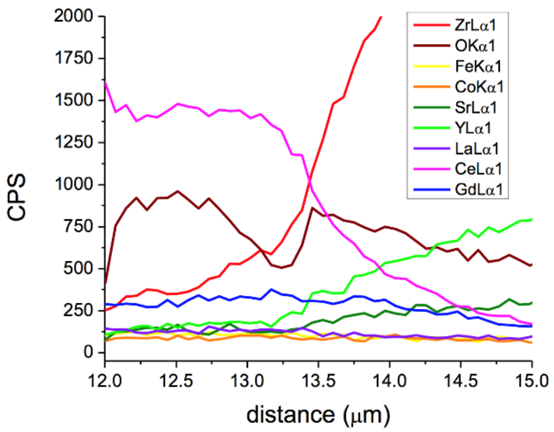
- Sr:
  - Present at ~ 0.2% in YSZ/GDC
  - Higher concentration at boundary
  - Depleted around boundary
- Co
  - present only near boundary
- Fe:
  - Used as sintering aid at 0.2%
  - Strongly segregated at boundary

Barrier layers by EPD (early)
LSCF Fired at 1000 C: SEM-EDS

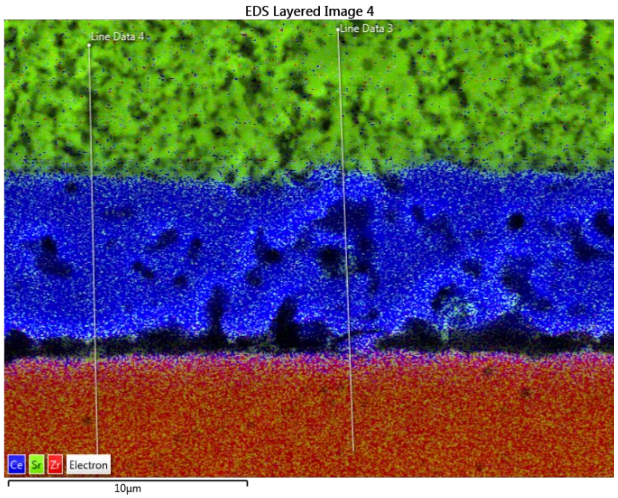


- Barrier layer shows limited porosity
- No evidence of Sr accumulation at GDC/YSZ interface
  - Apparent Sr in YSZ layer is an artifact of peak overlap (with Y)

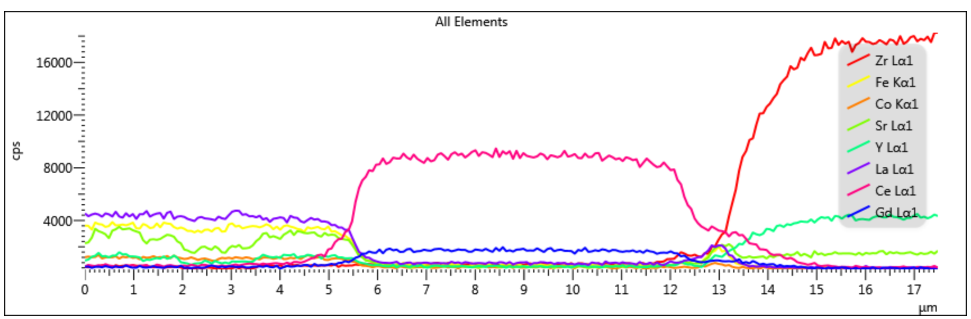


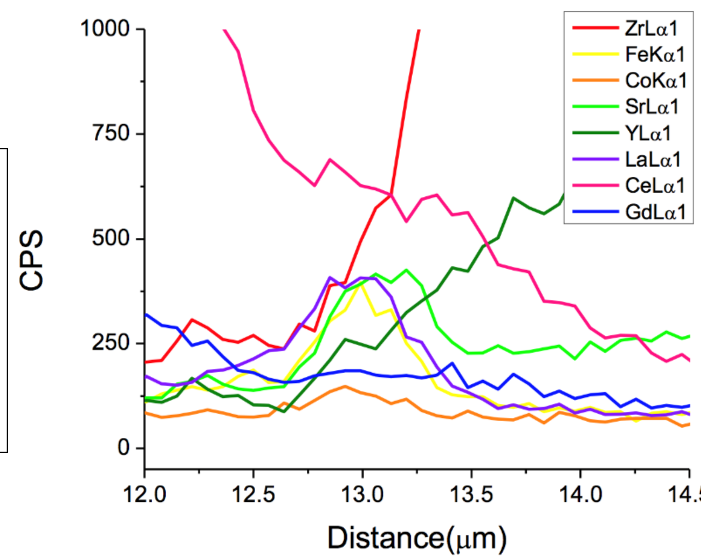


LSCF Fired at 1100 C: SEM-EDS



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





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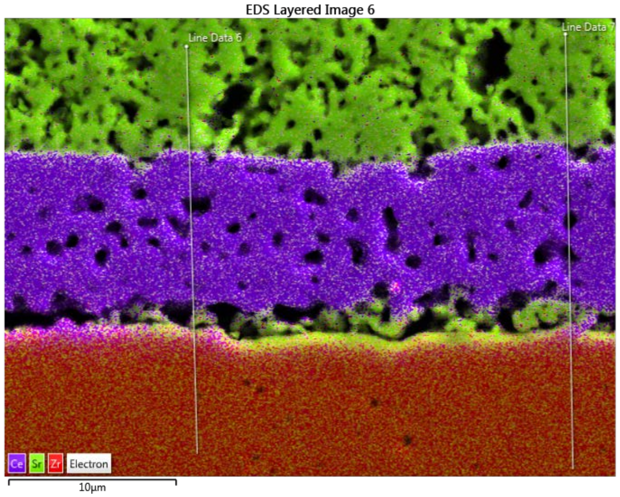
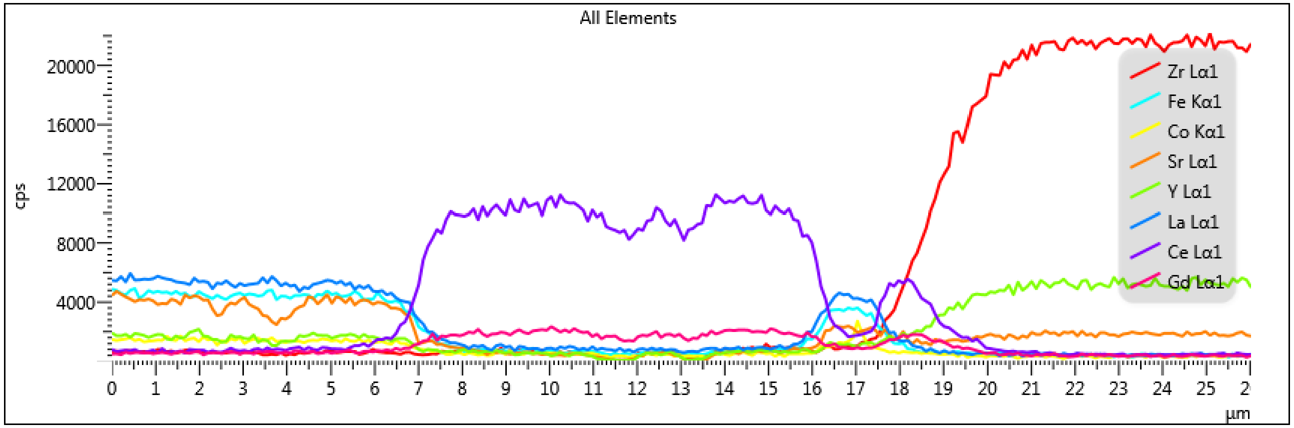
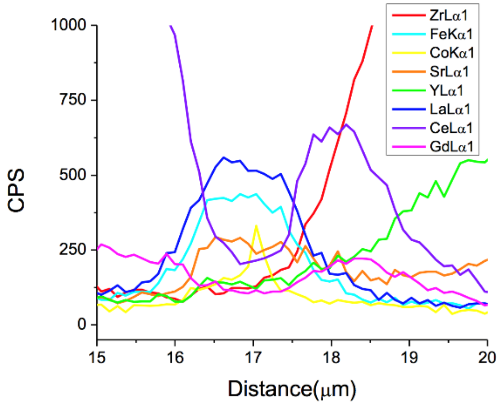
LSCF Fired at 1200 C



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





Summary & Take-home Message

EPD is an effective method to deposit GDC on non-shrinking YSZ electrolyte

- –DC EPD coating can be densified @ 1300C
- –AC EPD coating can be densified @ 1250C

4.5-6 microns dense GDC seems to be enough as barrier layer

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