Impurity effects in Solid Oxide Fuel Cells

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Outline

- Project Goals
- Effect of Cr on cell performance (full & half cell testing)
- Protective coatings
- Alternate Cathode compositions
- Future work

Project Goals

- Insights into mechanisms of Cr impurity attack on SOFCs
- Design of protective coatings for interconnections
- Cr resistant cathode compositions

Single cell testing of complete cells in the presence of Cr

Test conditions and EDS analysis

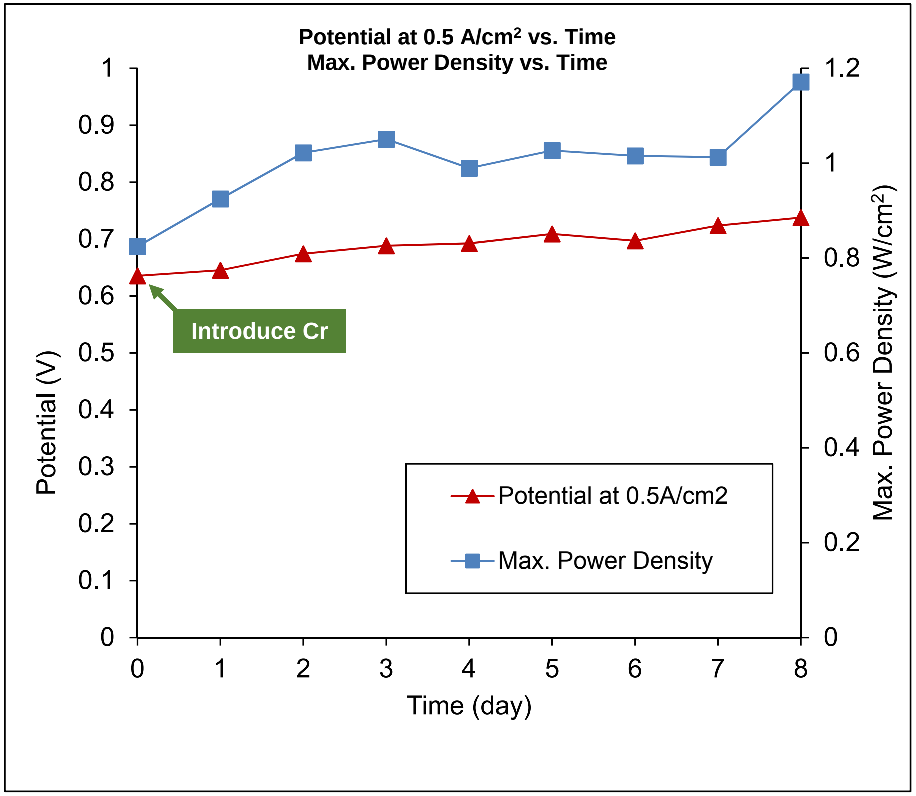
1. **Anode-supported SOFC Performance Measurements**
    a. With indirect contact of interconnect (Crofer® 22 APU), with dry air, without applied current
    b. With indirect contact of interconnect (Crofer® 22 APU), with 10% humid air, without applied current
    c. With indirect contact of interconnect (Crofer® 22 APU), with 10% humid air, with constant applied current
    d. With no interconnect involved (for comparison with c.), with 10% humid air, with constant applied current

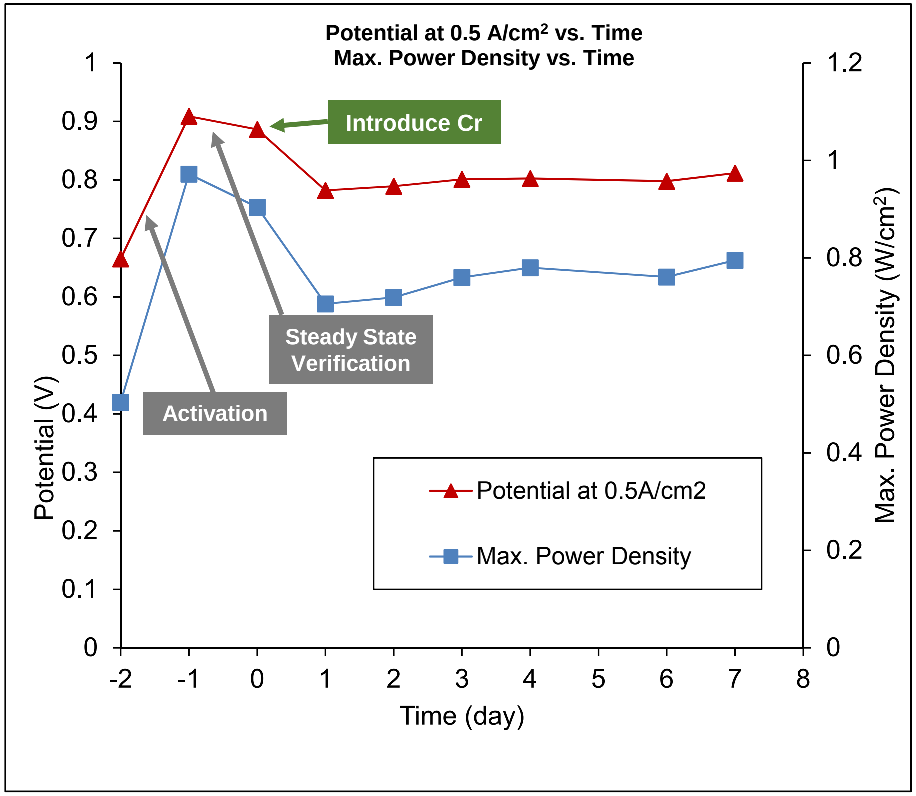
2. **EDS: Point Analysis & Spectrum Deconvolution**
    a. Baseline EDS point analysis (noCr-10%H_2O-Current)
    b. EDS of Cr-poisoned cathode (withCr-10%H_2O-Current)
    c. EDS of Cr-poisoned cathode (withCr-10%H_2O-noCurrent)

1. Anode-supported SOFC Performance Measurements

a. With indirect contact of interconnect (Crofer® 22 APU), with dry air, without current applied in between measurements.

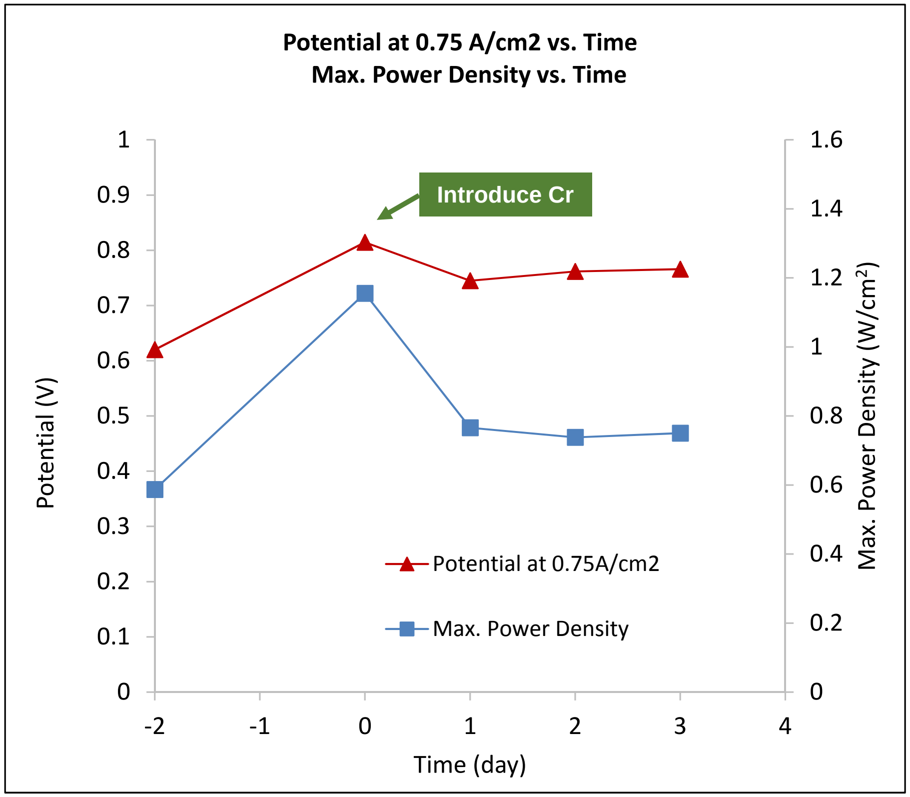
b. With indirect contact of interconnect (Crofer® 22 APU), with 10% humid air, without current applied in between measurements.



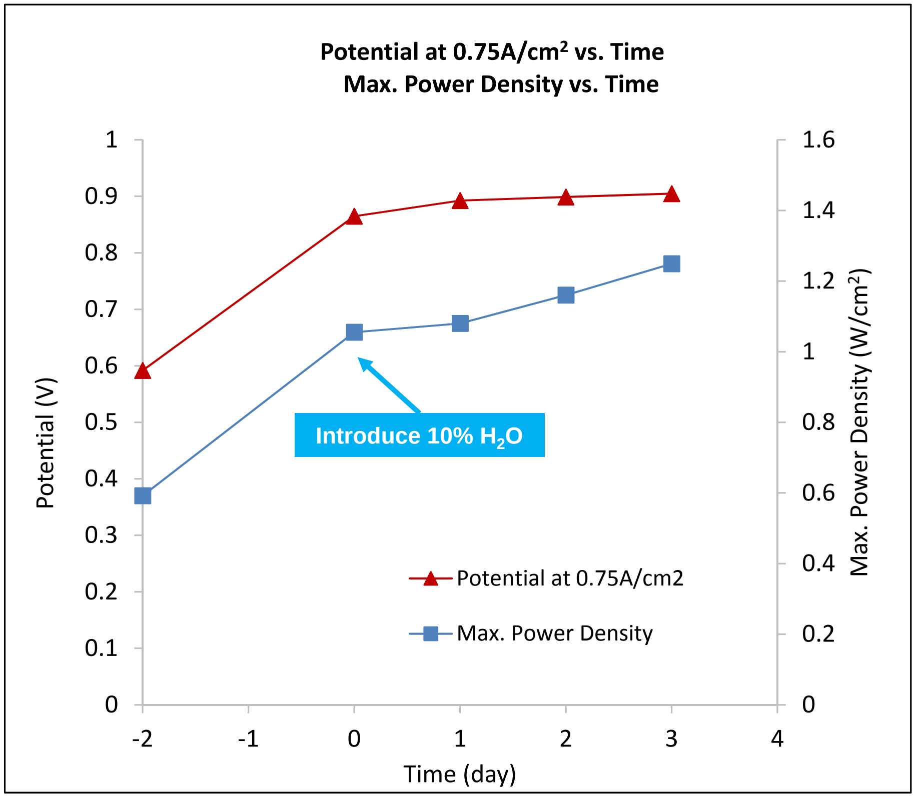


1. Anode-supported SOFC Performance Measurements

c. With indirect contact of interconnect (Crofer® 22 APU), with 10% humid air, with constant current applied in between measurements.



d. With no interconnect involved (for comparison with **c.**), with 10% humid air, with constant current applied in between measurements.



2. EDS: Point Analysis & Spectrum Deconvolution

a. Baseline EDS point analysis (no Cr-10%H_2O-Current)

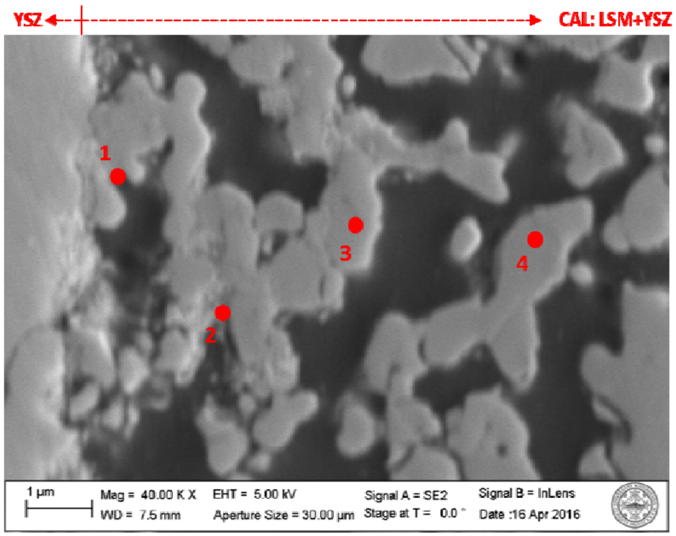
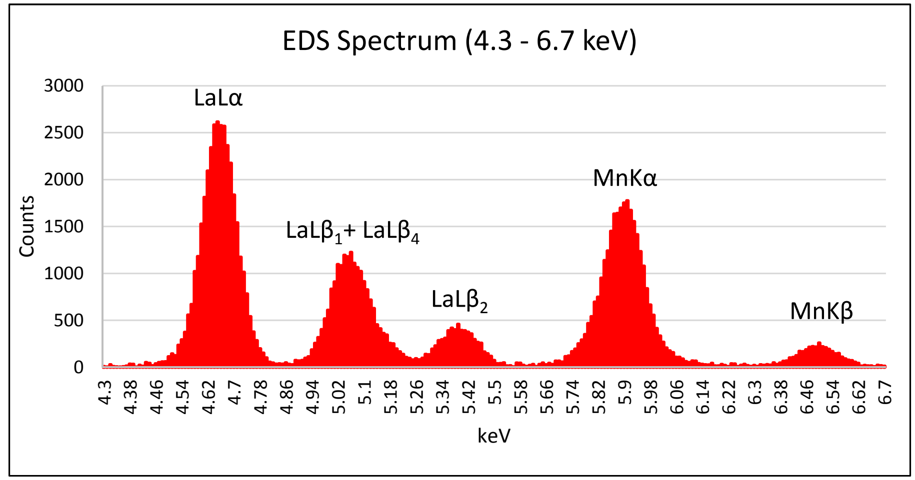
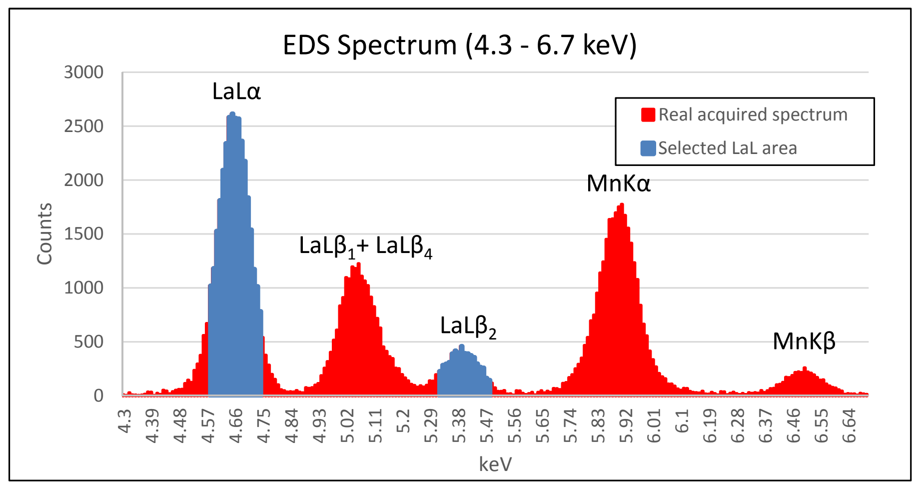


Fig. SEM image of cathode cross section close to TPB

Position	Intensity ratio (area) $\frac{La L\alpha}{La L\beta_2} = \frac{\sum_{4.58}^{4.74} Count}{\sum_{5.32}^{5.48} Count}$
1	5.30
2	5.19
3	5.54
4	5.78
Average	**5.45**

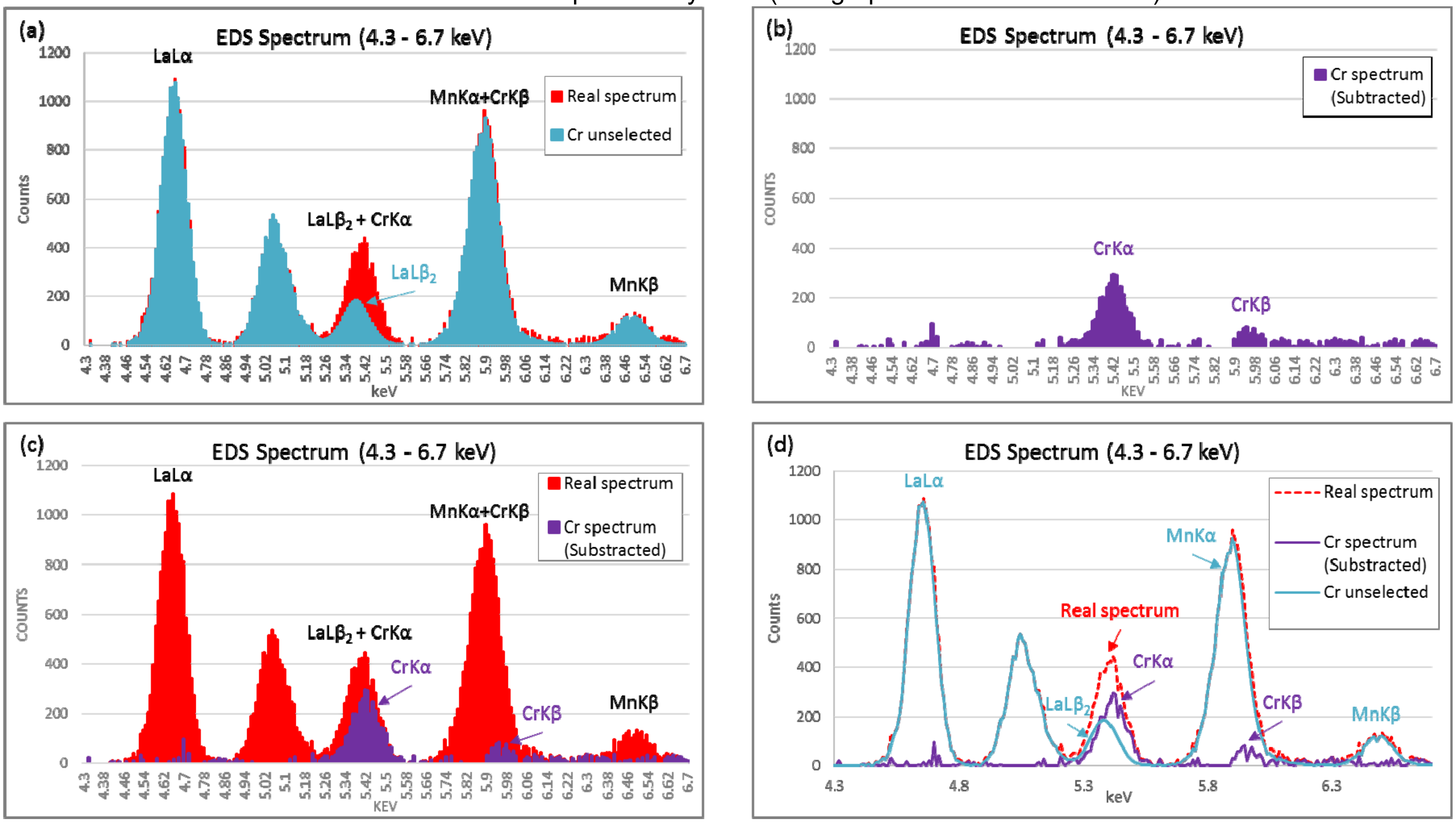




2. EDS: Point Analysis & Spectrum Deconvolution

(with Cr-10%H2O-Current)

Deconvolution of EDS Spectrum by HPD (Halographic Peak Deconvolution)



2. EDS: Point Analysis & Spectrum Deconvolution

b. EDS of Cr-poisoned cathode (withCr - 10%H2O-Current)

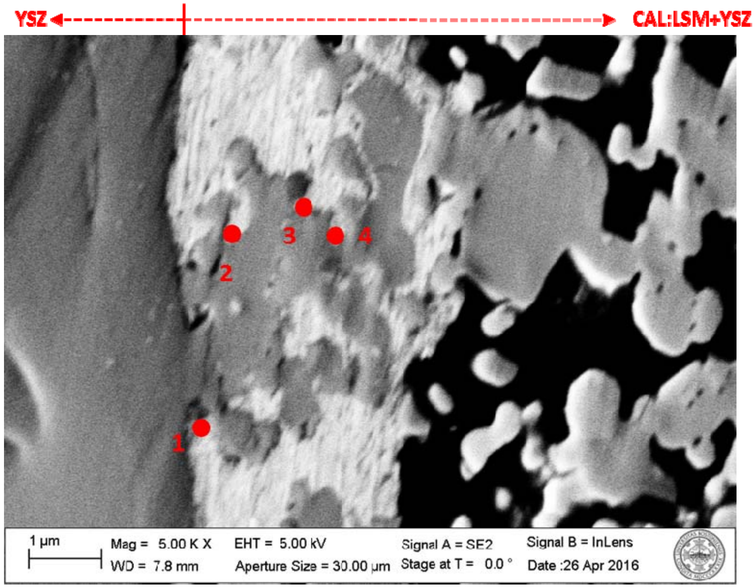
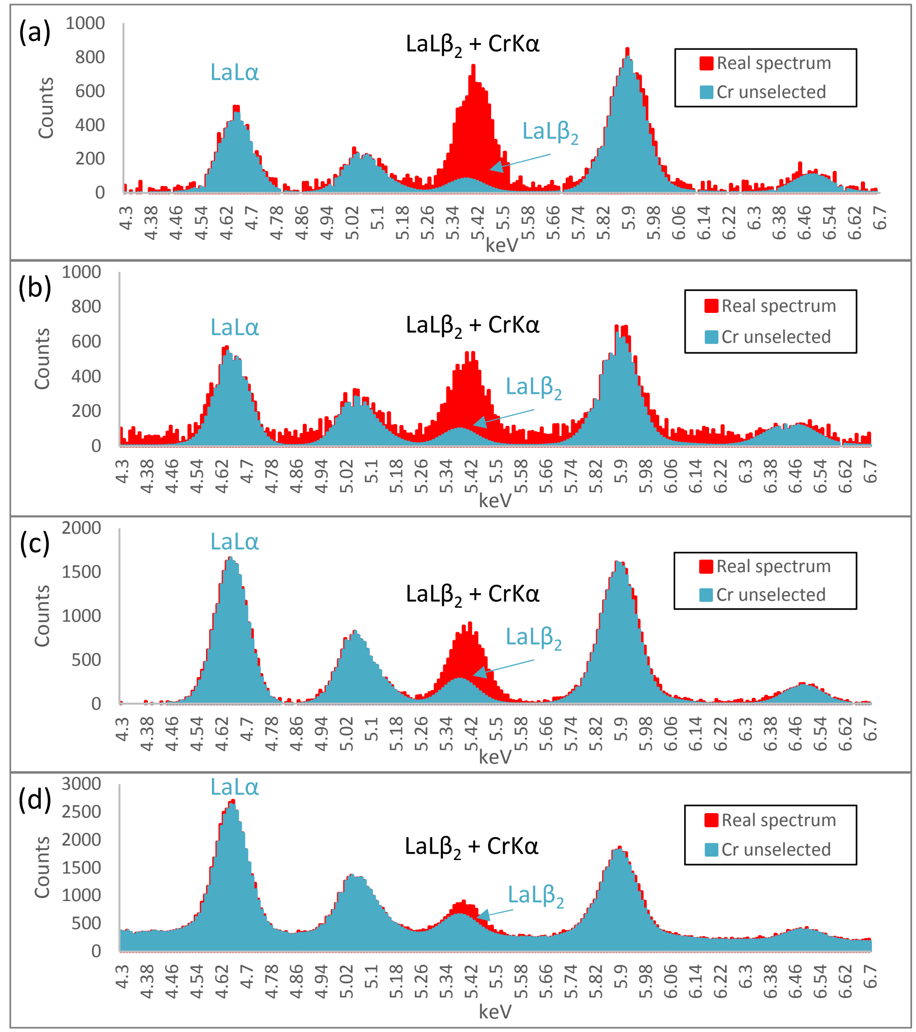


Fig. SEM image of cathode cross section close to TPB

Position	Intensity ratio (area)
	$\frac{LaL\alpha}{LaL\beta_2 + (CrK\alpha)} = \frac{\sum_{4.58}^{4.74} Count}{\sum_{5.32}^{5.48} Count}$
1	0.67
2	1.05
3	1.83
4	2.77



2. EDS: Point Analysis & Spectrum Deconvolution

c. EDS of Cr-poisoned cathode (withCr-10%H_2O-noCurrent)

Position	Intensity ratio (area)
	$\frac{LaL\alpha}{LaL\beta_2 + (CrK\alpha)} = \frac{\sum_{4.58}^{4.74} Count}{\sum_{5.32}^{5.48} Count}$
1	5.20
2	3.75
3	4.93
4	5.43
5	4.64
6	4.12
Average	**4.68**

(a)

(b)

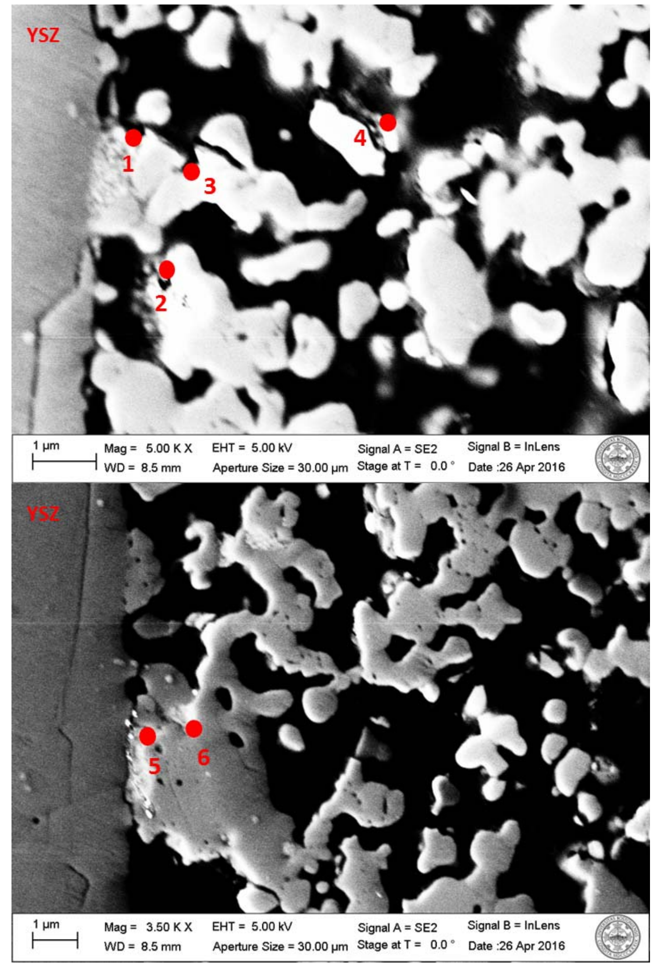


Fig. SEM image of cathode cross section close to TPB: (a) region 1, (b) region 2

Summary of Observations of Single Cell Tests

- Presence of humidity by itself moderates performance increase during the initial break-in period (presumably due to increase in polarization resistance at 750 mA/cm^2).

- In indirect contact experiments with current, significant degradation leading to drop in performance occurs over a period of days.

- EDS analysis clearly shows deposition of Cr at the TPBs, with decreasing Cr deposition away from the electrolyte-cathode interface.

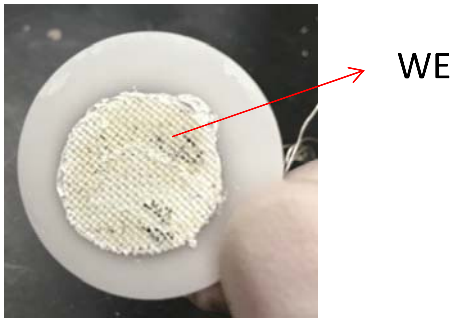
Half cell testing

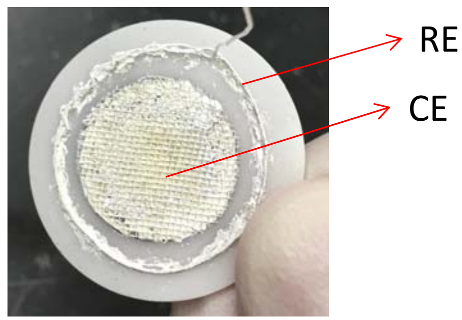
Experimental Conditions:

I. Electrolyte-support half-cell of SOFC Measurements with Indirect Contact of Interconnect, with Dry Air
II. Electrolyte-support half-cell of SOFC Measurements with Indirect Contact of Interconnect, with 10% Humidified Air
III. Electrolyte-support half-cell of SOFC Measurements with Indirect Contact of Interconnect, with 10% Humidified Air, with current

Cell Architecture and Details

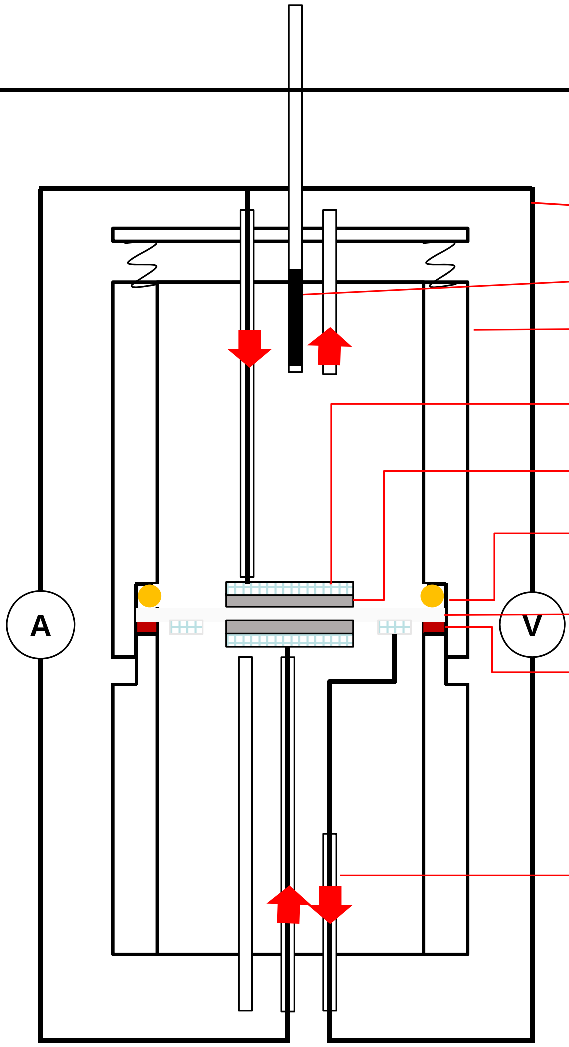
- The dimension of the cell





- Electrolyte:
  - Diameter: ~28mm
  - Thickness: 740μm
- Electrodes:
  - Working electrode & Counter electrode: LSM
  - Current collector : Silver mesh & silver paste
  - Diameter: ~15mm
- Reference Electrode
  - ID: ~20mm
  - OD: ~22mm

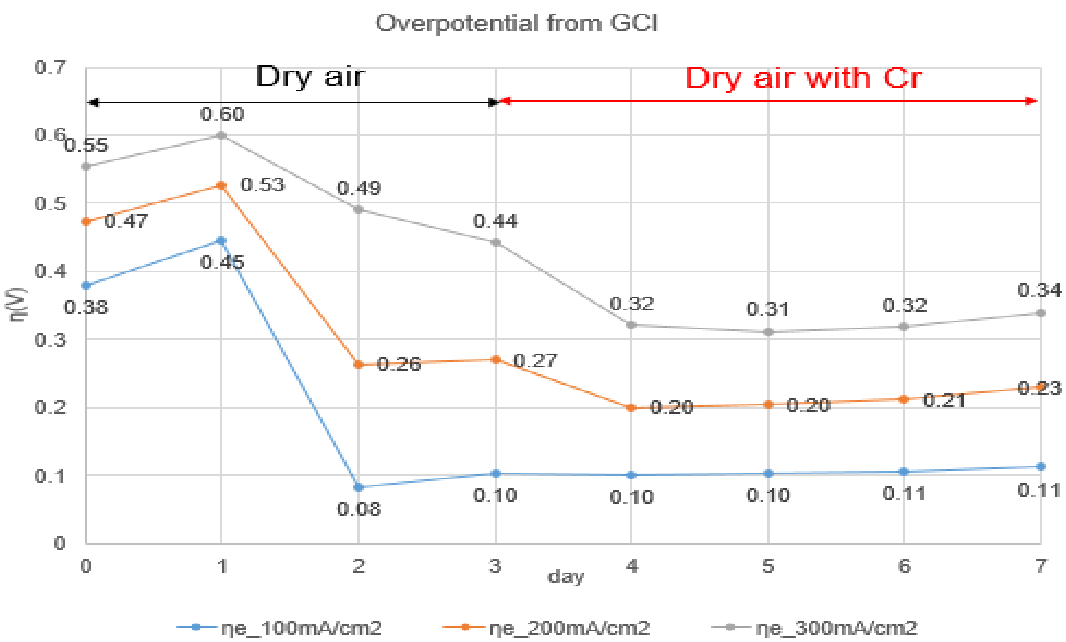
Experimental Set-Up

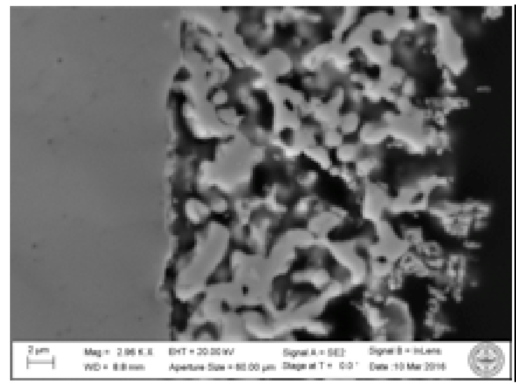


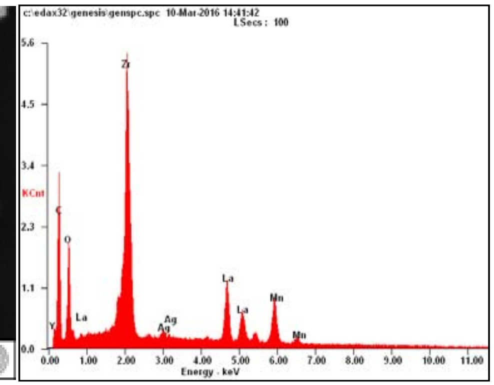
- **Test Condition:**
  - Spring load: ~18 lbs
  - Temperature: 800 °C
  - Gas: Dry air(21% oxygen)
  - Interconnect: Crofer® 22 APU strips (surface area: ~48 cm^2)

- **Electrochemical measurements:**
  - Galvanostatic Current Interruption(GCI)
  - Electrochemical Impedance Spectroscopy(EIS)

Electrolyte-support half-cell of SOFC Measurements with Indirect Contact of Interconnect, with Dry Air

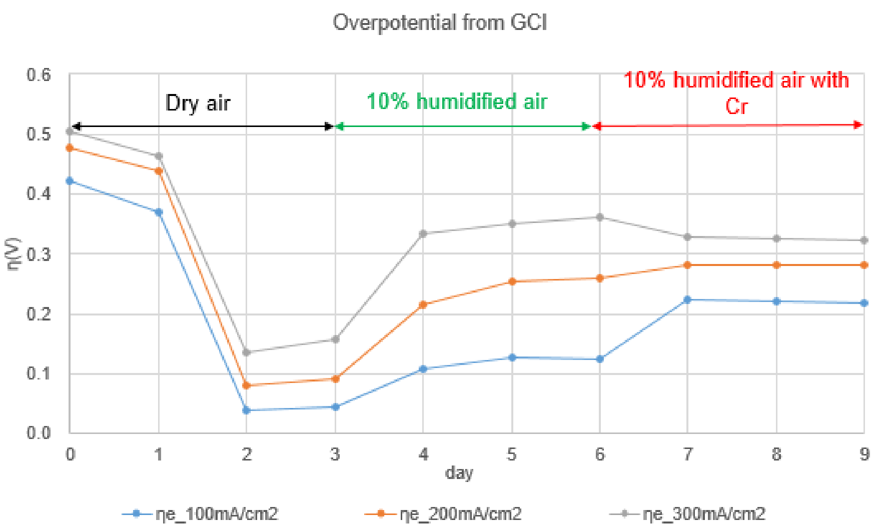


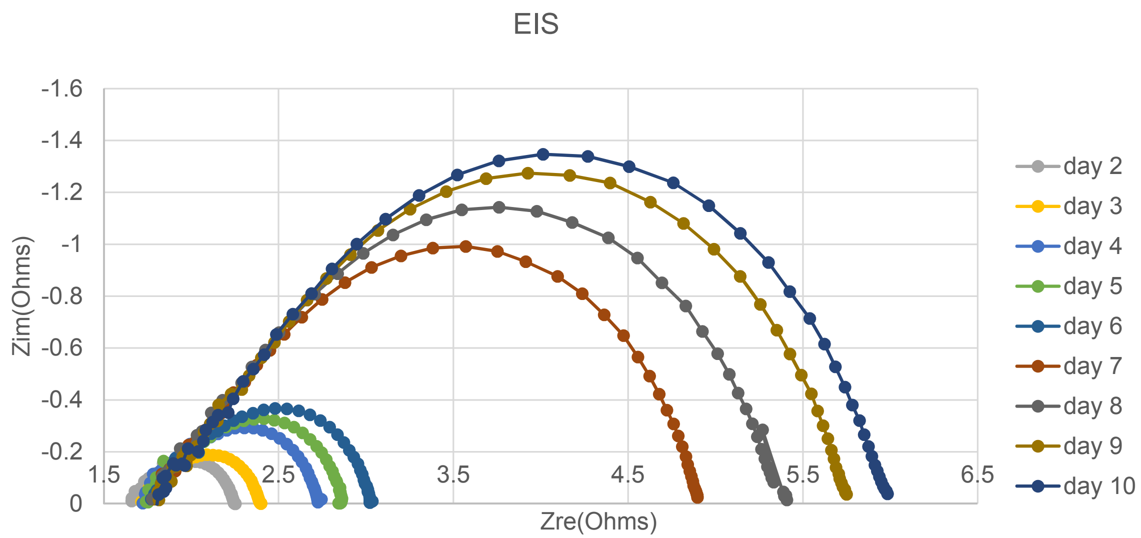




- After "activation" process (day1 to day 2), the polarization resistance decreased.
- The resistance on day 2 did not change much from day 3 (in figure 1 and 2), and it verified that the cell was broken-in .
- The polarization overpotential didn't change after introducing Cr in dry air, which means no Cr deposited on the TPBs.
- In the SEM and EDX, no Cr could be found.

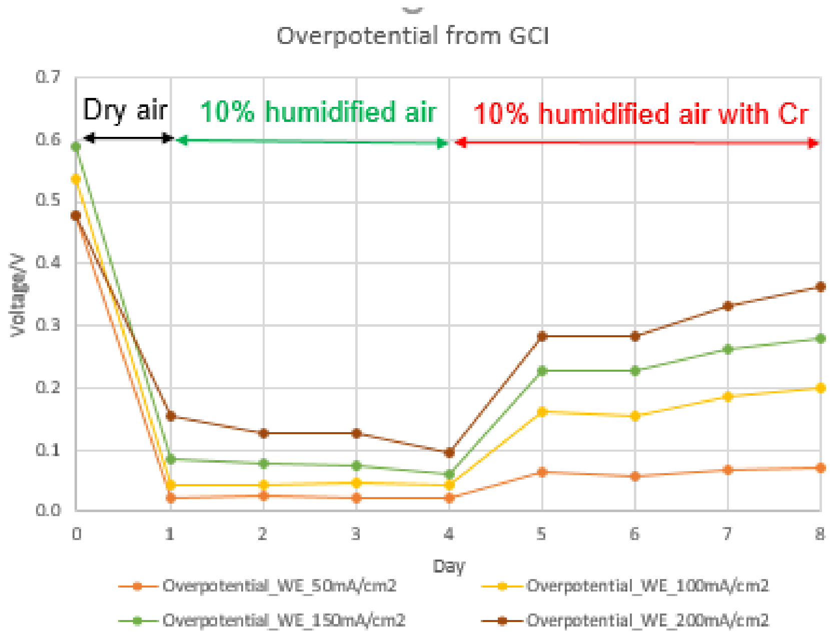
Electrolyte-support half-cell of SOFC Measurements with Indirect Contact of Interconnect, with 10% Humidified Air

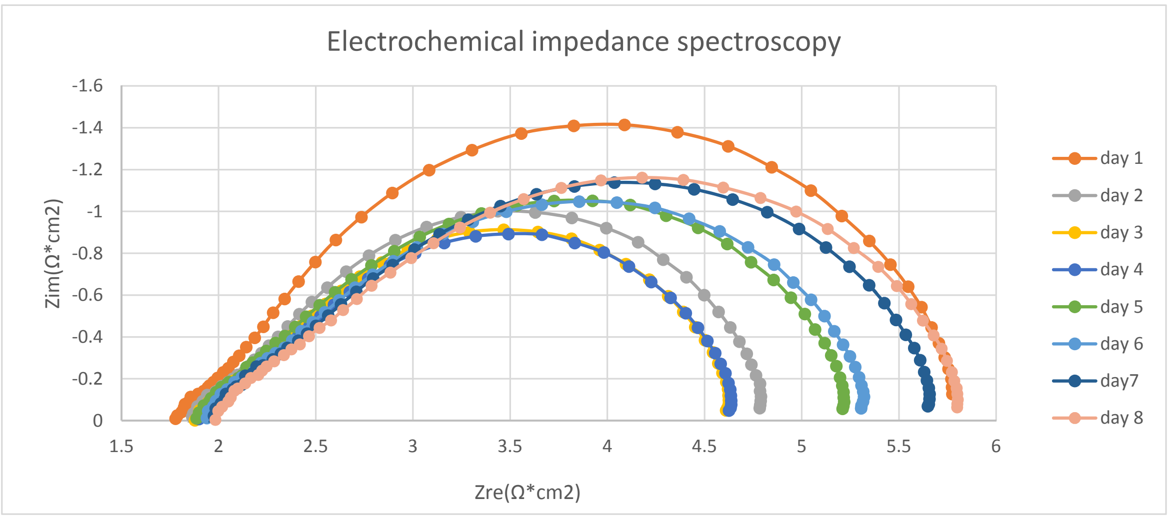




- After "activation" process, the polarization resistance decreased
- After 10% humidified air introduced, polarization resistance increased, which indicates 10% humidified air degraded the cell
- After Cr with10% humidified air introduced, polarization resistance increased, which indicates Cr degraded the cell
- In SEM and EDX, Cr was found

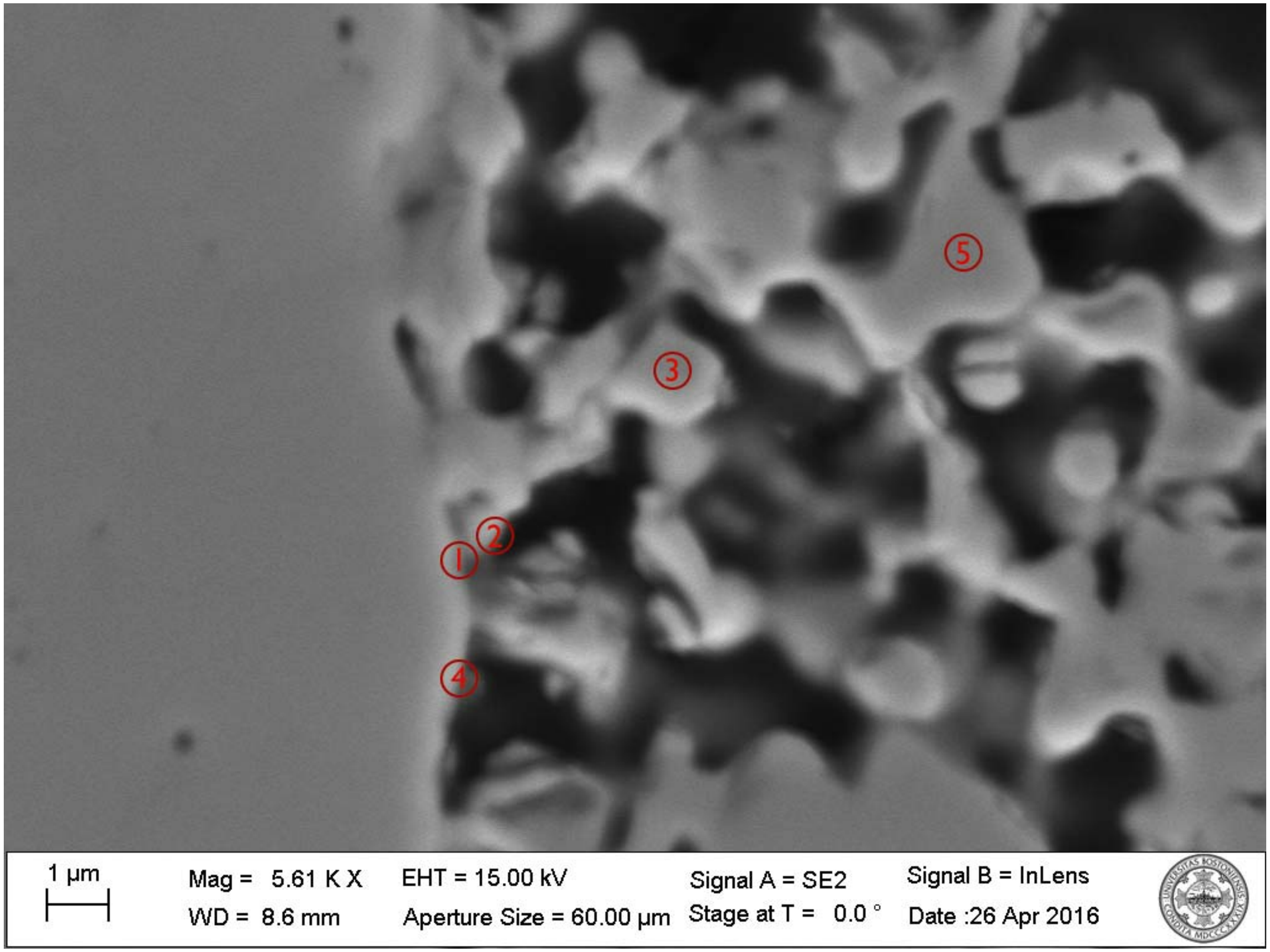
Electrolyte-support SOFC Measurements with Indirect Contact of Interconnect, with 10% Humidified Air, with current





- After "activation" (or break-in) process, the polarization resistance decreased
- After 10% humidified air introduced, polarization resistance decreased (these current densities are far lower than 750 mA/cm^2 in the complete cell experiments), which indicates 10% humidified air did not degrade the cell at low current densities
- After Cr with10% humidified air introduced, polarization resistance increased, which indicates Cr clearly degraded the cell

Microstructure of the cell before the test (without Cr)



Point scan

1. LSM and YSZ Boundary
2. LSM edge
3. Center of LSM grain near YSZ
4. YSZ edge
5. Center of LSM grain away from YSZ

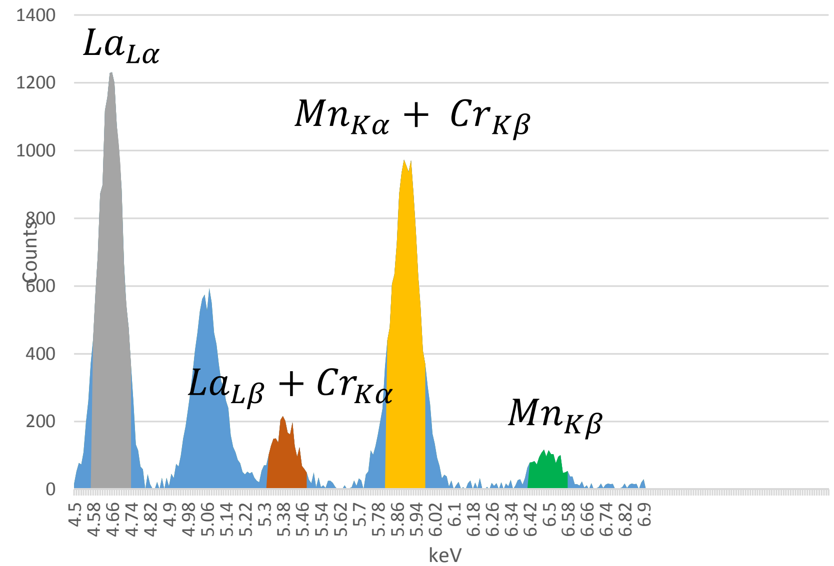
Microstructure of the cell before the test(without Cr)

Point scan
LSM and YSZ Boundary

Baseline ratio
Energy range: $La_{L\alpha}$: 4.58keV to 4.74keV

$La_{L\beta}$& $Cr_{K\alpha}$: 5.32keV to 5.48keV

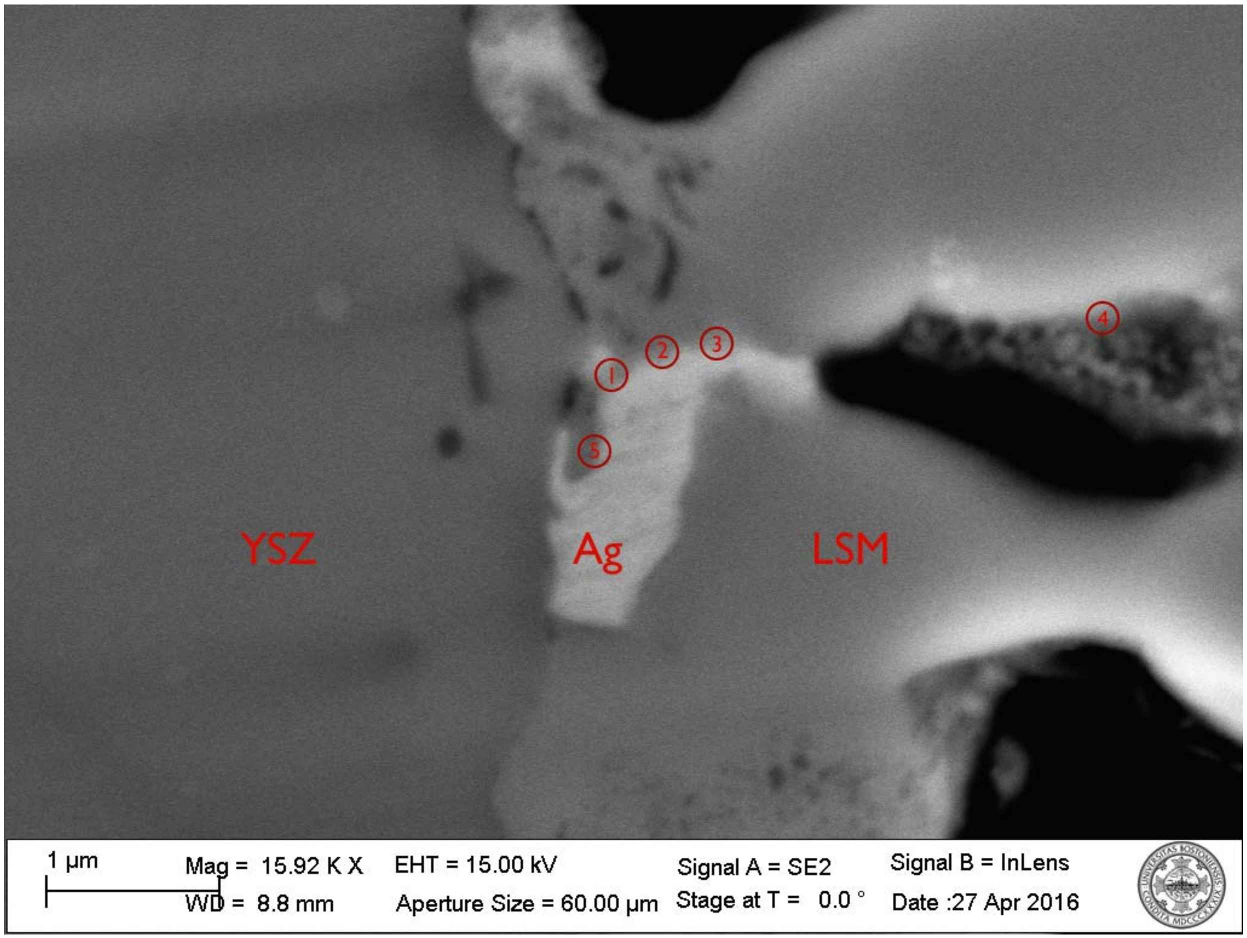
$$\frac{La_{L\alpha}}{(La_{L\beta} + Cr_{K\alpha})} = \frac{\sum_{4.74keV}^{4.58keV} counts}{\sum_{5.48keV}^{5.32keV} counts} = 6.16$$



Points	Area ratio
1.LSM and YSZ Boundary	6.61
2. LSM edge	5.53
3. Center of LSM grain near YSZ	5.62
4. YSZ edge	5.21
5. Center of LSM grain away from YSZ	5.61

- The peak ratio $\frac{La_{L\alpha}}{(La_{L\beta})}$ is without $Cr_{K\alpha}$ is around 5.6

Microstructure of the cell after electrochemical testing (with Cr, with 10% humidified air and with 200 mA/cm^2 current)



Point scan

1. Silver, LSM and YSZ boundary
2. Silver and LSM boundary
3. Silver and LSM boundary
4. LSM edge
5. Silver and LSM

Microstructure of the cell after the test(with Cr, with 10% humidified air and with 200mA/cm2 current)

Point scan

Silver, LSM and YSZ boundary

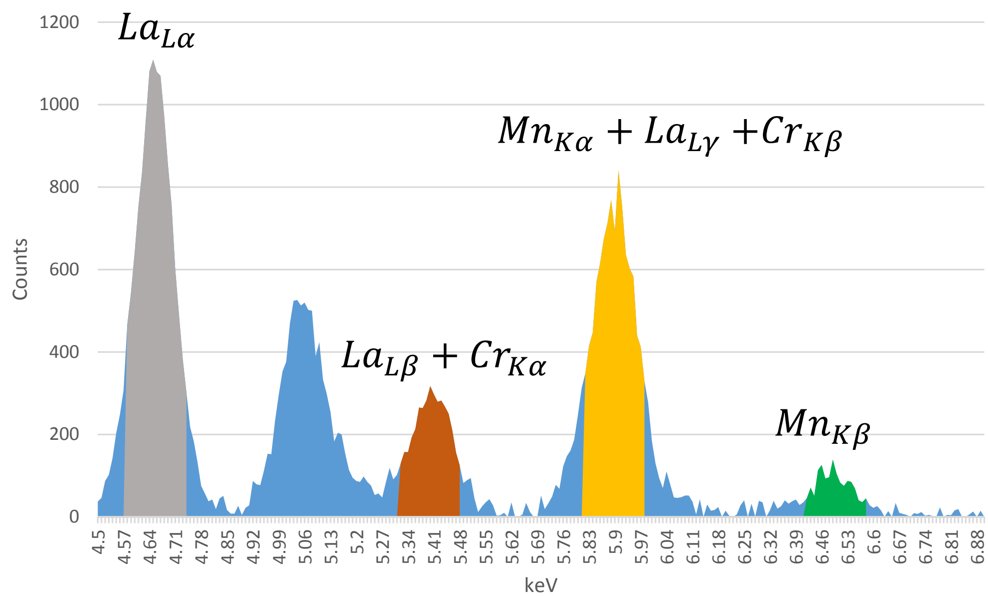
Baseline ratio
Energy range:

$La_{L\alpha}$: 4.58keV to 4.74keV

$La_{L\beta}$& $Cr_{K\alpha}$: 5.32keV to 5.48keV

$$\frac{La_{L\alpha}}{(La_{L\beta} + Cr_{K\alpha})} = \frac{\sum_{4.74keV}^{4.58keV} counts}{\sum_{5.48keV}^{5.32keV} counts} = 3.36$$

Points	Area ratio
1.Silver, LSM and YSZ boundary	3.36
2. Silver and LSM boundary	4.12
3. Silver and LSM boundary	4.78
4. LSM edge	5.35
5. Silver and LSM	5.29



- The peak ratio is much less than 5.6, which confirms Cr was deposited on the TPBs.

Summary of Observations from Half-Cell Testing

- At low current densities water vapor alone does not result in increased polarization with time.

- Introduction of Cr along with water vapor results in quadrupling of polarization resistance over four days under an applied current of 200 mA/cm^2.

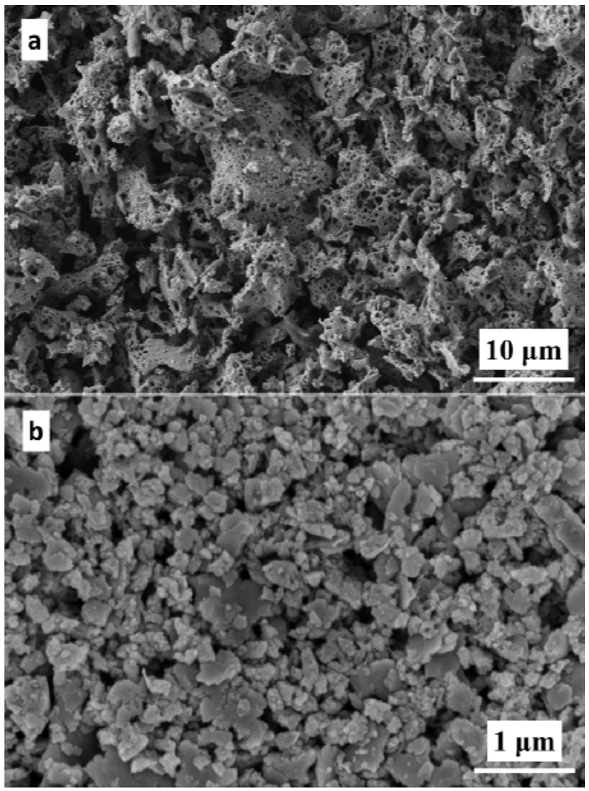
- Cr-deposition follows a similar pattern as observed in complete cells – at TPBs and electrochemically active locations.

Development of Protective Coating

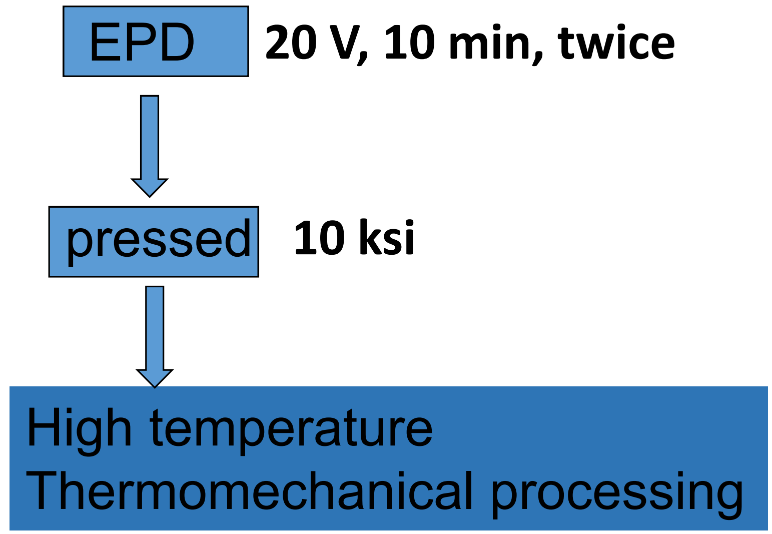
$Cu_{1.3}Mn_{1.7}O_4$ powders by GNP

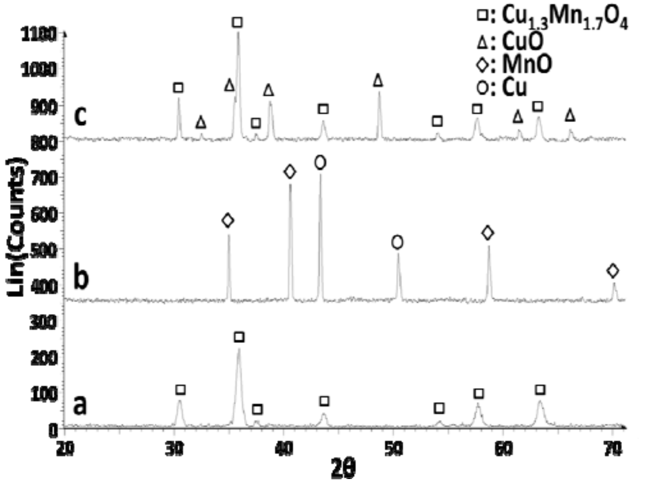
a) after calcination

b) after ball milling

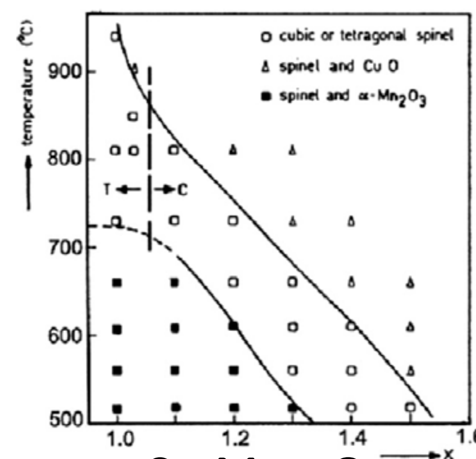


EPD and subsequent densification procedures

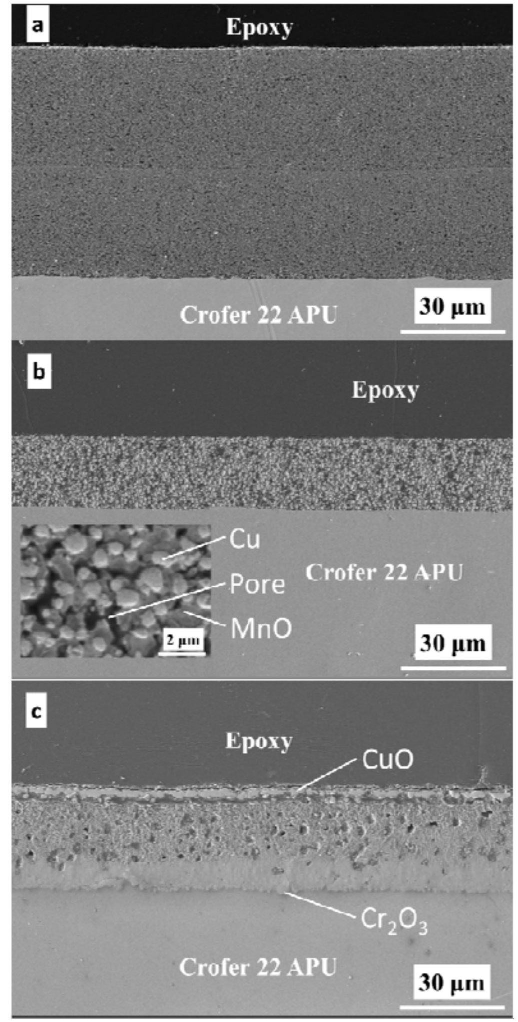




a) $Cu_{1.3}Mn_{1.7}O_4$ powders after calcination;
b) intermediate
c) coating layer after annealing



$Cu_xMn_{3-x}O_4$

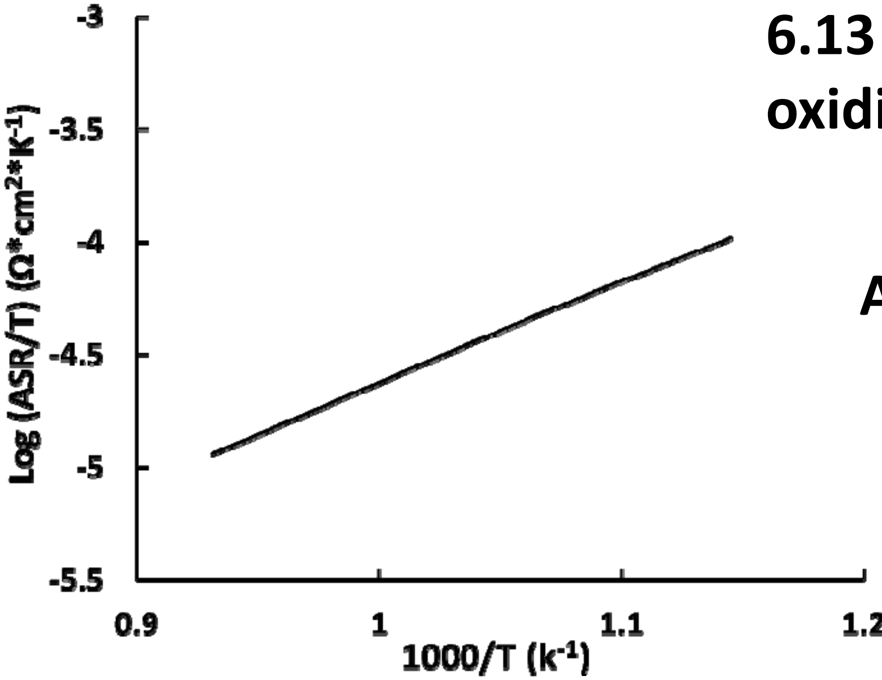


as-deposited
66 µm

intermediate
21 µm

after annealing
27 µm

ASR Measurements

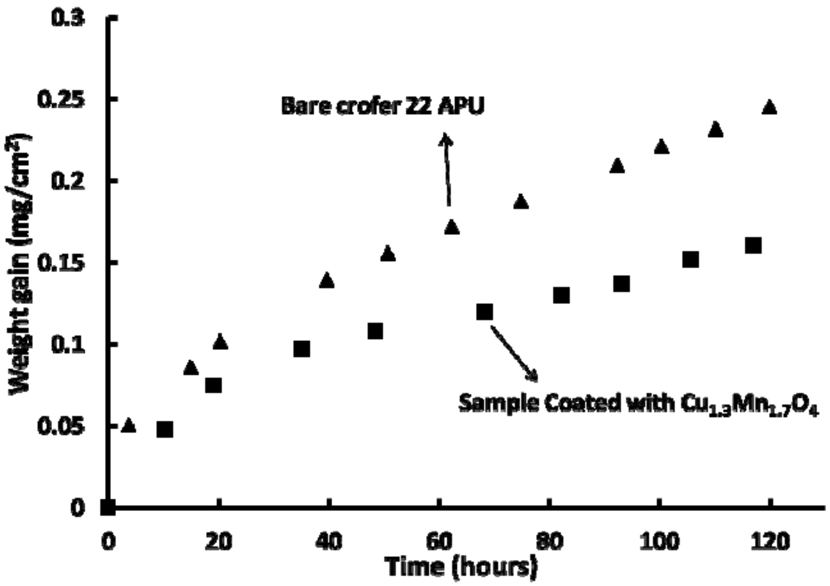


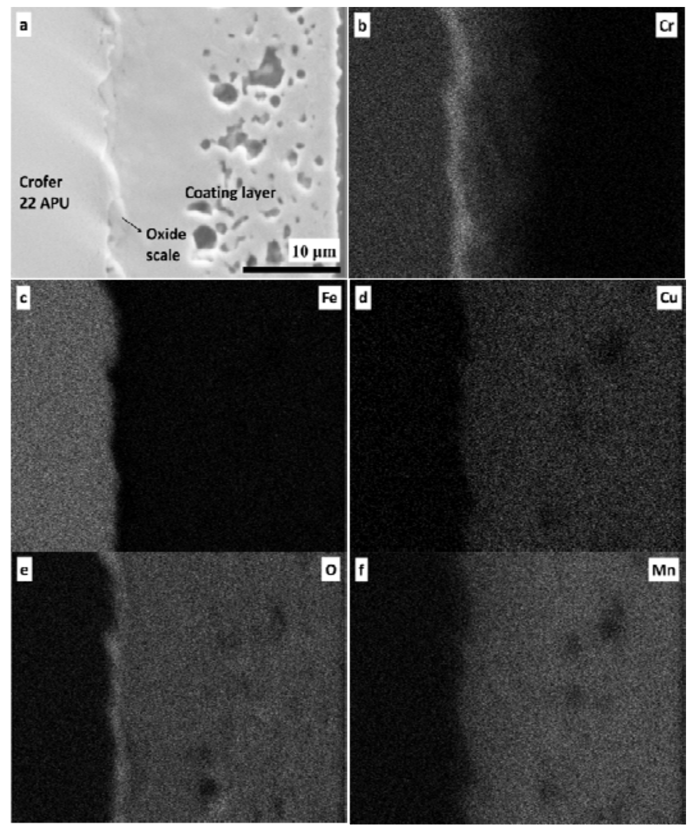
6.13 mΩ*cm² after 185 h oxidization at 800 ℃ in air

$$ASR/T = A \exp(E_a/kT)$$

$$E_a=0.9\ eV$$

Thermogravimetry (800 ℃, 120 h)

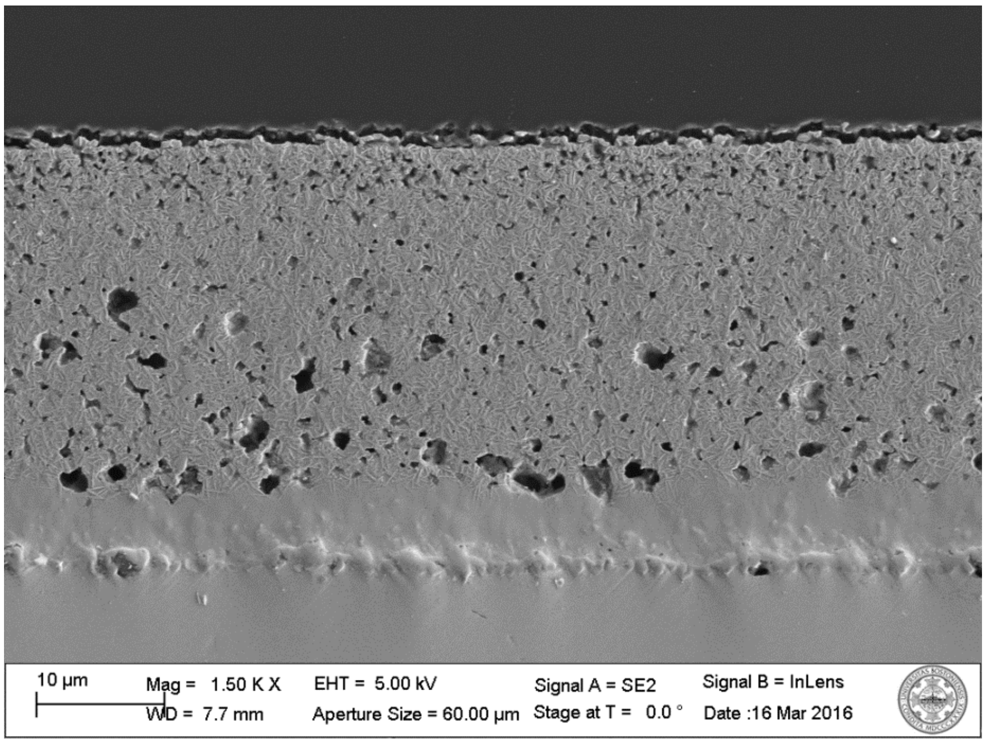


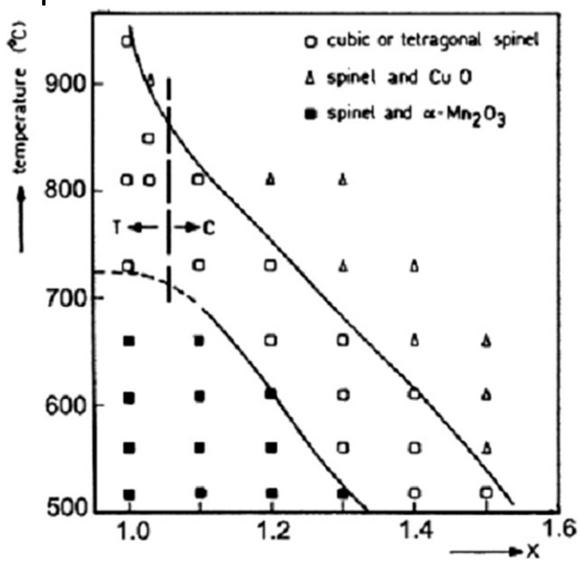


$Cu_{1.3}Mn_{1.7}O_4$ is effect as a barrier to Cr and O diffusion

Coating with $CuMn_{1.8}O_4$

No CuO surface layer after same EPD and densification procedures as $Cu_{1.3}Mn_{1.7}O_4$





$Cu_xMn_{3-x}O_4$

Summary of Observations of EPD Coating Experiments

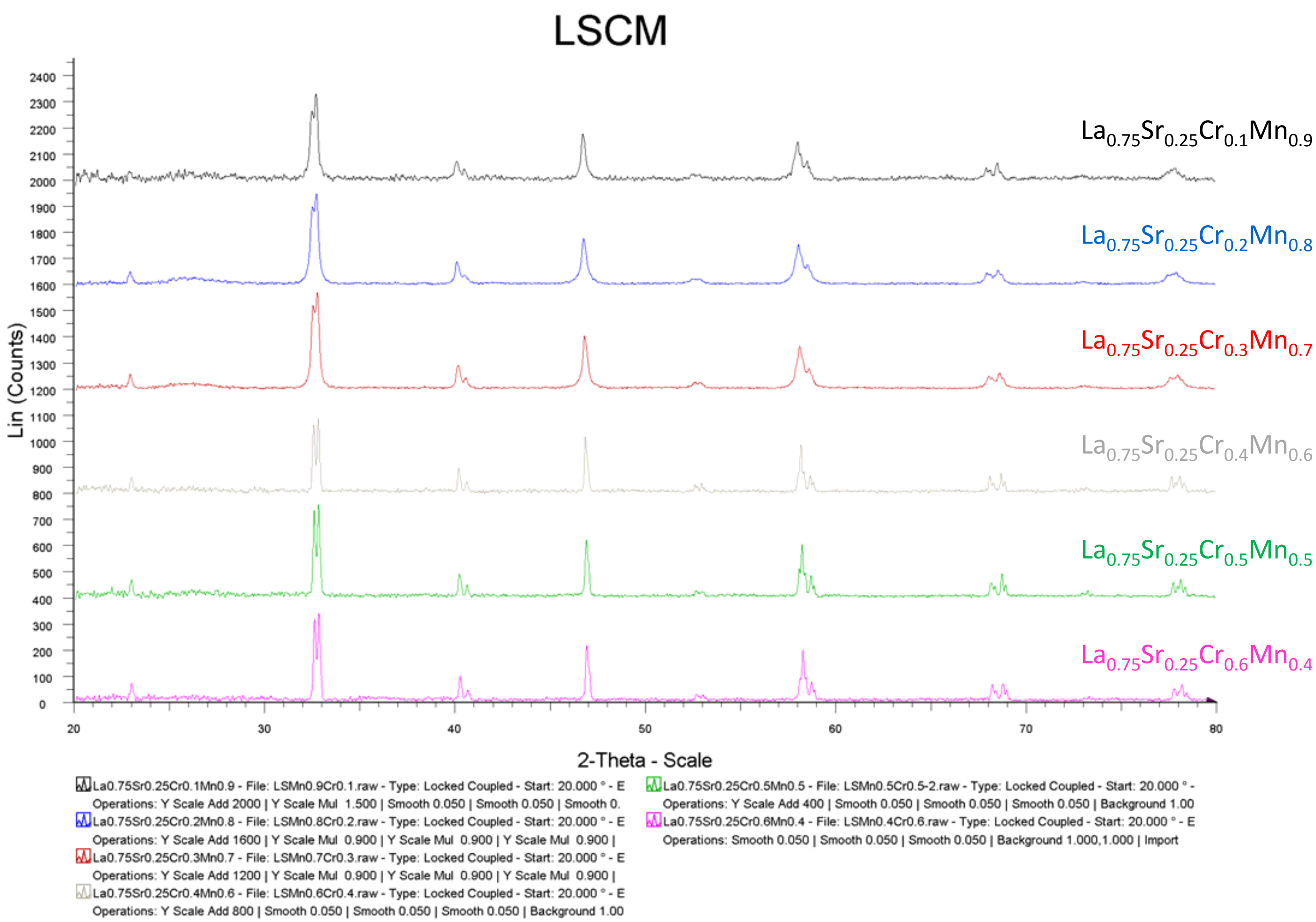
- Electrophoretic deposition is an effective method to deposit thick coatings on conducting stainless steel substrates.

- ASR is ~ 6 $m\Omega*cm^2$ after 185 hours.

- Morphology of coating highly dependent on composition of spinel.

Alternate Cr-resistant cathode compositions

Result and Discussion(Xrd)



Structure: rhombohedral

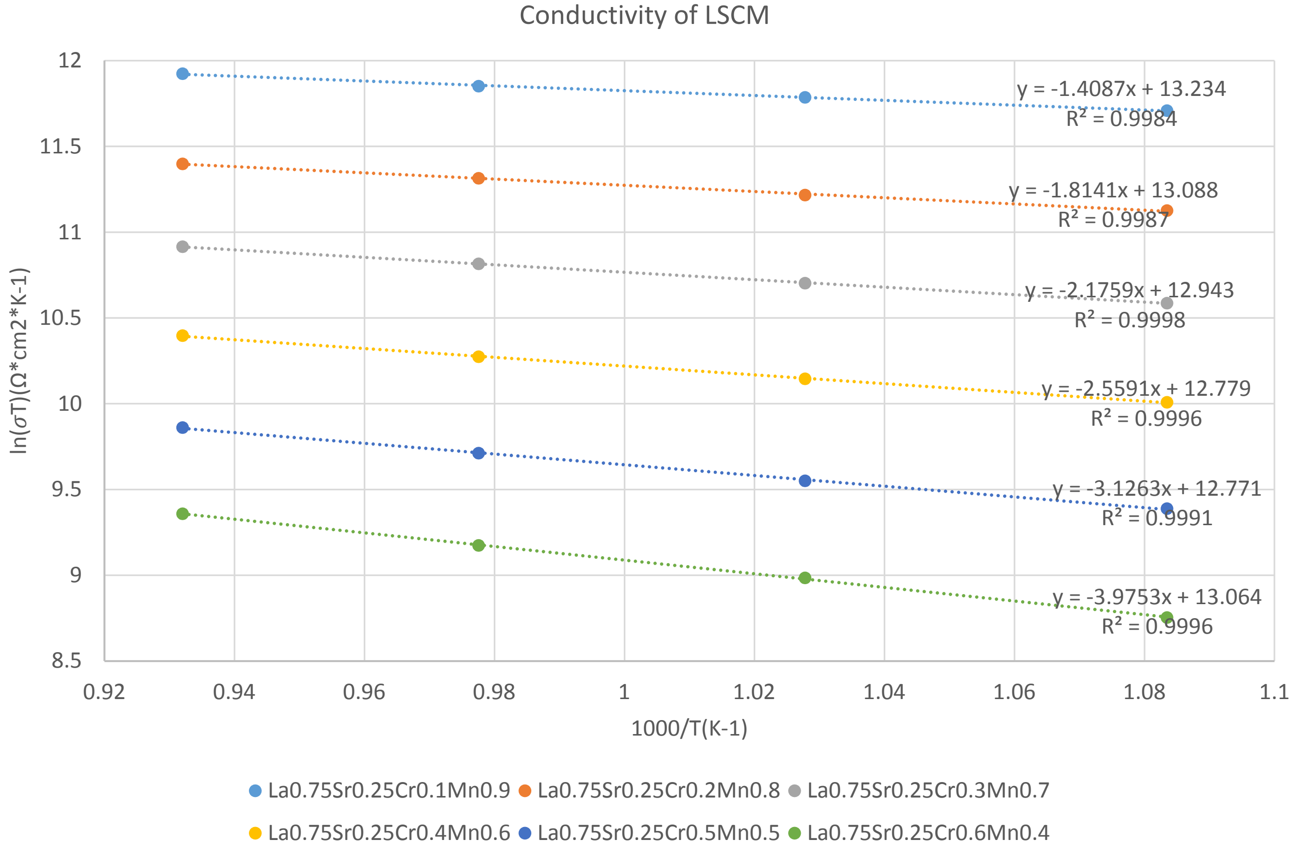
Result and Discussion(Xrd)

Structure: rhombohedral

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk^2 + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Material	$La_{0.75}Sr_{0.25}Cr_{0.1}Mn_{0.9}$	$La_{0.75}Sr_{0.25}Cr_{0.2}Mn_{0.8}$	$La_{0.75}Sr_{0.25}Cr_{0.3}Mn_{0.7}$
d-spacing(Peak (1,1,0)	2.75969	2.75805	2.75554
d-spacing(Peak (1,0,4)	2.74344	2.74056	2.73831
a(Å)	5.51938	5.5161	5.51108
c(Å)	13.40078	13.38371	13.37331
V(Å^3)	353.54212	352.67241	351.75716
Material	$La_{0.75}Sr_{0.25}Cr_{0.4}Mn_{0.6}$	$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}$	$La_{0.75}Sr_{0.25}Cr_{0.6}Mn_{0.4}$
d-spacing(Peak (1,1,0)	2.75597	2.75226	2.7474
d-spacing(Peak (1,0,4)	2.73478	2.73250	2.72859
a(Å)	5.51194	5.50452	5.49480
c(Å)	13.34662	13.33883	13.32194
V(Å^3)	351.16463	350.01563	348.33871

Result and Discussion



$$ln(\sigma T) = -\frac{Q}{1000R}\left(\frac{1000}{T}\right) + ln(\sigma_0)$$

- The Cr concentration increased, the electrical conductivity decreased.
- Cr acts as a block for polaron transfer

Future work

- Cr-impurity effects will be re-examined using Cr-resistant cathode compositions; to also include LSCF based compositions.
- EPD spinel coating process conditions will be optimized to obtain uniform, single-phase, dense coatings in Cu-Mn-O family that suppress Cr transport.
- Defect chemistry of spinels as a will be analyzed as a function of composition.
- Recommendation of coating composition and Cr-resistant cathode composition will be provided to commercial partner (FuelCell Energy).

Acknowledgments

- Helpful conversations with Steve Markovich, Harry Abernathy, Patcharin Burke are acknowledged.

- Financial support via DOE –FE 0023325