BOSTON UNIVERSITY

Mitigation of Chromium Impurity Effects and Degradation in SOFCs

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Outline

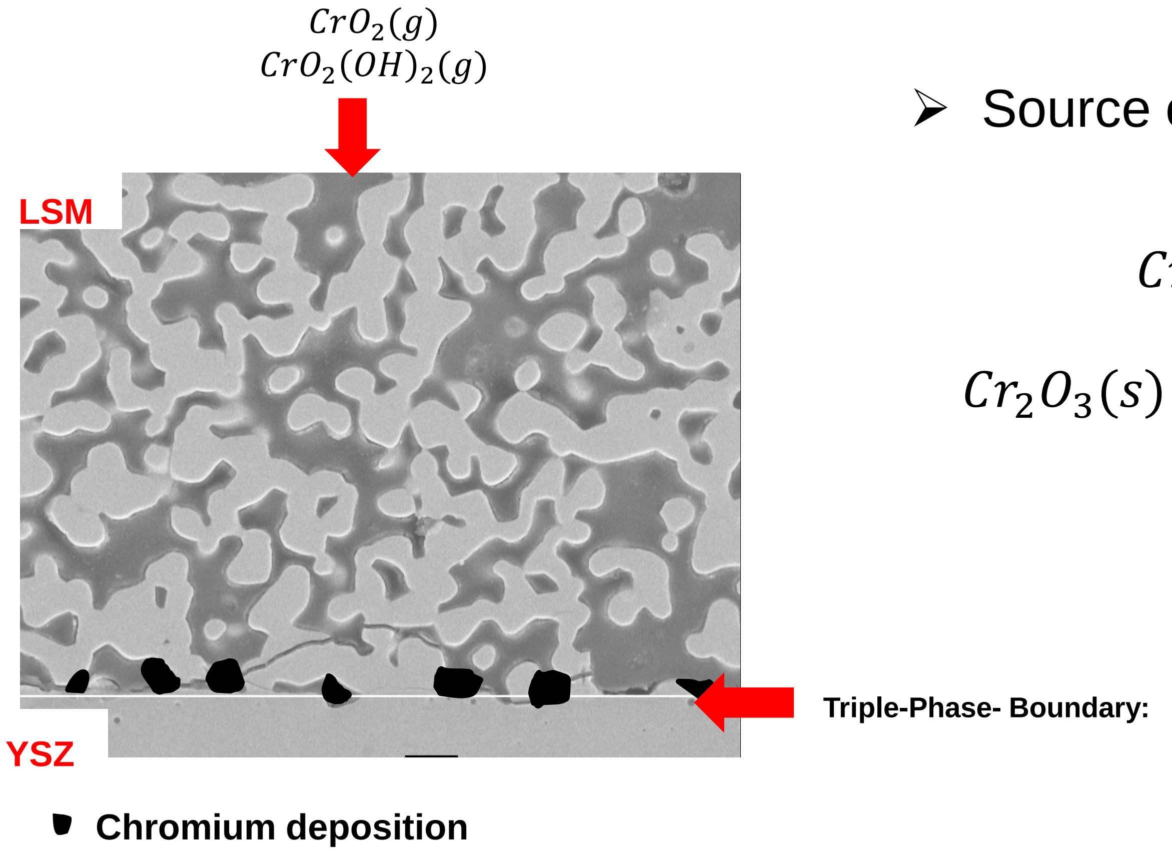
- Motivation and goals
- Understanding of Cr impurity attack – role of current density, humidity, temperature
  - Effect of Cr impurity using half cells and complete cells
- Protective coatings
- Ongoing work
- Summary and conclusions

Motivation and Goals

- Understand the mechanism and kinetics of Cr impurity attack at the SOFC cathode

- Develop effective strategies to combat Cr impurity effects:
  - Protective coatings
  - Cathode compositional modifications

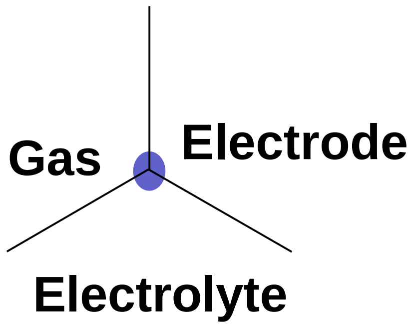
Current Understanding of Cr Attack Mechanism



- Source of Cr from interconnect and BOP:

$$Cr_2O_3(s) + \frac{3}{2}O_2 \rightarrow 2CrO_3(g)$$

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



Kinetic Studies: Electrochemical Measurement Tools

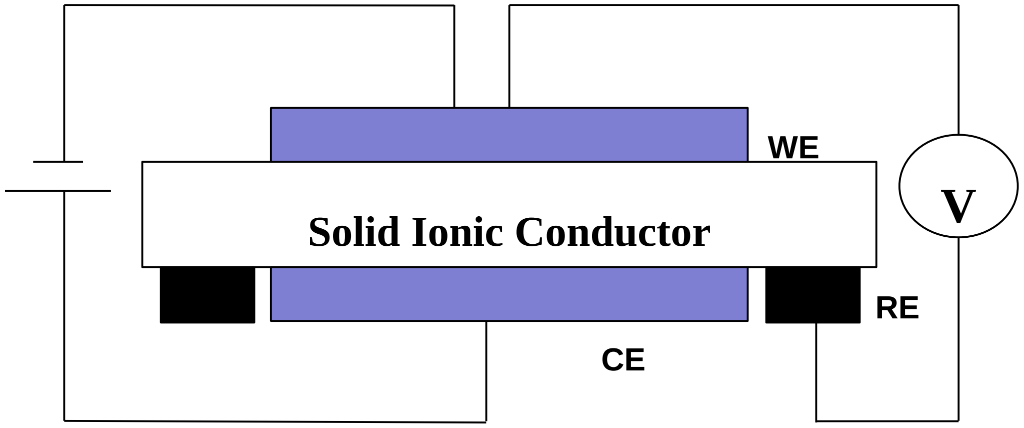
- Half-cells in contact with Cr source

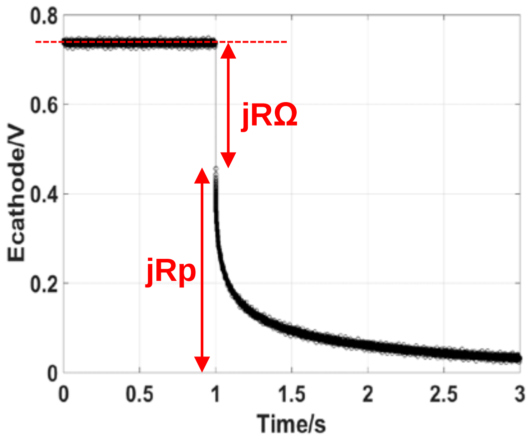
- Complete SOFCs in contact with Cr source

- SEM-EDX analysis

Cell Configuration: Half-cell measurements

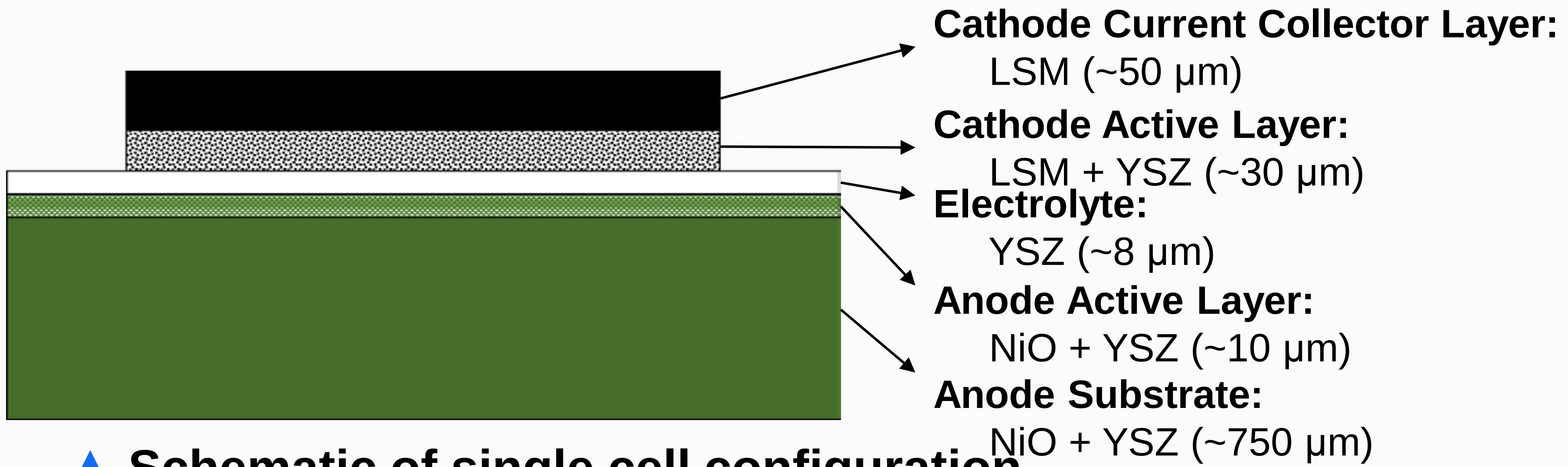
- Galvanostatic Current Interruption Technique(GCI)



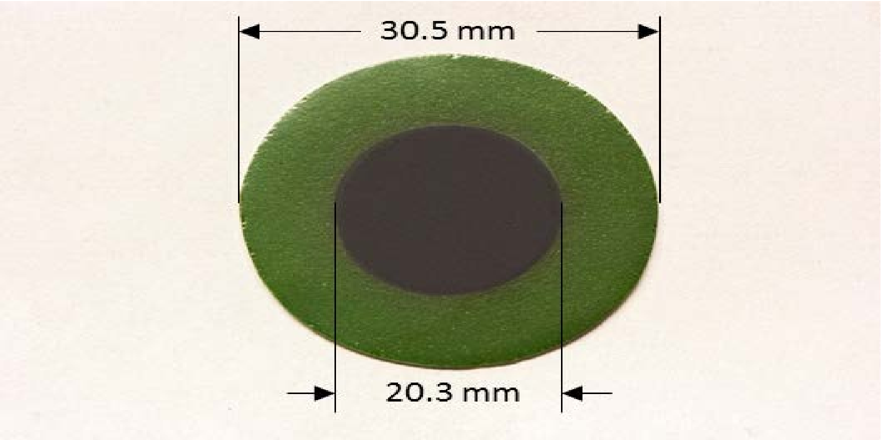


Parameter	Units	Description
$E_{cathode}$	V	The cathodic potential
R_p	$\Omega.cm^2$	The polarization resistance
R_Ω	$\Omega.cm^2$	The ohimc resistance

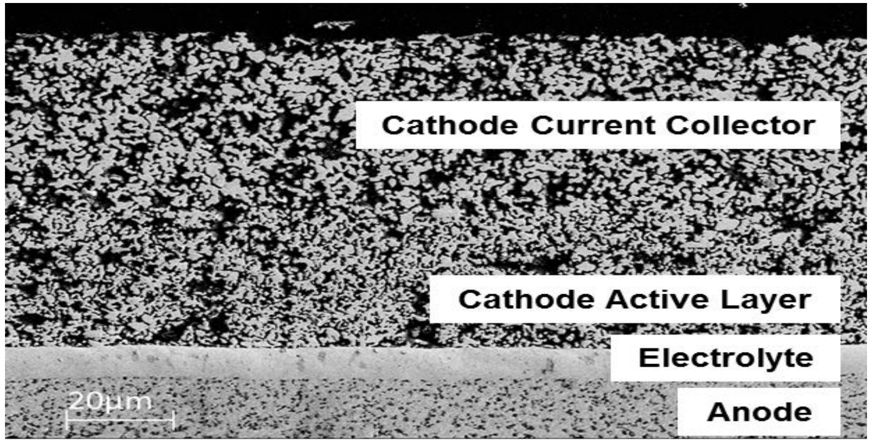
Cell Configuration: Complete Cells



▲ **Schematic of single cell configuration**



▲ **As-sintered cell**

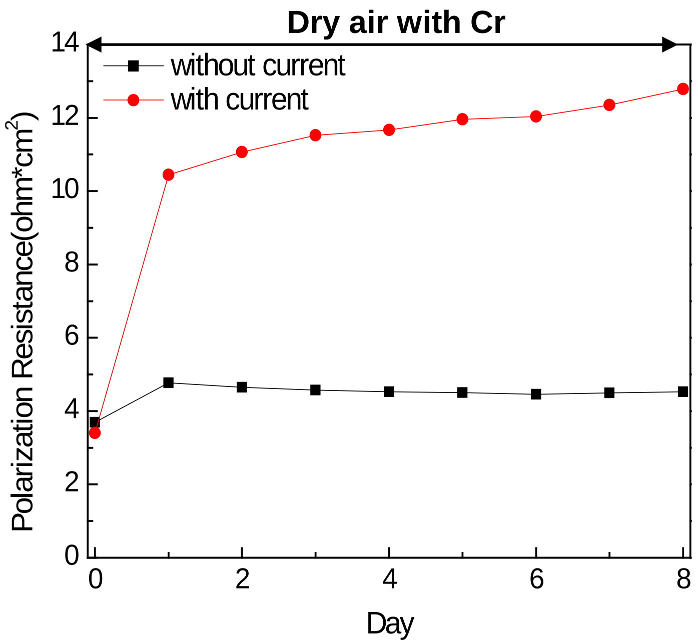


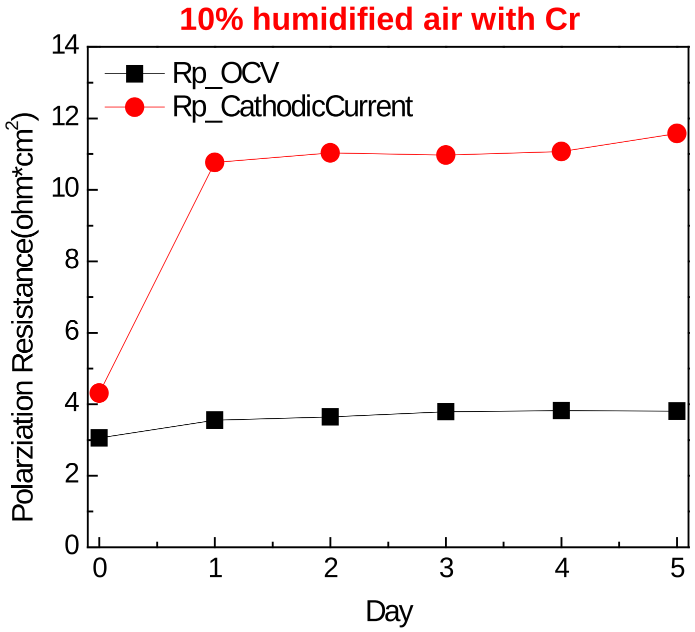
▲ **SEM micrograph of cell cross section**

Results & discussions

- Effect of Current
- Effect of Humidity
- Effect of Time under Cathodic Current
- Effect of Temperature

Effect of Current and Humidity (Cathode Polarization): Half-Cells

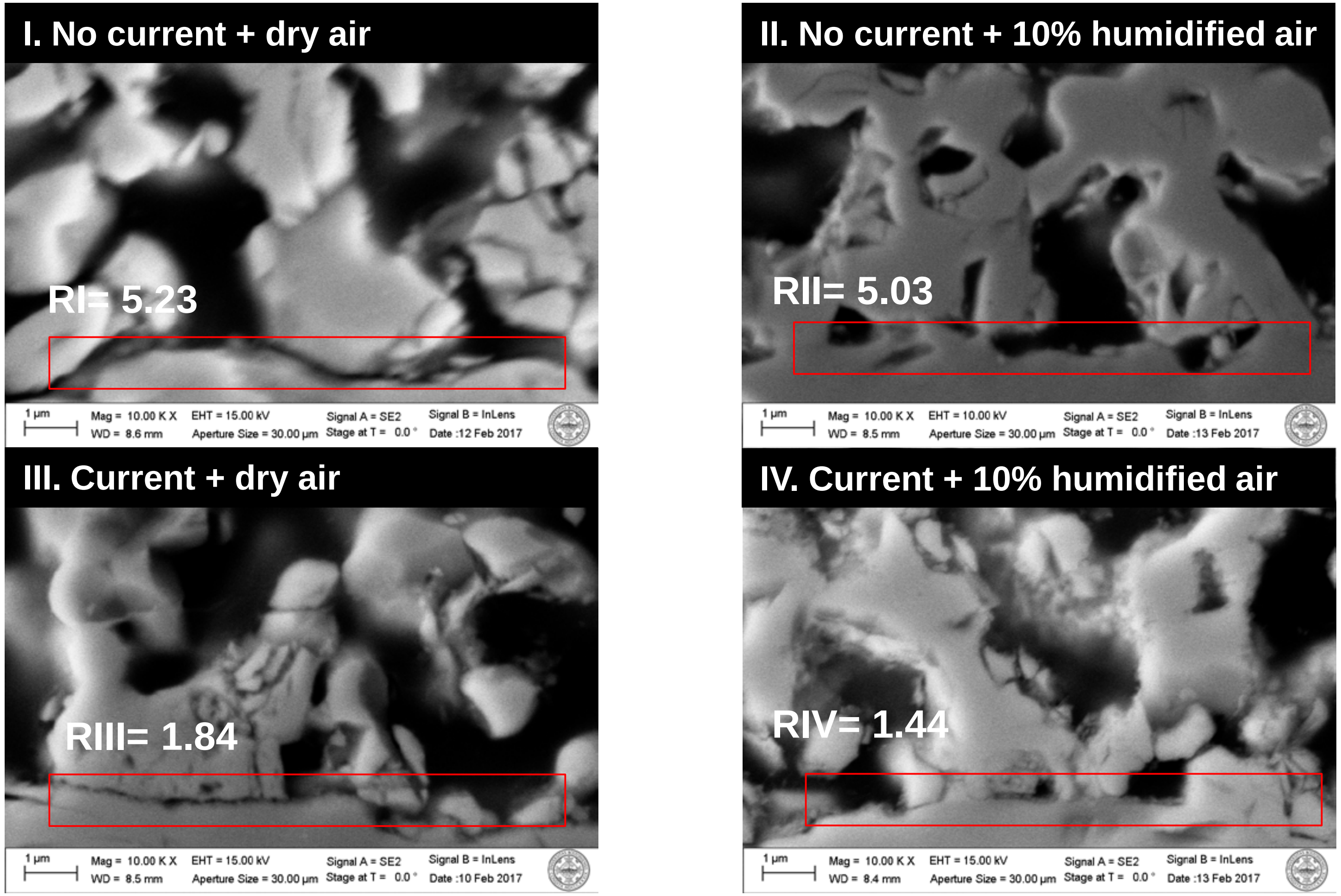




- **Without current:**
  - The polarization resistance was stable.
- **With current:**
  - The polarization resistance increased dramatically on the first day in dry air <u>and</u> 10% humidified air.

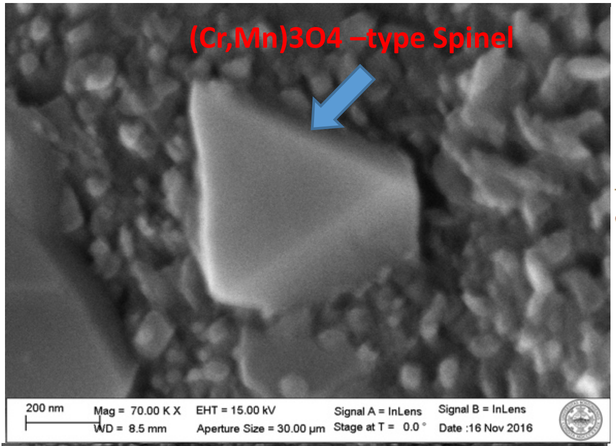
$$R = \frac{(La_{L\alpha} + Cr_{K\alpha})}{La_{L\alpha}}$$

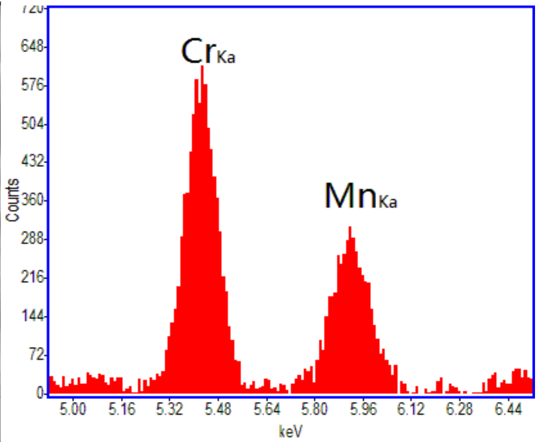
Microstructure-TPBs



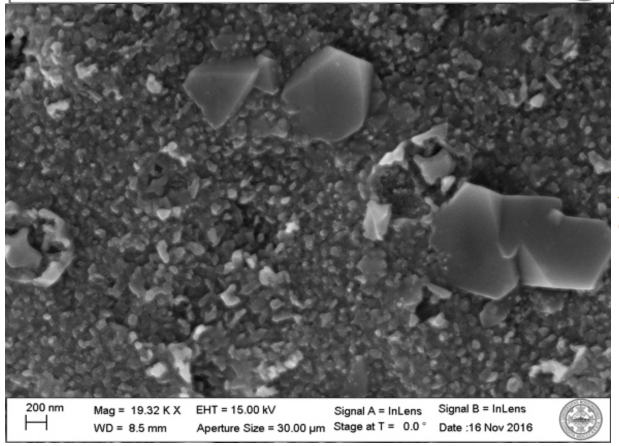
- $R_{I} < R_{II} < R_{III} < R_{IV}$
- Chromium deposition is heaviest in R_{IV}

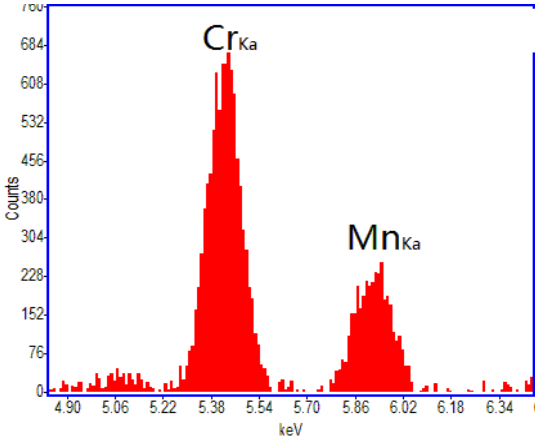
Cathode-Electrolyte Interface Microstructure after HCl Etching of Cathode (Half Cells)





- The faceted grains: $Mn(Mn,Cr)_2O_4$[1]
- The atomic ratio Cr:Mn = 2 on the large grains



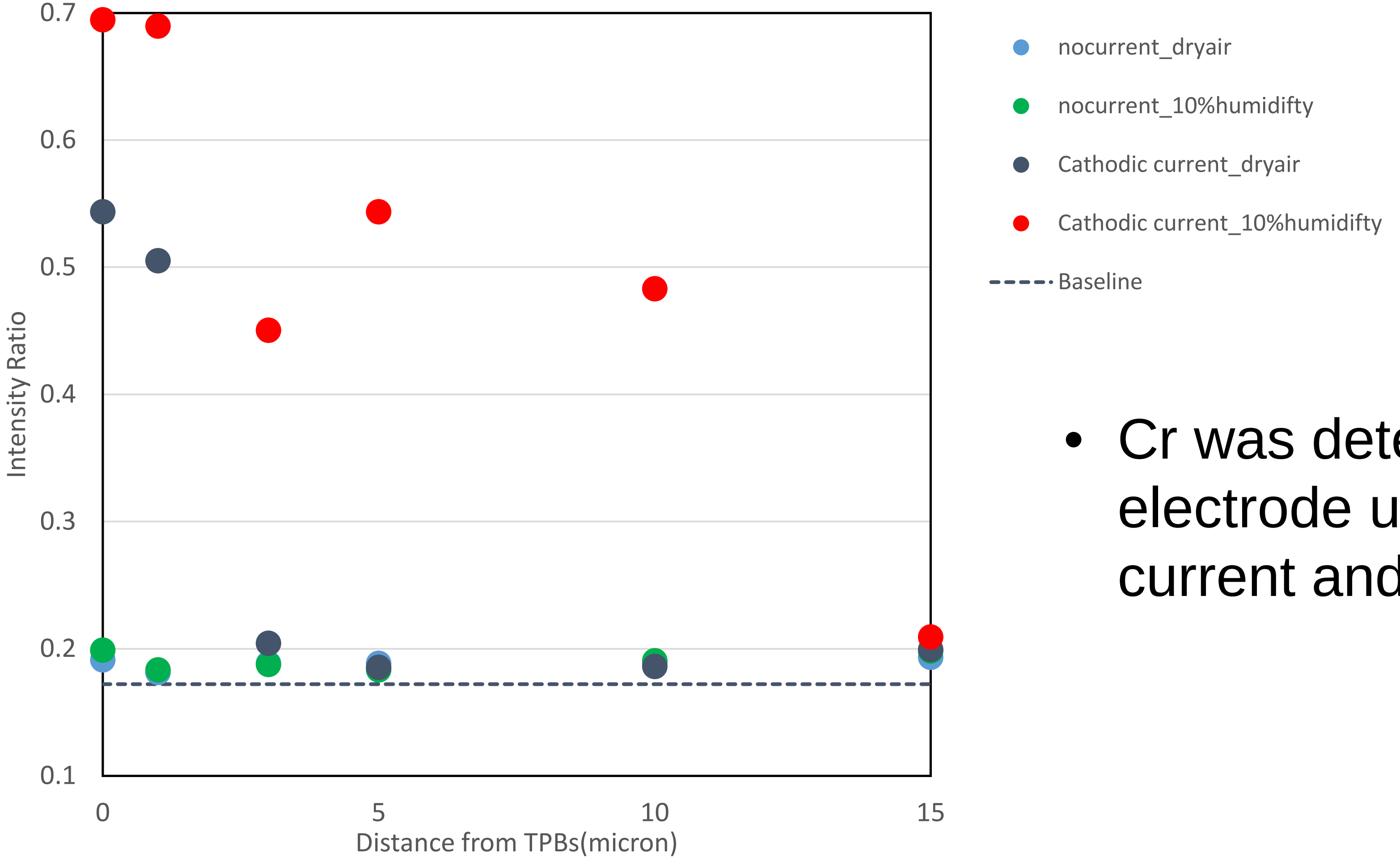


- The atomic ratio Cr:Mn > 2 over the whole area.
- The small fine grains: Cr-rich

$(Cr,Mn)_3O_4$ and Cr-rich phase such as Cr_2O_3 could be detected.

1. Badwal S P S, Deller R, Foger K, et al. Interaction between chromia forming alloy interconnects and air electrode of solid oxide fuel cells[J]. Solid State Ionics, 1997, 99(3-4): 297-310.

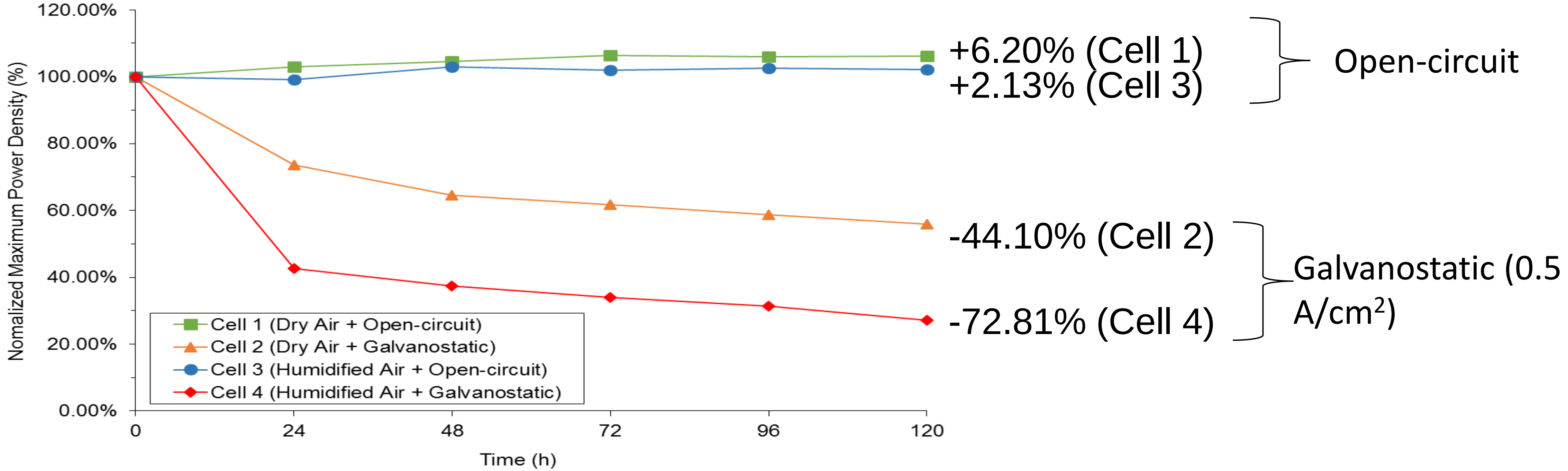
Post Test Microstructure (Half-Cells)



$$R = \frac{(La_{L\alpha} + Cr_{K\alpha})}{La_{L\alpha}}$$

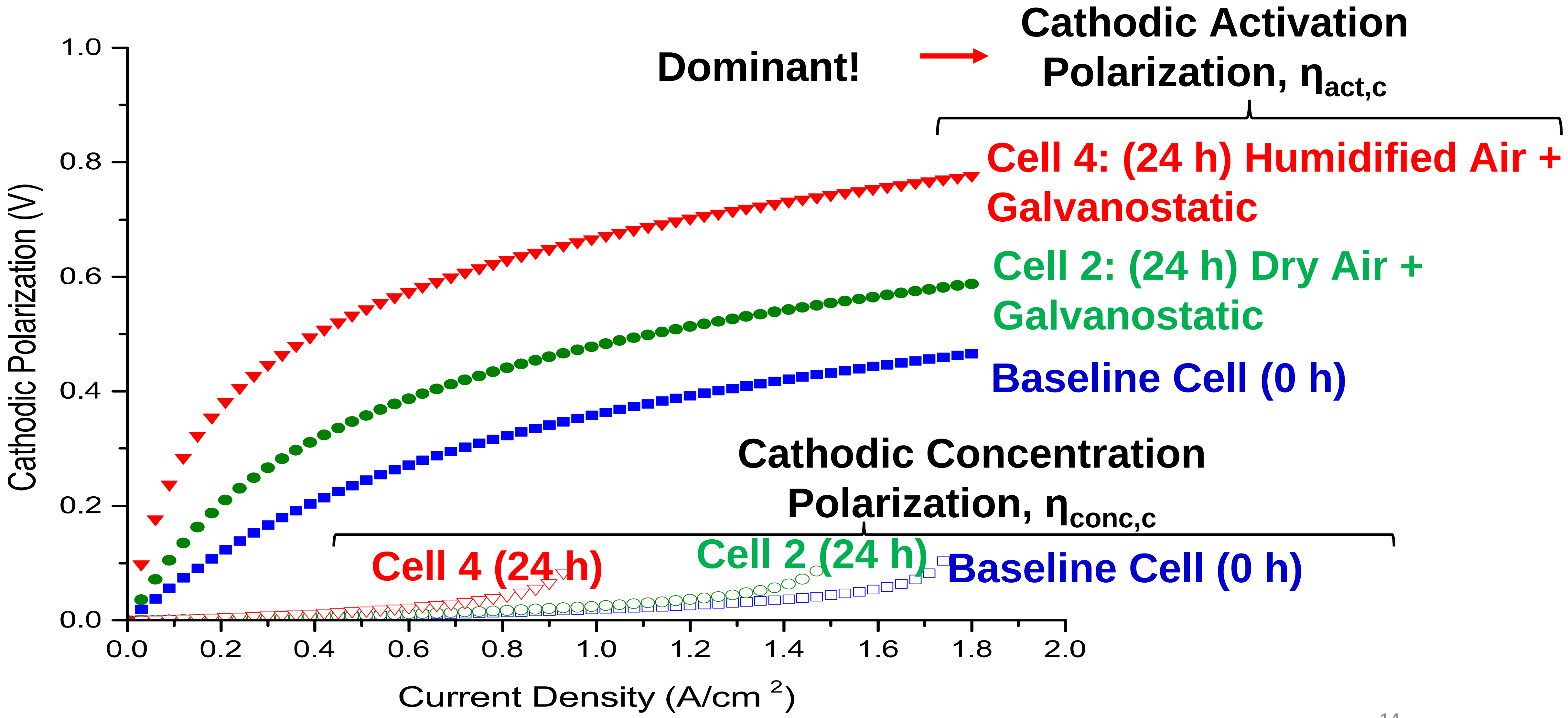
- Cr was detected over the whole electrode under cathodic current and 10% humidified air

Effect of Current and Humidity (Cathode Polarization): Complete Cells



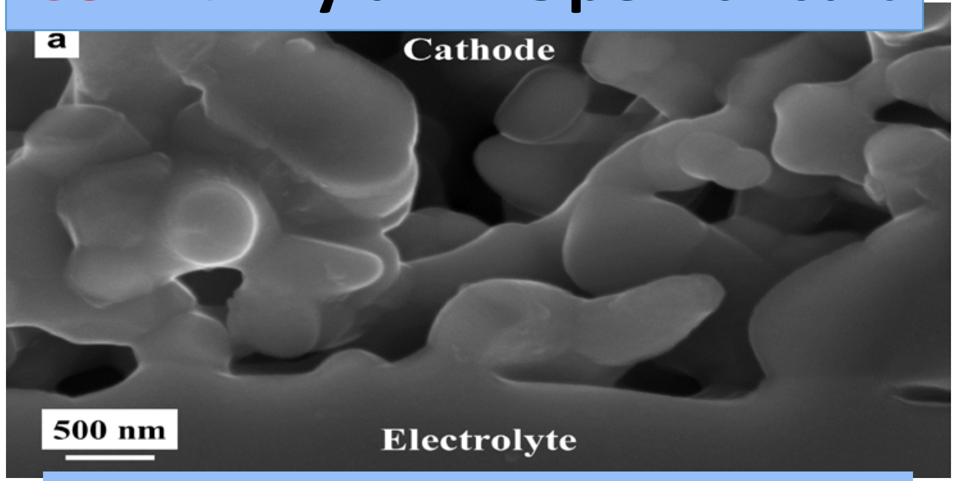
- Rate of degradation: Cell 4 > Cell 2 > Cell 3 ≥ Cell 1
- Degradation appeared to occur significantly when constant current was applied.
- Humidity appeared to promote the performance degradation.

Cathode Polarization Losses (Complete Cells)

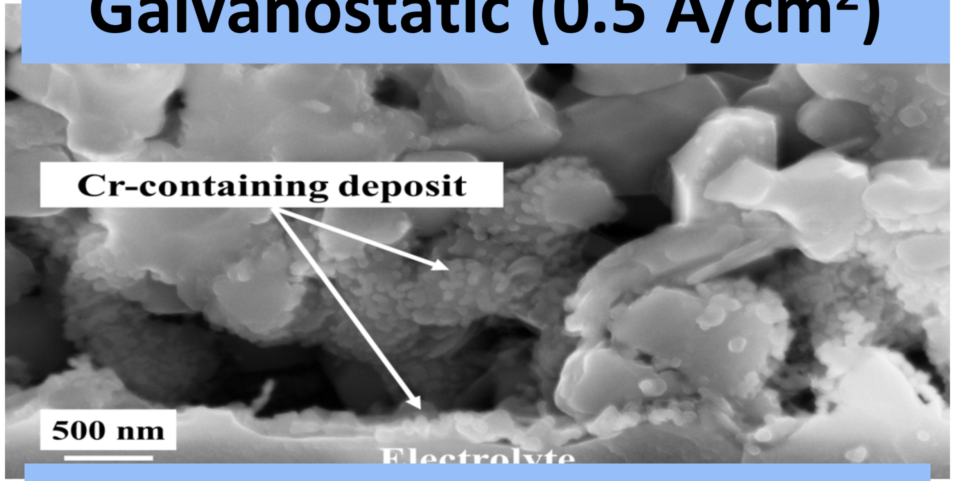


Post-Test Microstructure Characterization (SEM)

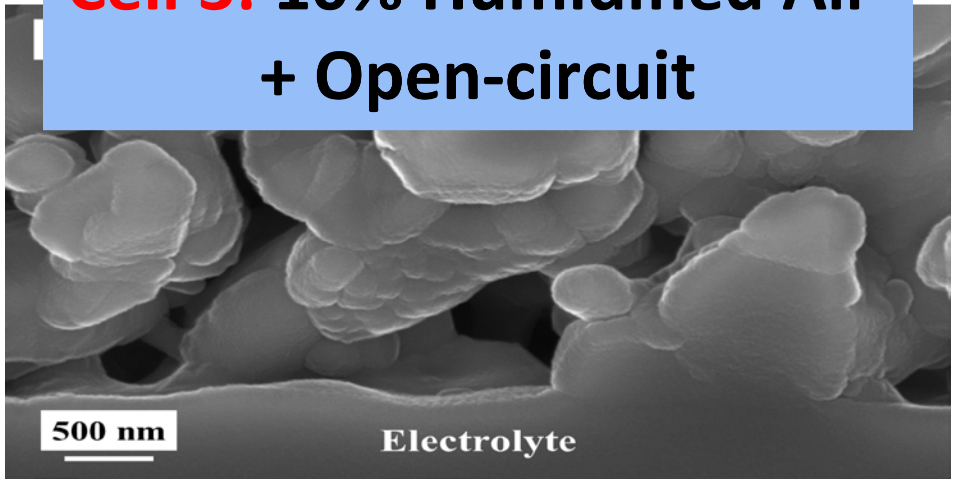
Cell 1: Dry air + Open-circuit



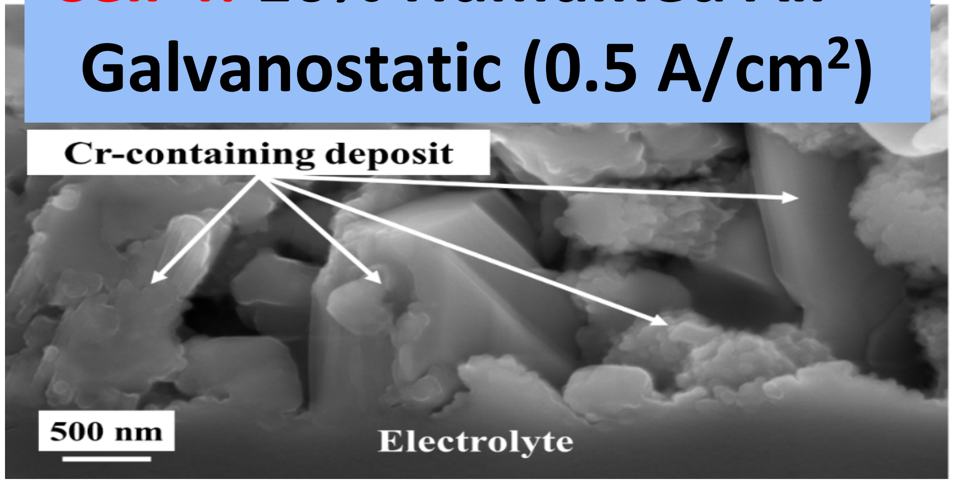
Cell 2: Dry air + Galvanostatic (0.5 A/cm^2)



Cell 3: 10% Humidified Air + Open-circuit

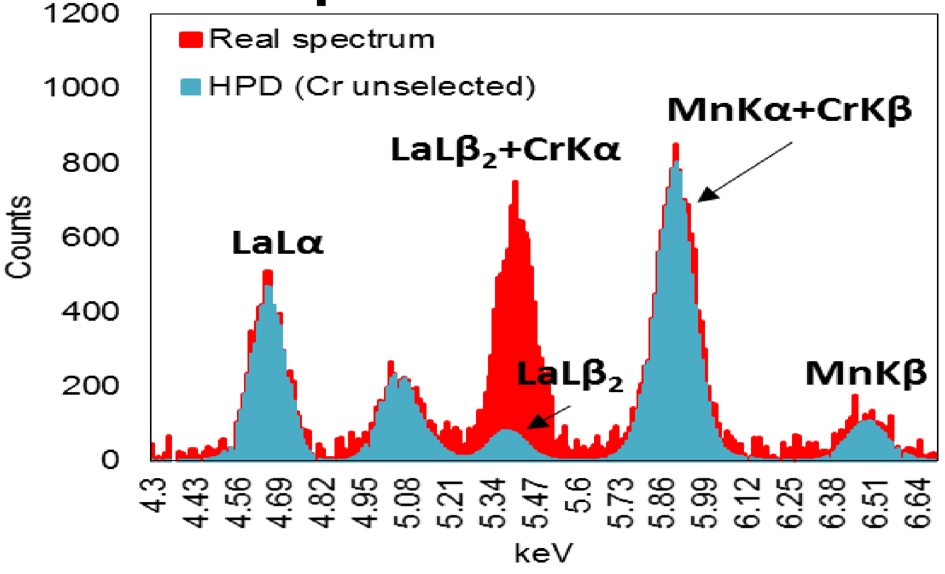


Cell 4: 10% Humdified Air + Galvanostatic (0.5 A/cm^2)



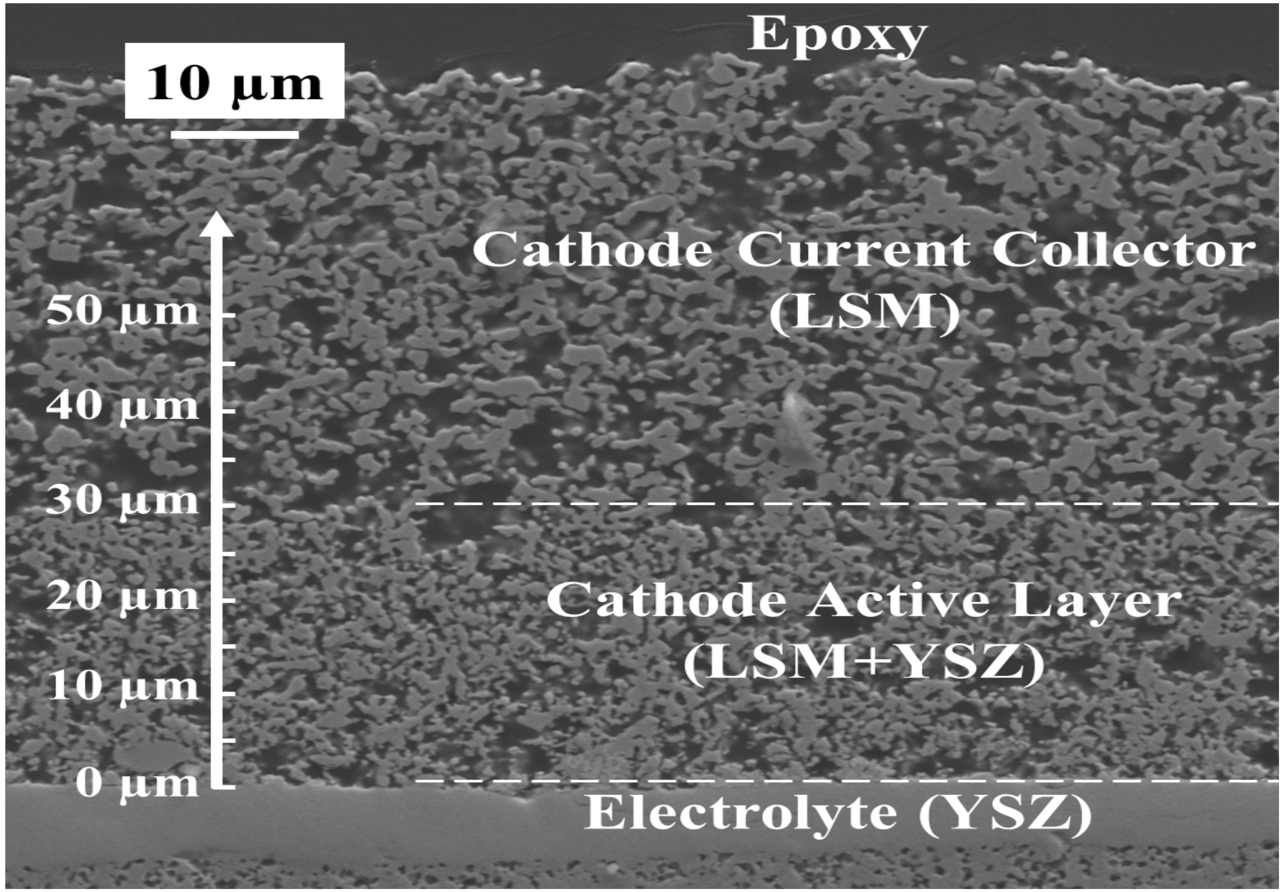
Post-Test Microstructure Characterization (EDX)

Example: A Spectrum of Cr-poisoned Cathode



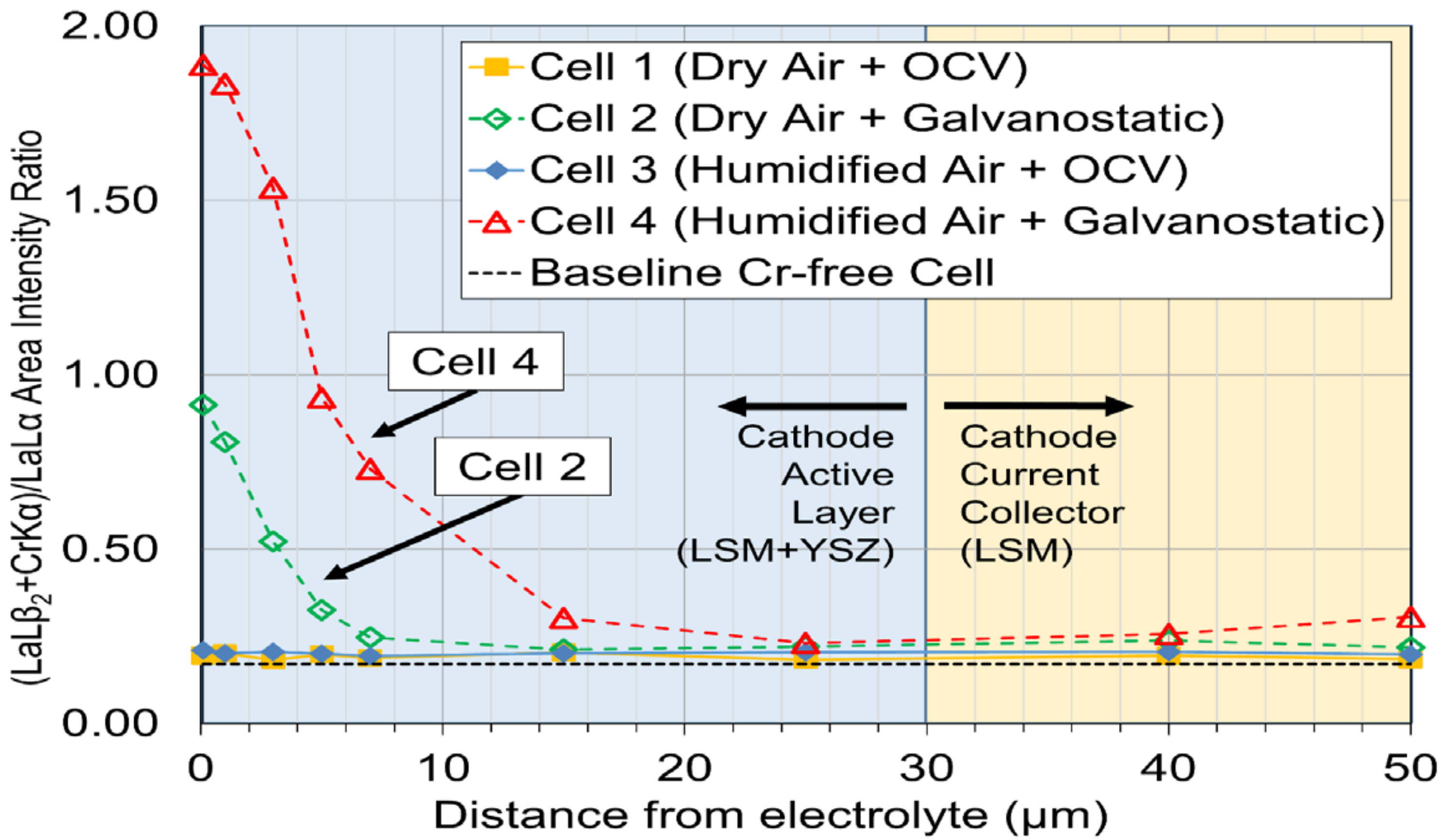
- **Metric for Cr deposition:**

Intensity Ratio: $\frac{LaL_{\beta2}(+CrK_{\alpha})}{LaL_{\alpha}}$



Area intensity ratios were measured at different cathode distances from the electrolyte.

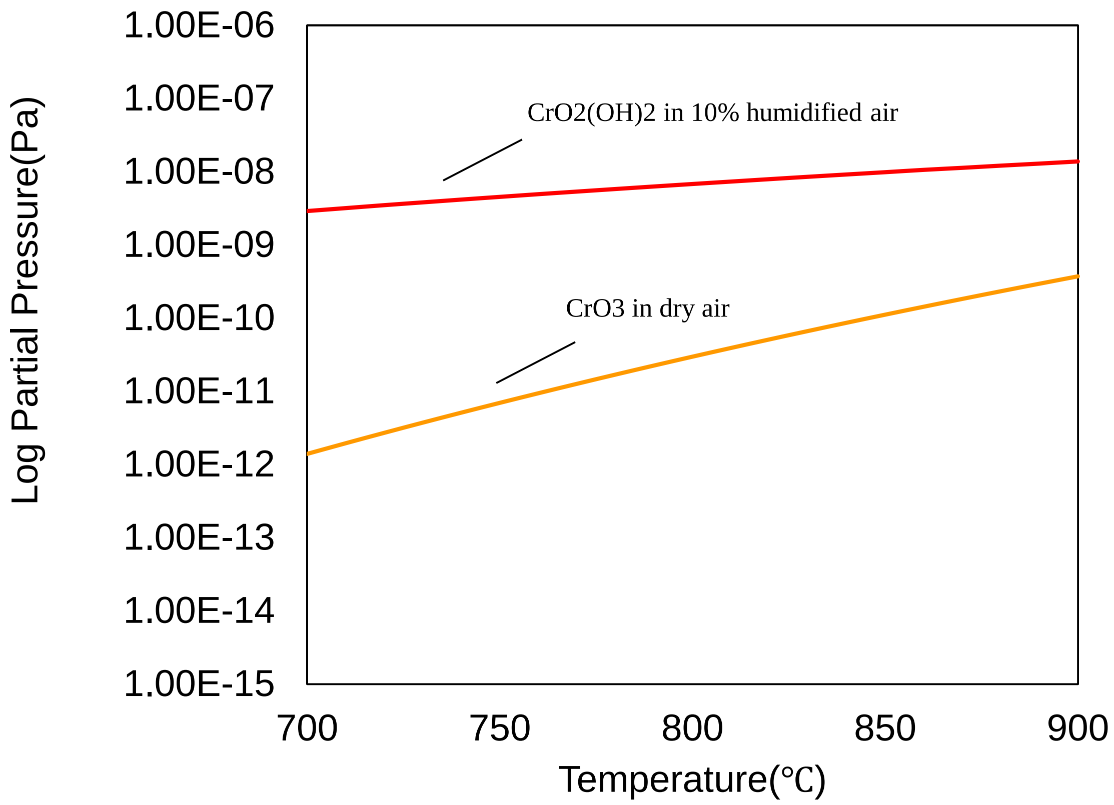
Post-Test Microstructure Characterization (EDX)



- Cr intensity at cathode/electrolyte interface: Cell 4 > Cell 2 > Cell 3 ≈ Cell 1

- Cr deposition was promoted by current and extended to TPB's away from the electrolyte.

The Effect of Humidity

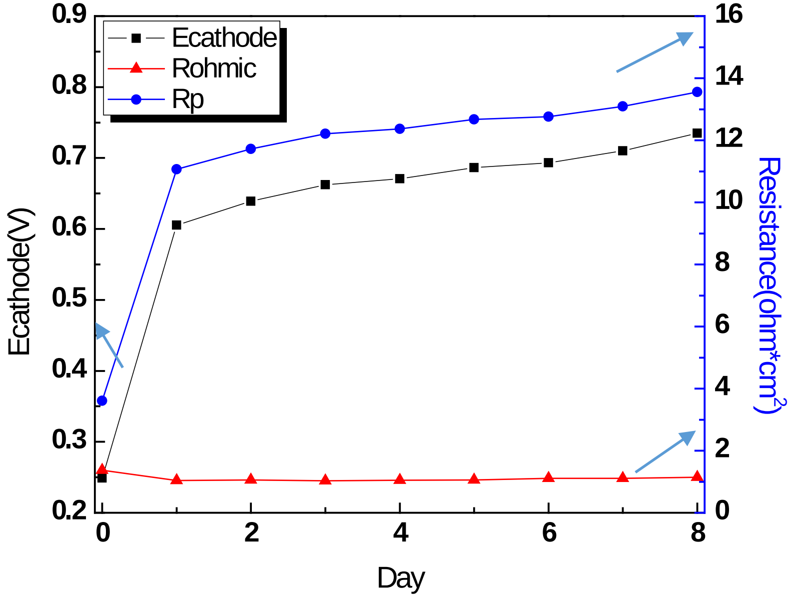


Vapor pressures of major chromium vapor species in air from thermodynamic calculation

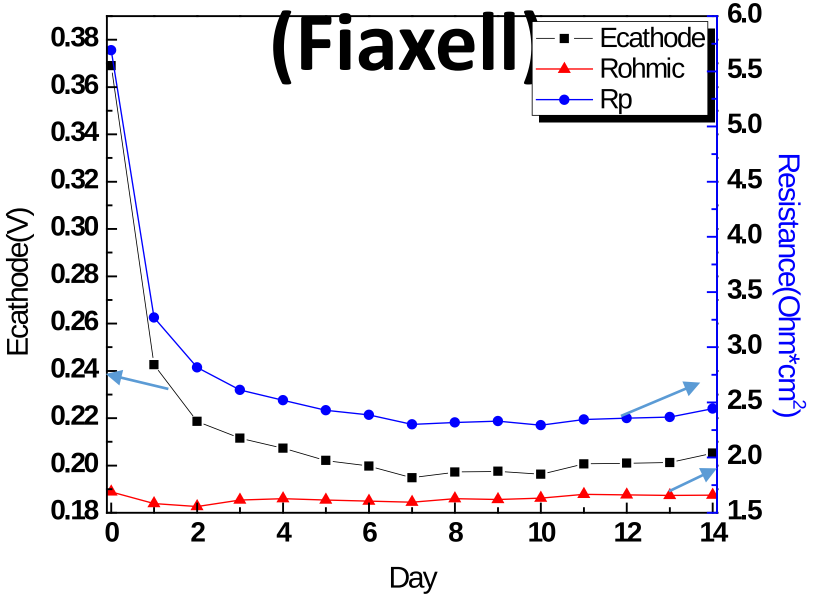
- The vapor pressure of the oxy-hydroxide is greater by a factor of 100 to 10000.

Effect of Protective Coating: Half-Cells

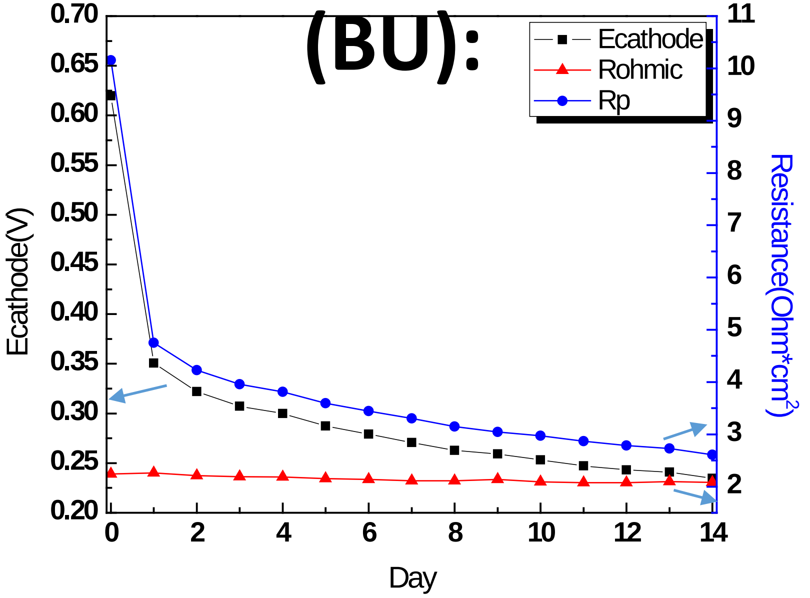
No coating



$CuMn_2O_4$ coating (Fiaxell)



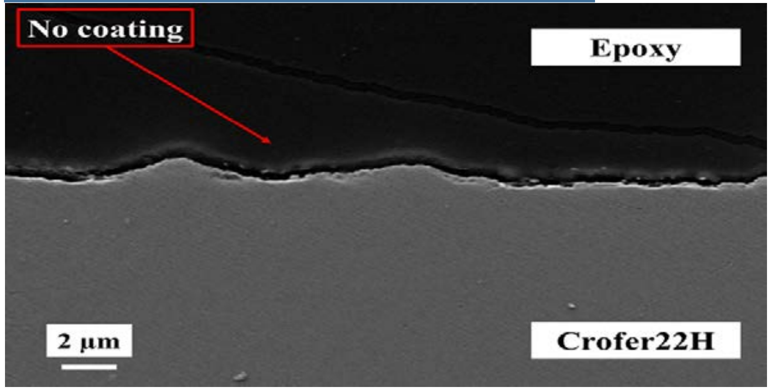
$CuMn_{1.8}O_4$ coating (BU):



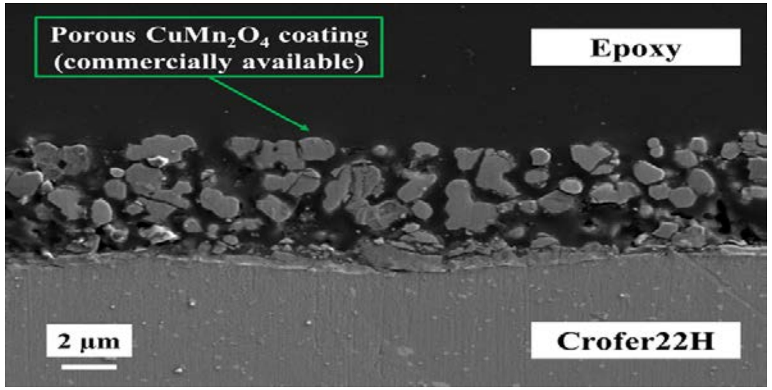
- **No coating :** Major degradation of performance was observed once the cathodic constant current was applied.
- **$CuMn_2O_4$ coating (Fiaxell):** Minor degradation was observed after the 240 hours’ current was applied.
- **$CuMn_{1.8}O_4$ coating (BU):** No degradation was observed during the 14-day test.

Effects of Protective Coating: Complete Cells

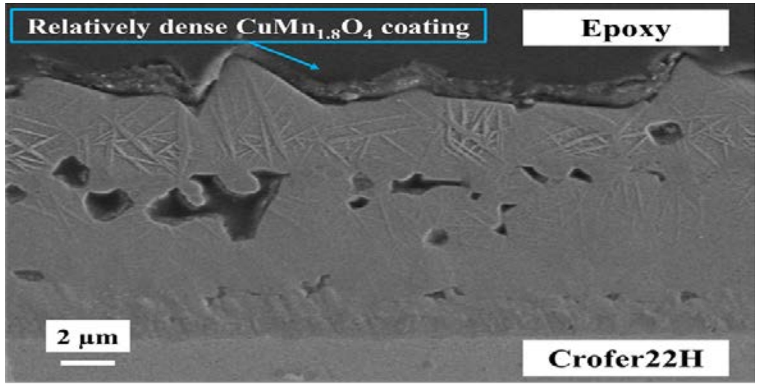
(a) No Coating



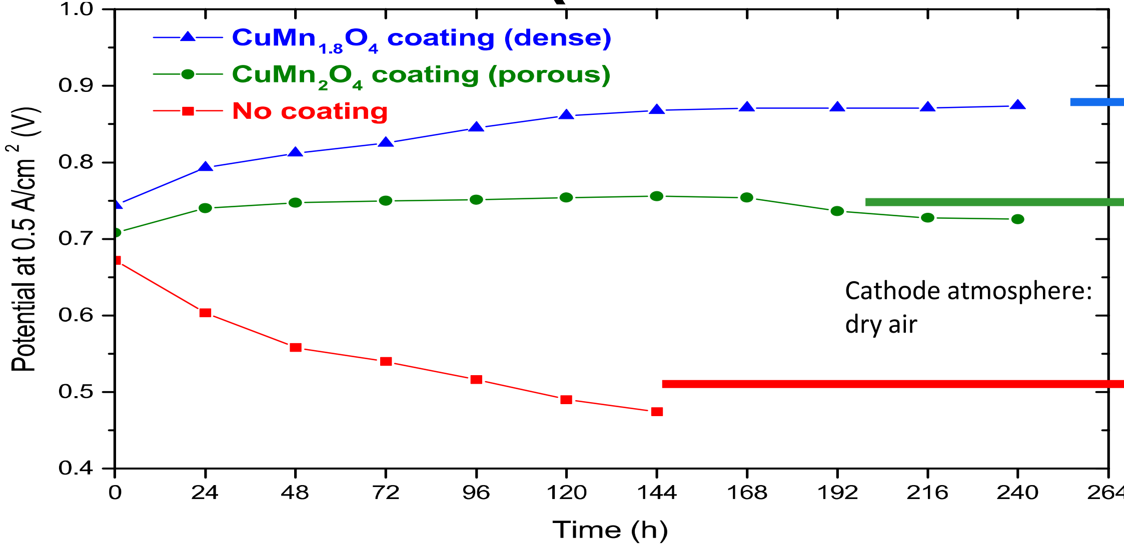
(b) Commercial (Fiaxell) $CuMn_2O_4$ Spinel Coating



(c) BU $CuMn_{1.8}O_4$ Spinel Coating



- Cell Performance (Potential at 0.5 A/cm^2) as a Function of Time:



No observable degradation

Degradation after Cr gettering capacity of coating exhausted

Degradation was observed from the begining

Electrophoretic Deposition of Protective Coatings

Electrophoretic Deposition of $CuMn_{1.8}O_4$ coatings

Deposition Process

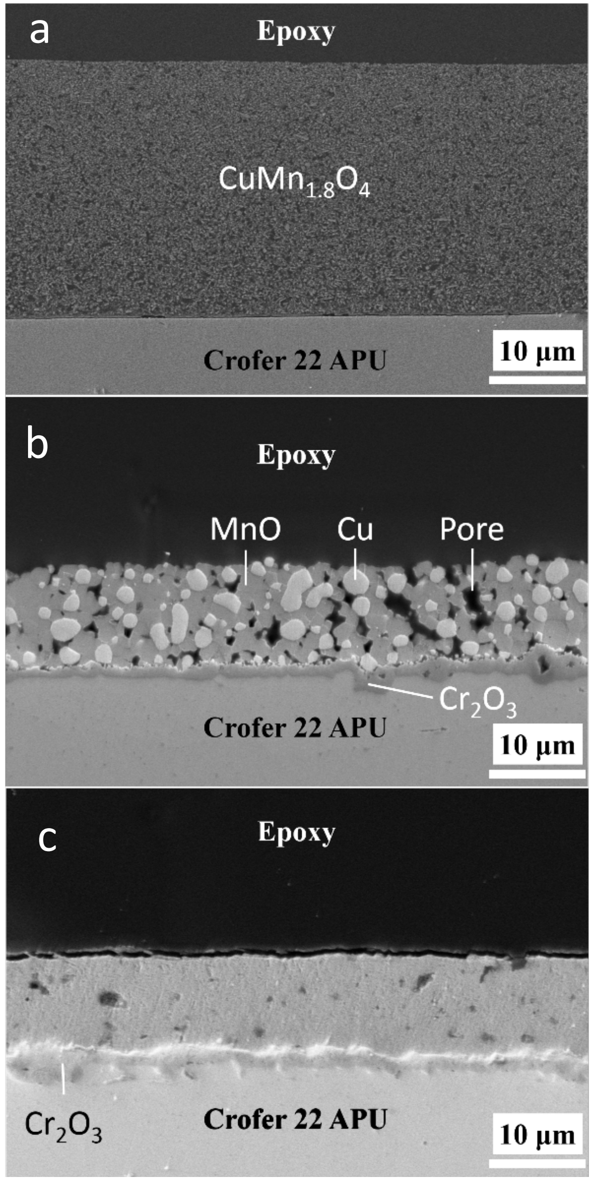
EPD

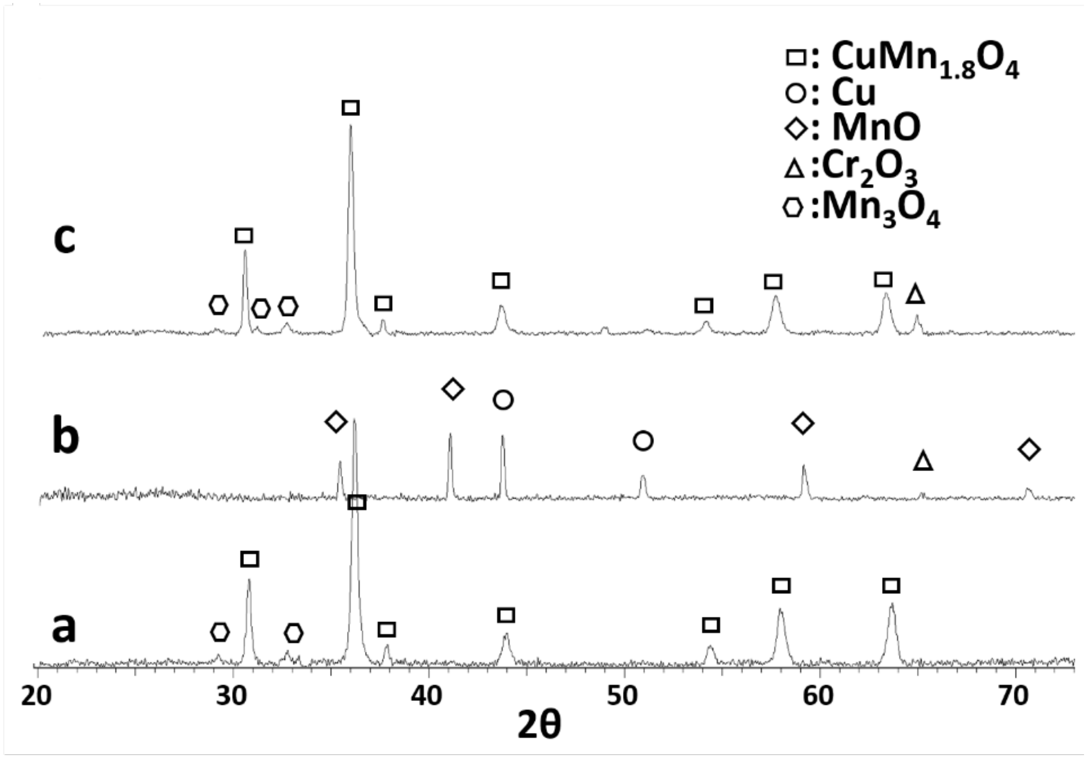
↓

Reduction annealing (1000 °C, 24 h)

↓

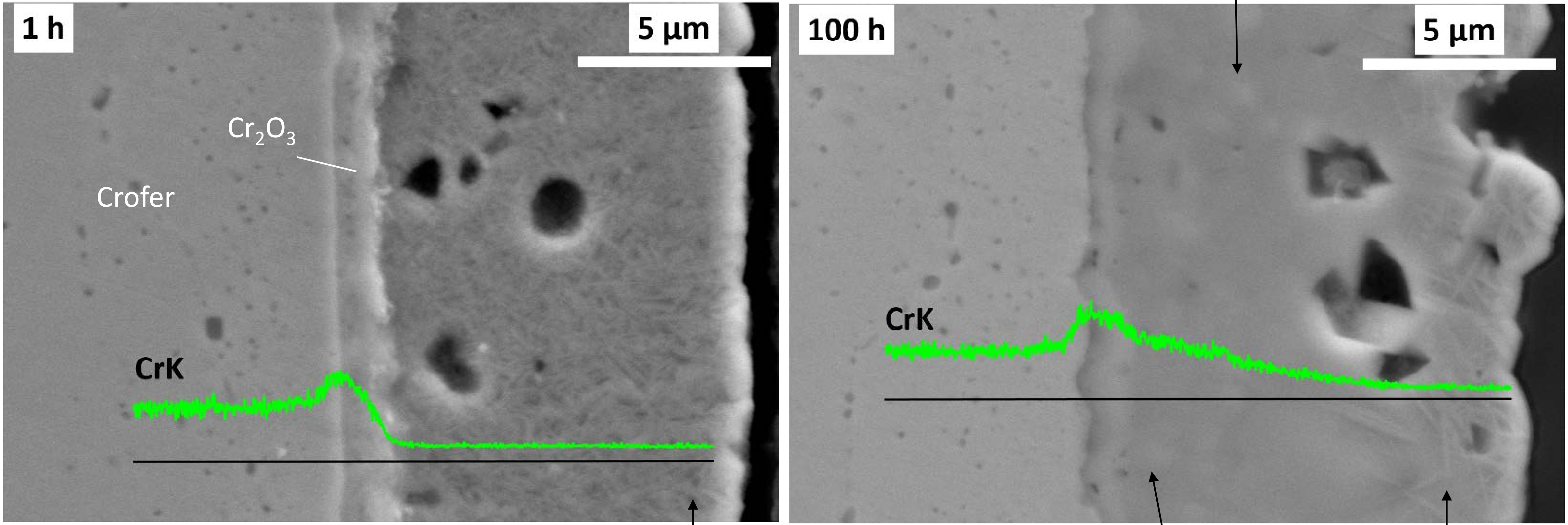
Oxidation annealing (850 °C, 1 h)



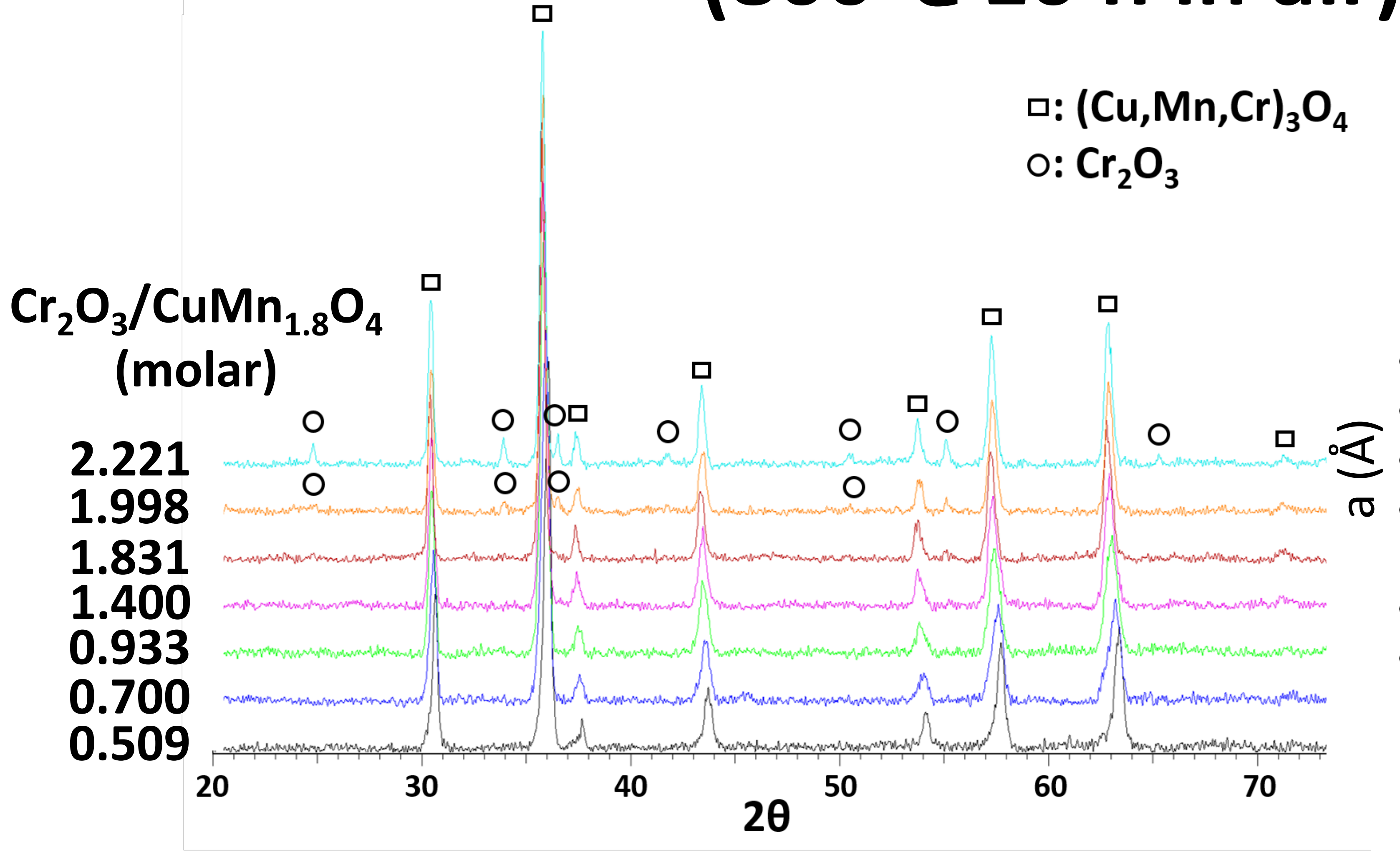


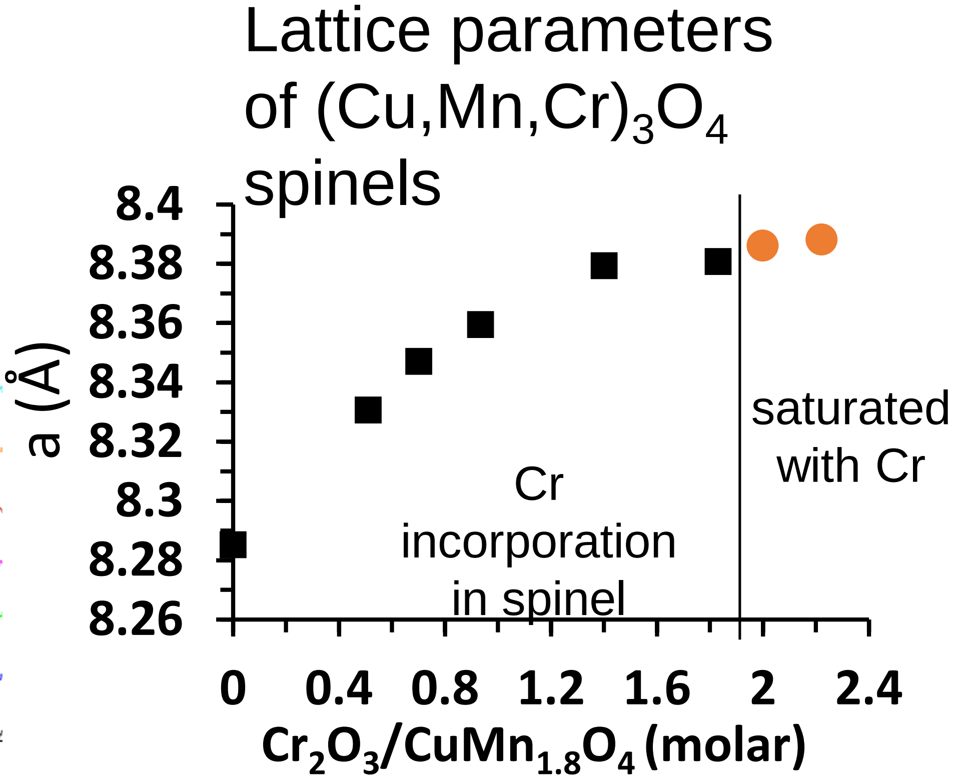
XRD: a) $CuMn_{1.8}O_4$ powders
b) after reduction anneal
c) after 1h oxidation anneal

Microstructure evolution during oxidation at 850ºC



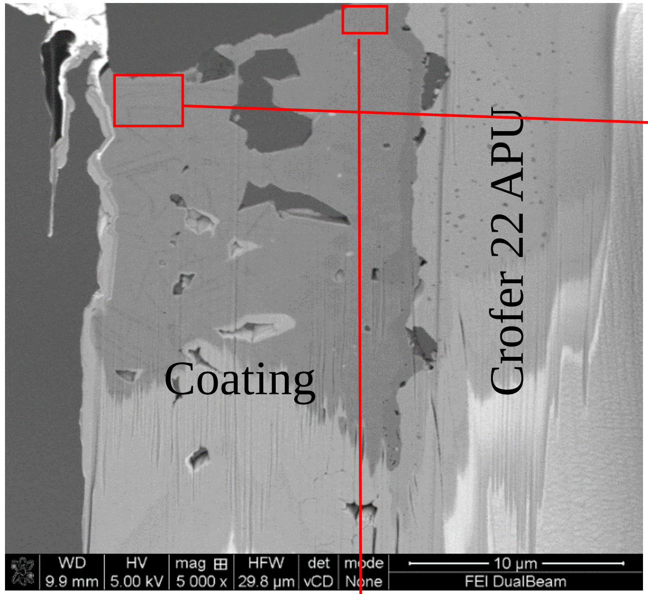
Reaction between $CuMn_{1.8}O_4$ and Cr_2O_3 (800℃ 10 h in air)





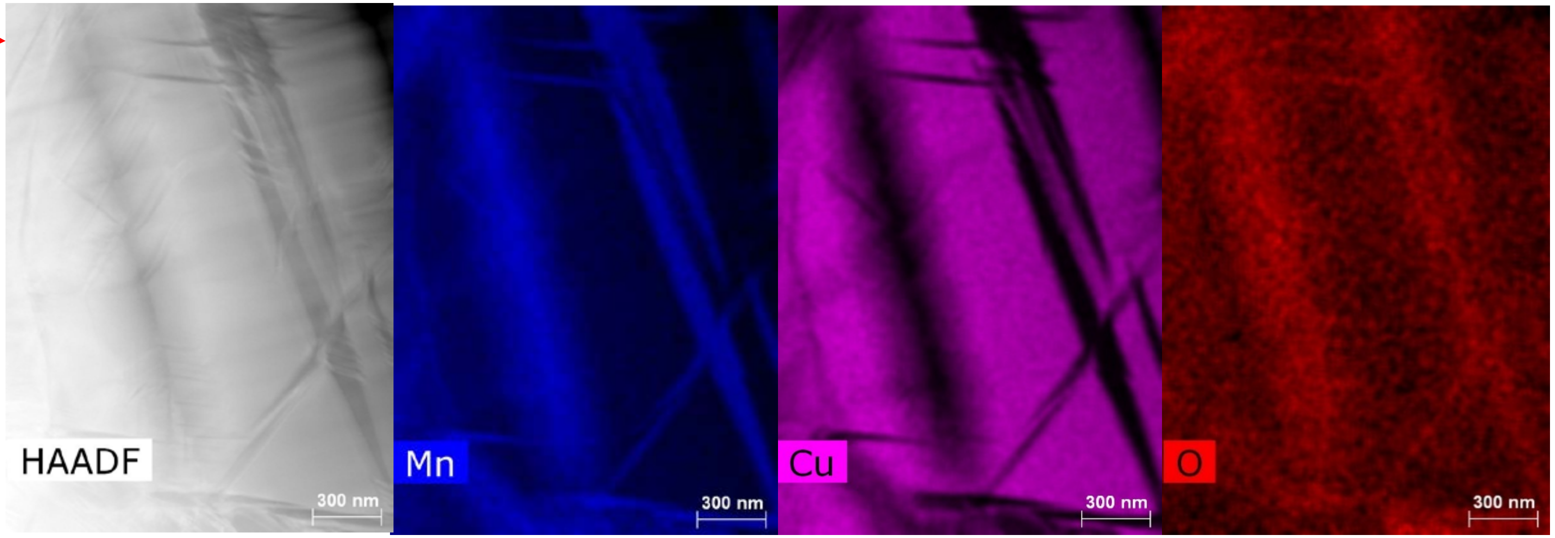
One mole of $CuMn_{1.8}O_4$ can getter ~ 2 moles of Cr_2O_3

TEM analysis of coating

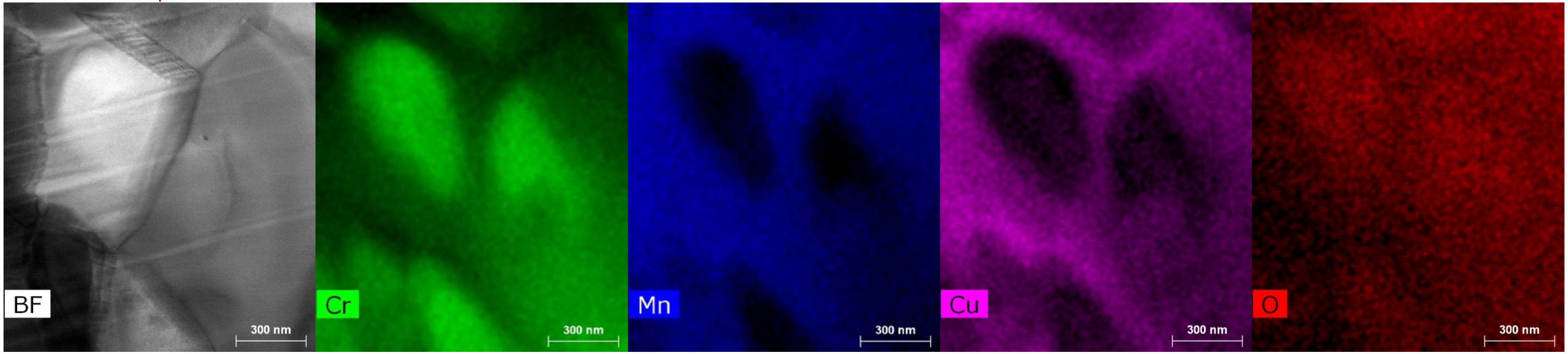


FIB-based cross sectional TEM sample

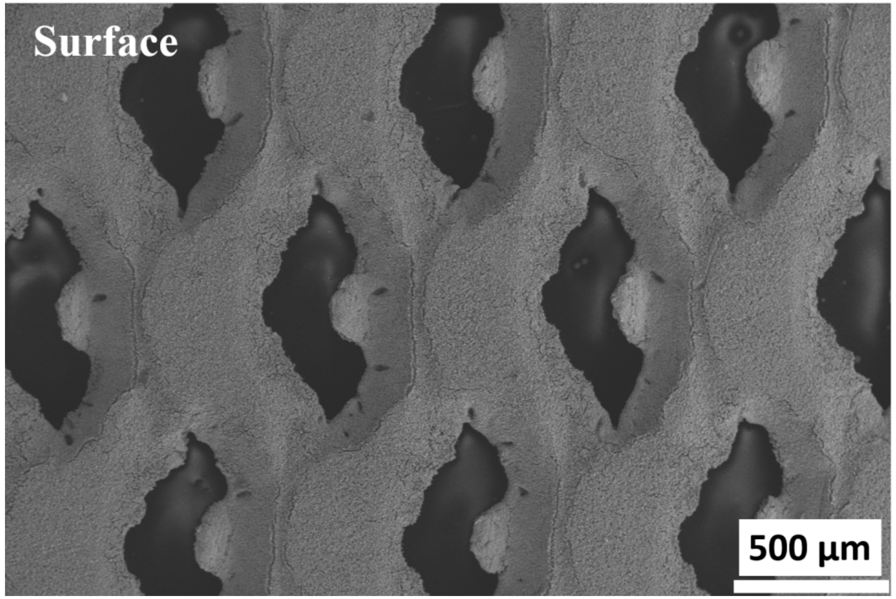
Needle structures: Mn-rich

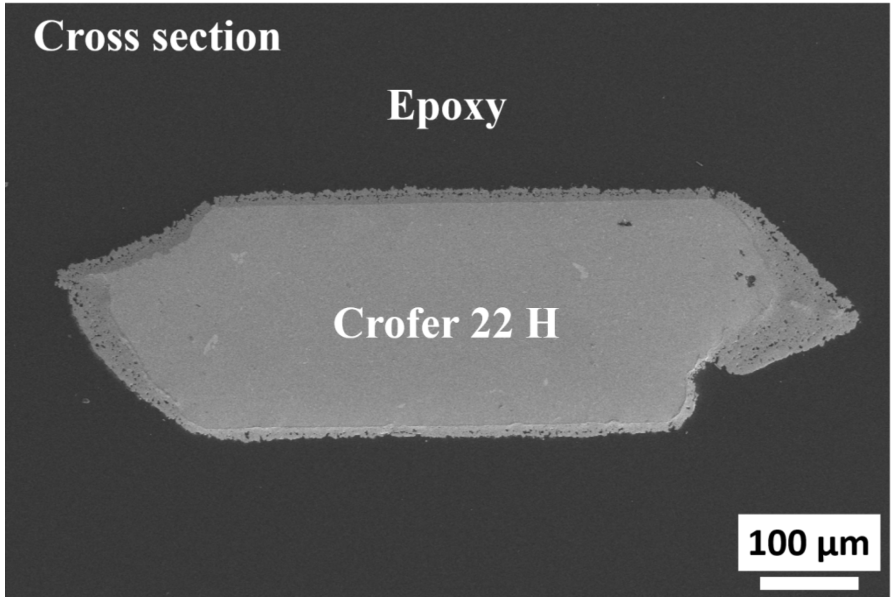


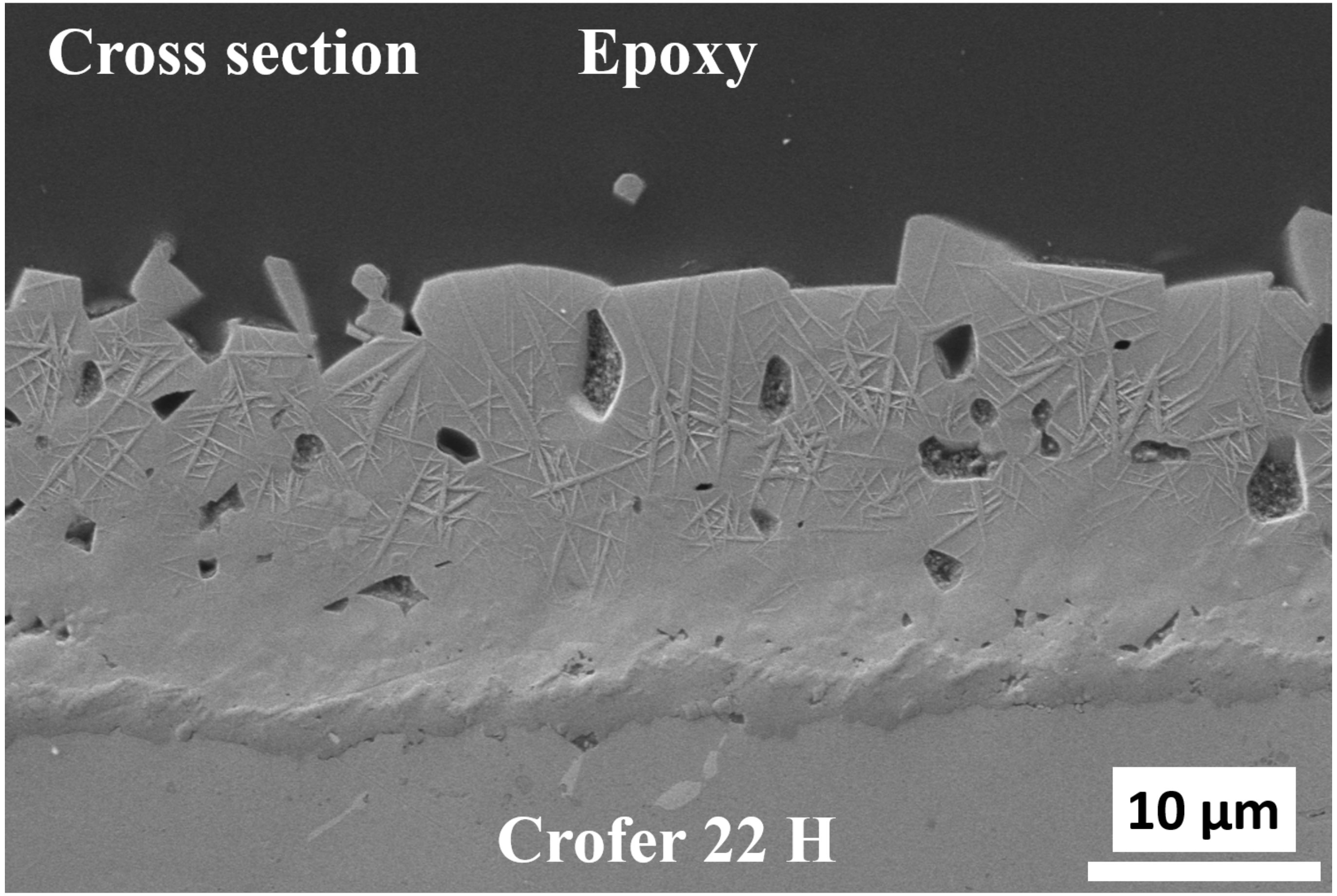
Particles in dense layer: Cr_2O_3



Coating on complex geometry (Crofer mesh)

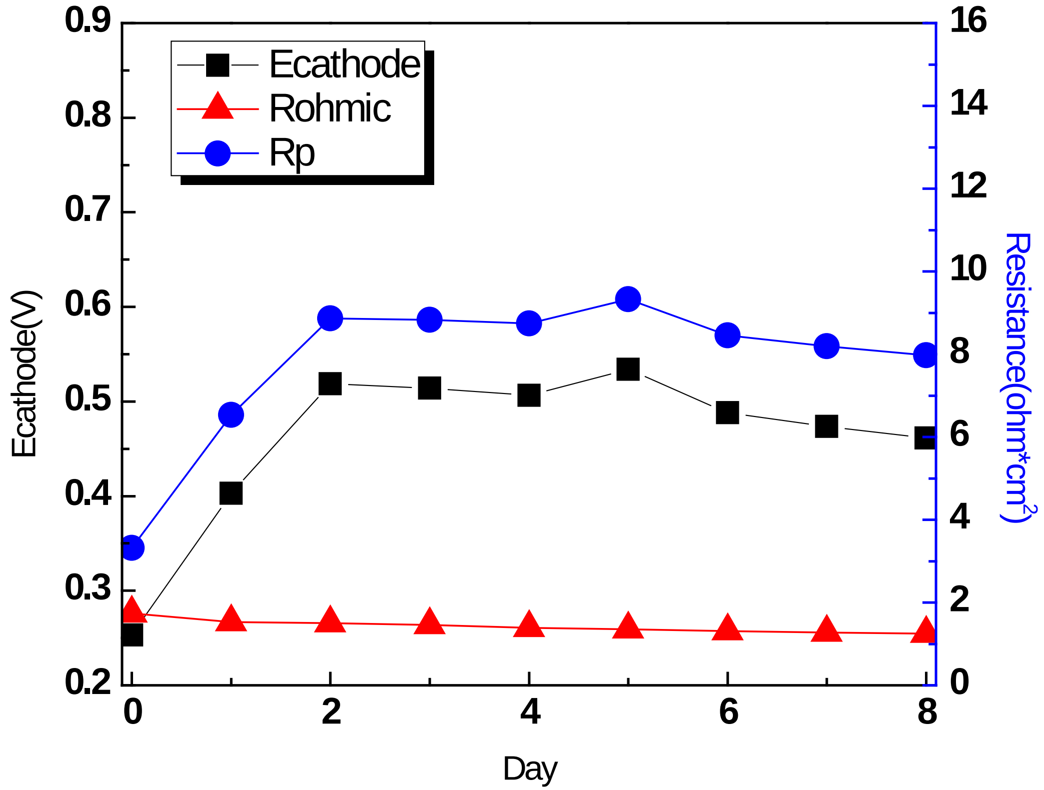




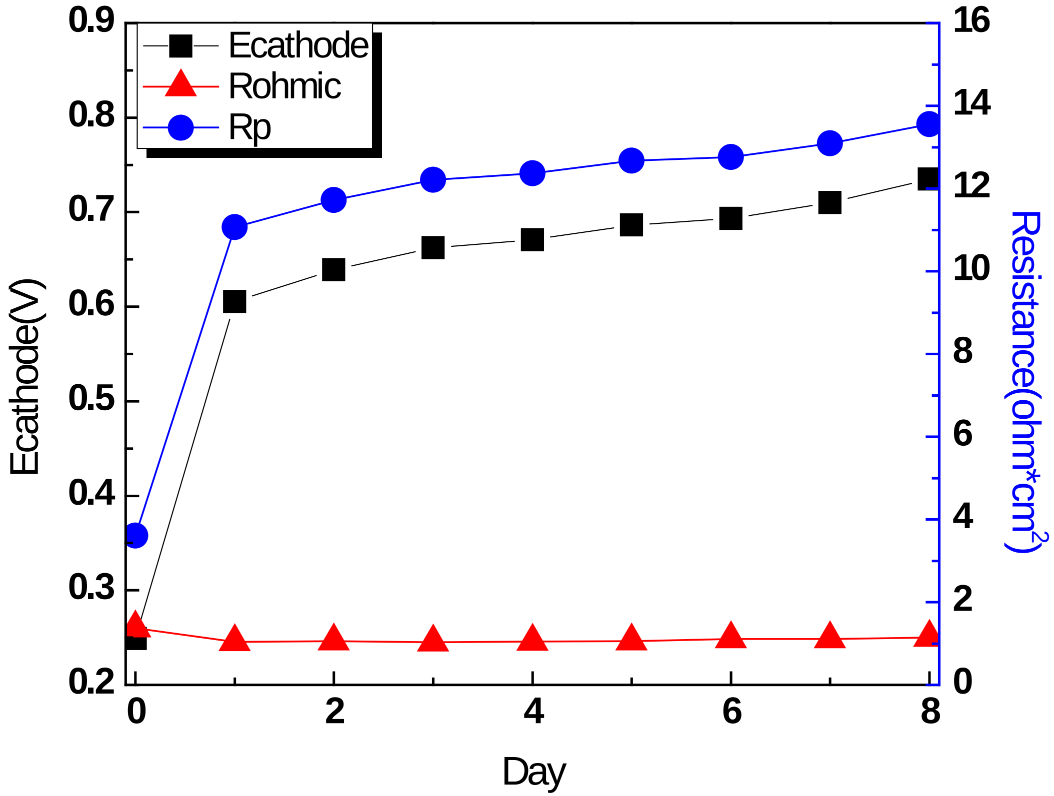


Ongoing Work: Cathode Compositional Modifications (Half Cells)

$(La_{0.8}Sr_{0.2})_{0.95}Cr_{0.2}Mn_{0.8}O_{3-\delta}$ cathode



$(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}$ cathode



- $(La_{0.8}Sr_{0.2})_{0.95}Cr_{0.2}Mn_{0.8}O_{3-\delta}$ cathode: The polarization resistance stabilized after 2 days' cathodic current.

- $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}$ cathode : The polarization resistance continued to increase after 8 days' cathodic current.

Summary and Conclusions

- Cr-impurity attack has been studied using half-cells and complete cells
- Cr-transport and attack occurs not only at TPBs, but also on internal pore surfaces in the cathode
- Attack occurs under cathodic polarization; magnified by humidity
- Can be mitigated/eliminated to a great extent by applying protective coatings on the interconnect
- Effective EPD technique has been developed – possible to apply dense conformal spinel coatings
- Cathode compositional modifications appear promising

Acknowledgments

- Financial support from DOE-NETL through contract # DE-FE0023325 is gratefully acknowledged
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- Useful discussions with Hossein-Ghezel Ayagh of FCE are acknowledged
- Experimental support from Yang Yu and Deniz Cetin is acknowledged