Mitigation of Chromium Impurity Effects and Degradation in Solid Oxide Fuel Cells

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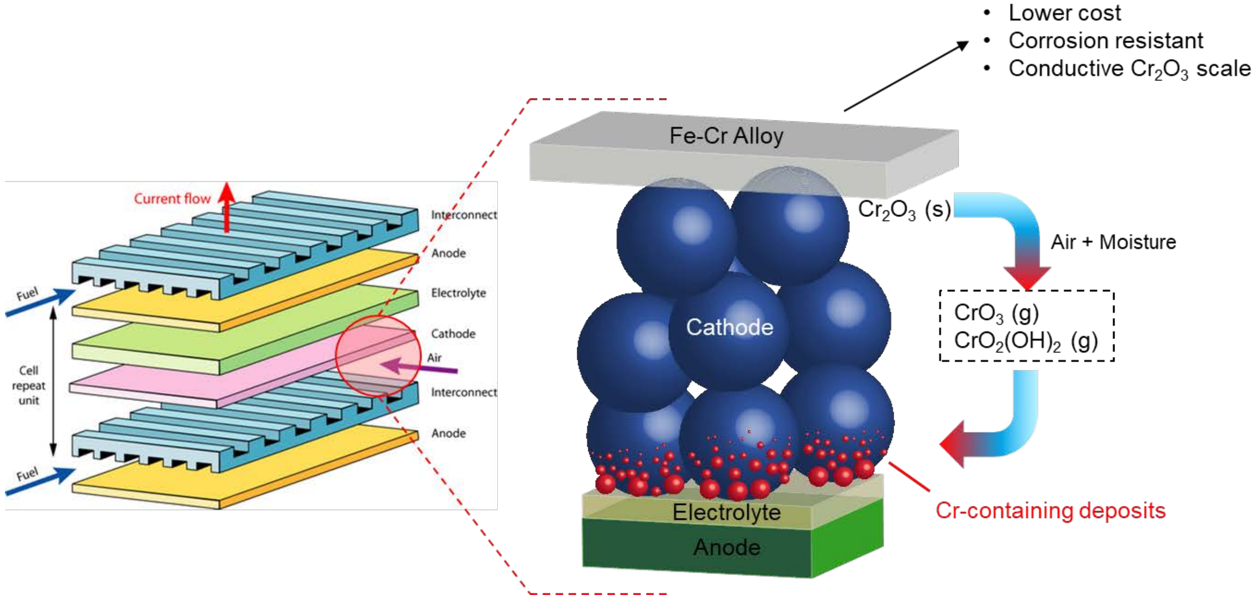
Outline

- Introduction
- Cell Fabrication
- Summary of Test Conditions
- Electrochemical Degradation
- Microstructural Evolution
- Degradation Mechanisms
- Development of Oxide Protective Coatings
- Summary

Introduction

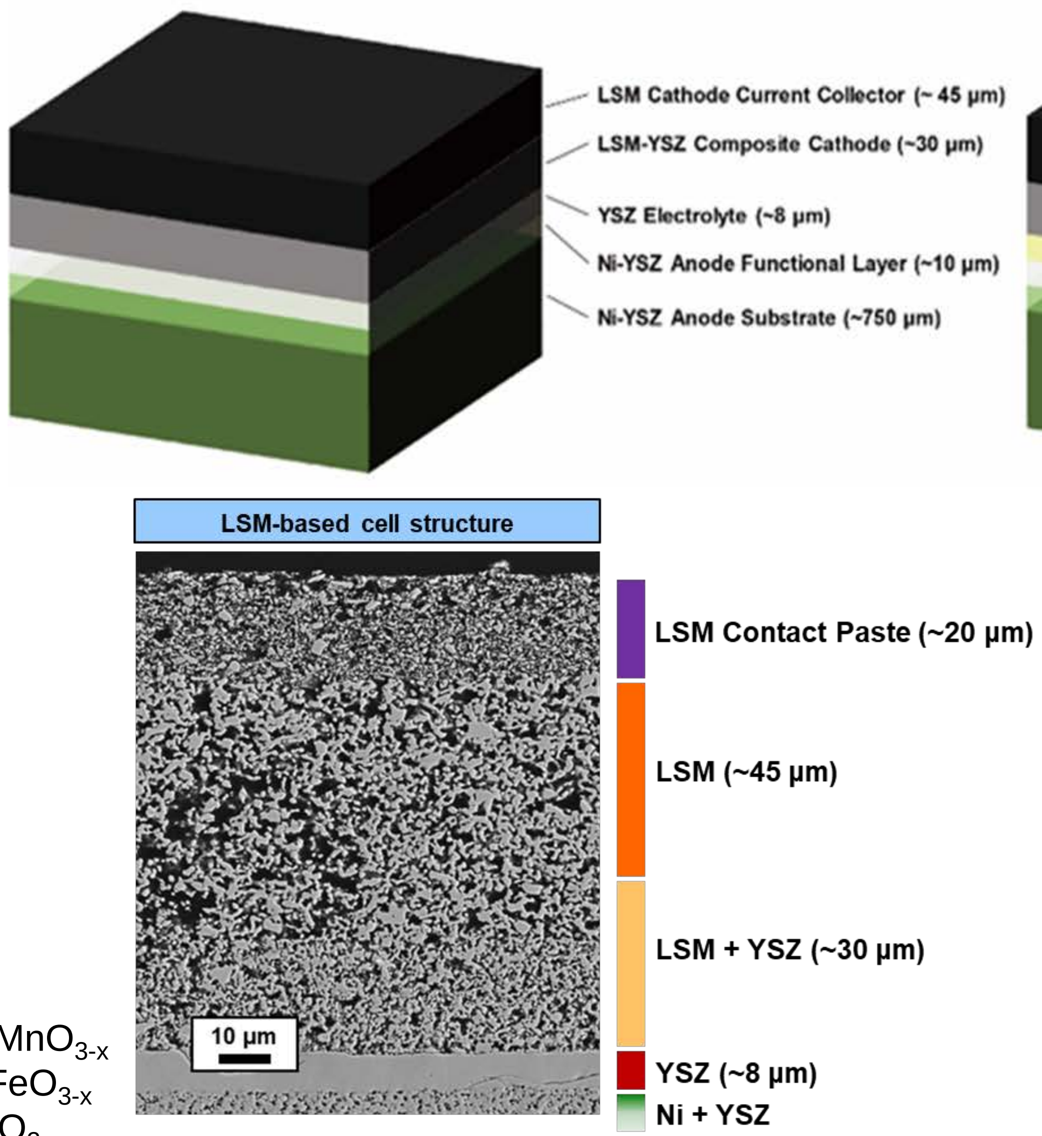
- **Background**

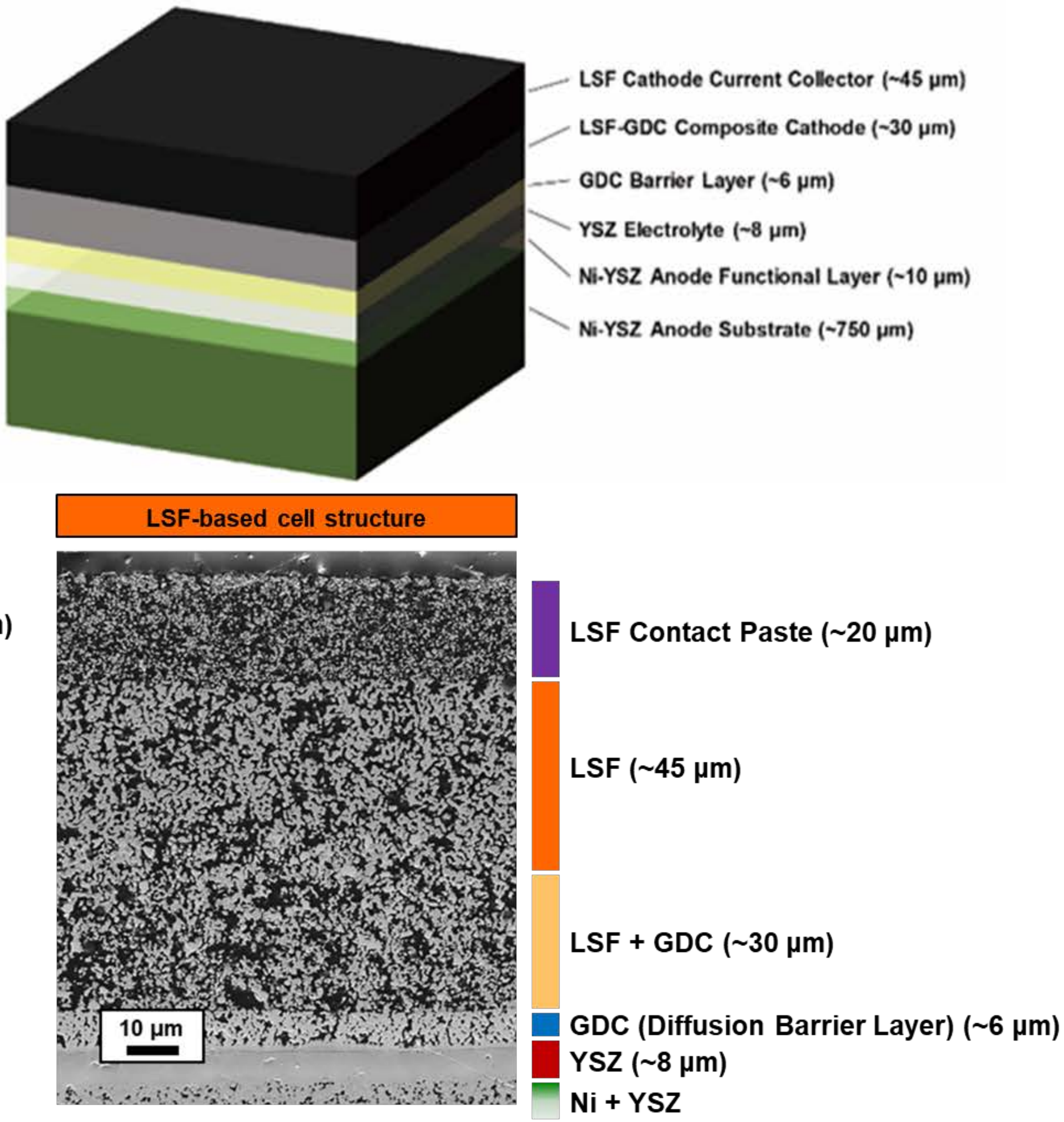


  - **Chromium (Cr) poisoning of cathode in solid oxide fuel cells (SOFCs) is considered to be one of the major reasons for performance degradation**
  - **For different cathode materials, the mechanisms of Cr-poisoning are complex.**

- **Project Goals**
  - **Compare the degradation phenomena in LSM, LSF, and LNO (La_2NiO_4) - based cathodes caused by Cr-poisoning**
  - **Through the comparative study, investigate the mechanisms of Cr-poisoning in these three types of cathodes in realistic full cell operating conditions**
  - **Design mitigating strategies based on applying protective coatings to ferritic stainless steel interconnects**

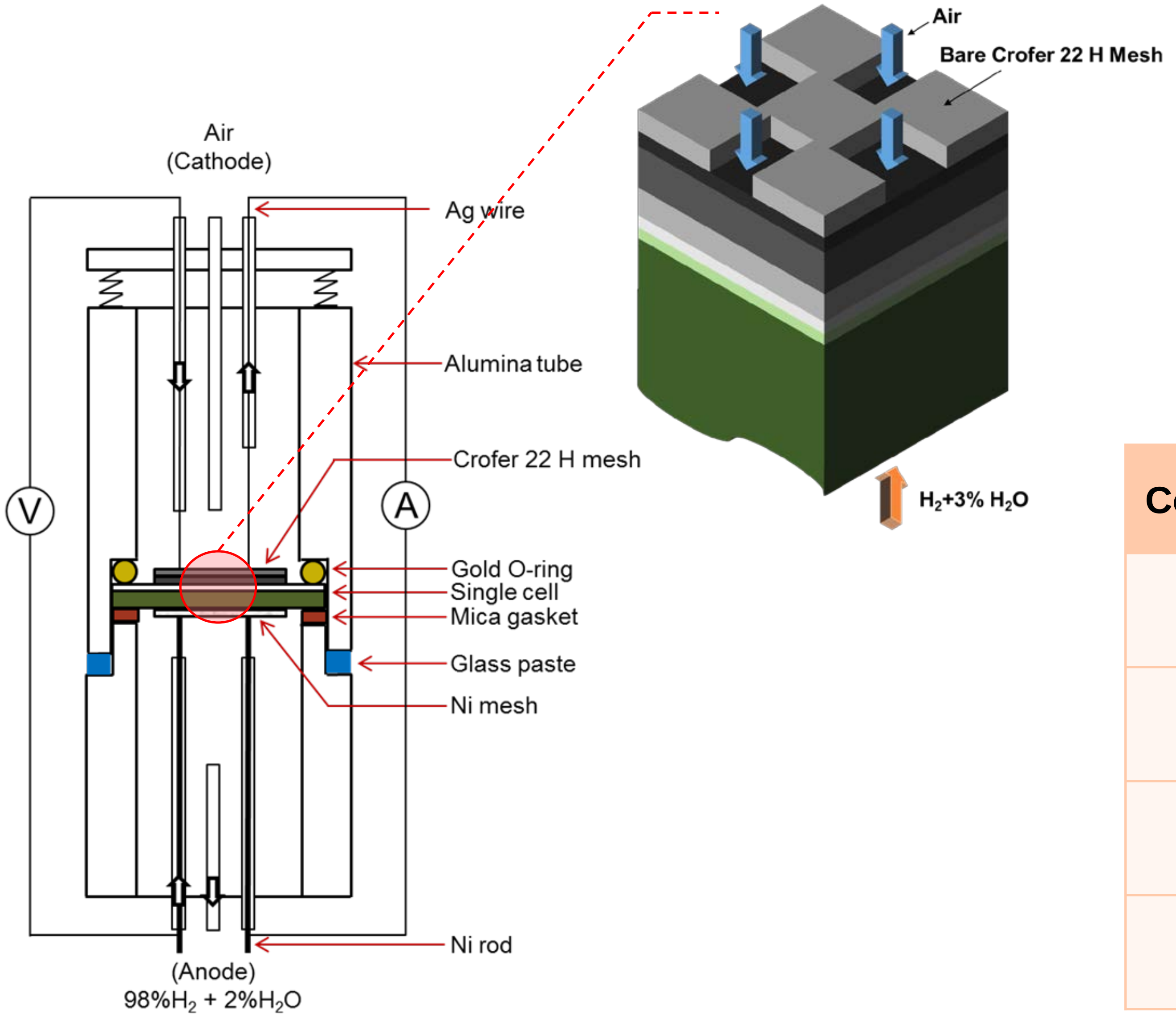
Cell Fabrication





LSM: $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-x}$
LSF: $(La_{0.8}Sr_{0.2})_{0.95}FeO_{3-x}$
GDC: $(Gd_{0.10}Ce_{0.90})O_{2-x}$

Summary of Test Conditions

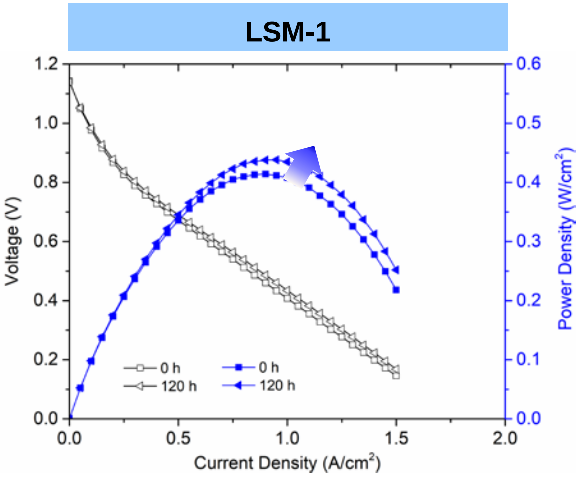
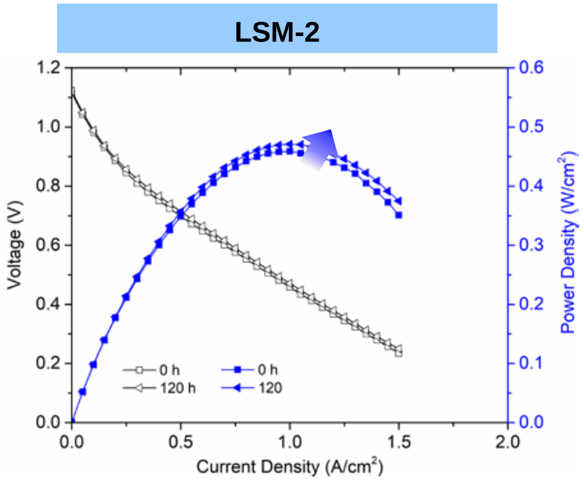
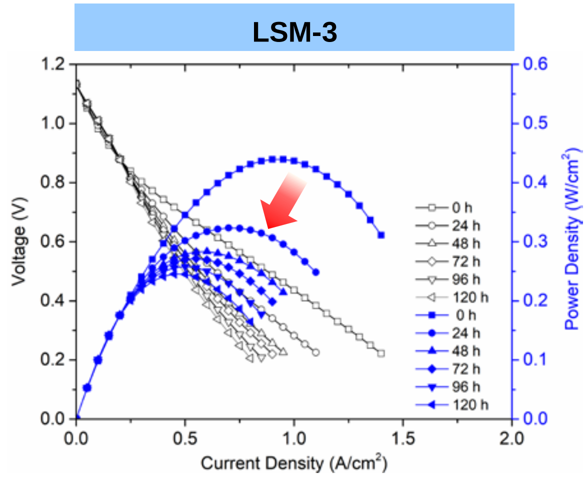
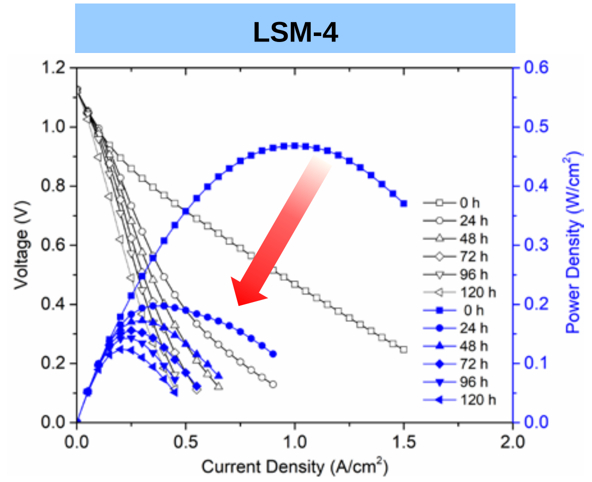
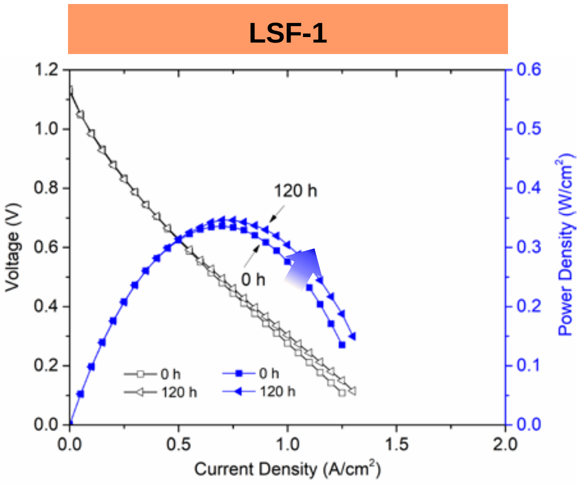
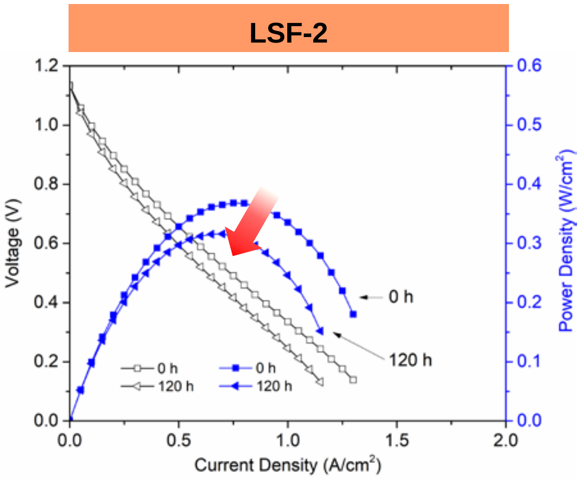
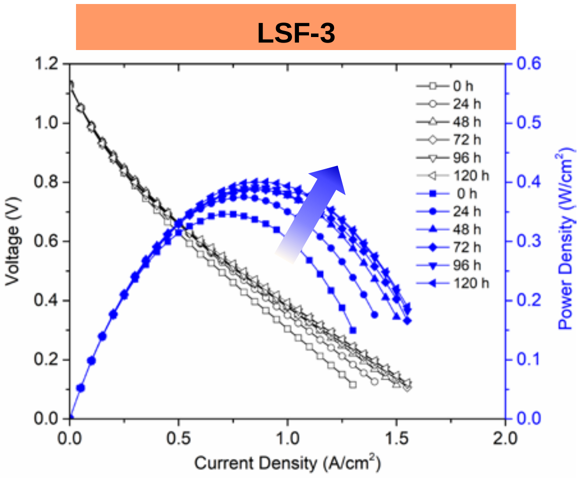
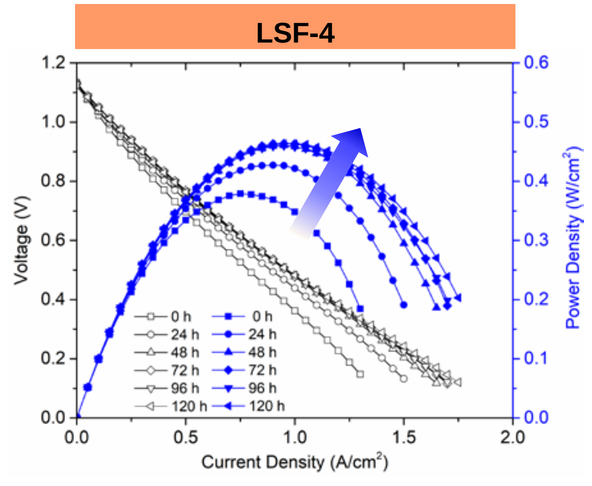


- **General test conditions:**
  - Fuel: 98% H_2+2% H_2O (300 cc/min): Fixed
  - Oxidant: Air (1000 cc/min)
  - Interconnect: Crofer 22 H mesh (used as cathodic current collector in cell tests)

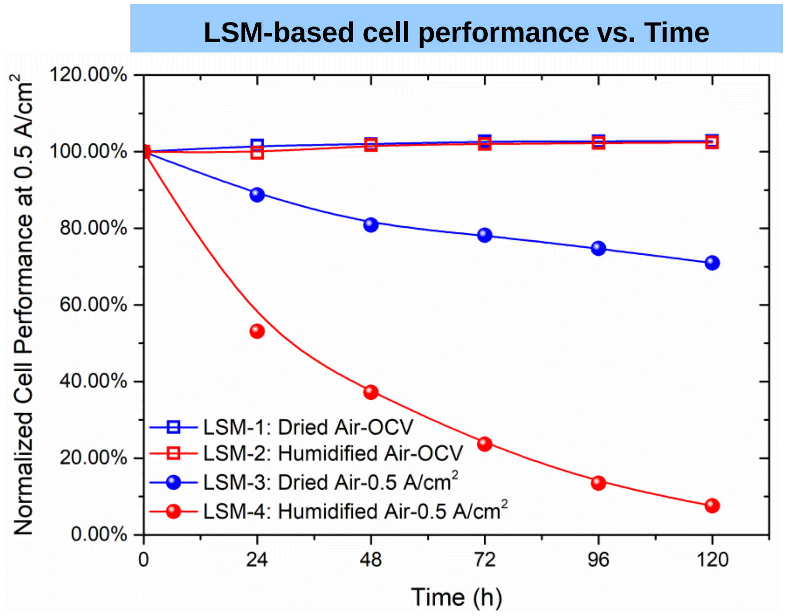
- **Conditions varied in the study:**

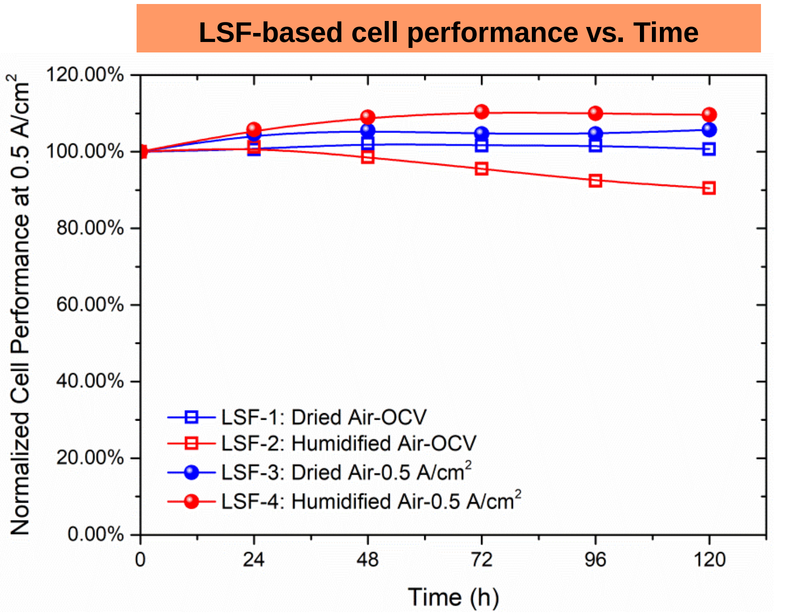
Conditions	Cathode Atmosphere	Current Condition	Cells
1	Dry Air	Open Circuit	LSM-1
			LSF-1
2	Humidified Air (10% H_2O)	Open Circuit	LSM-2
			LSF-2
3	Dry Air	Galvanostatic (0.5 A/cm^2)	LSM-3
			LSF-3
4	Humidified Air (10% H_2O)	Galvanostatic (0.5 A/cm^2)	LSM-4
			LSF-4

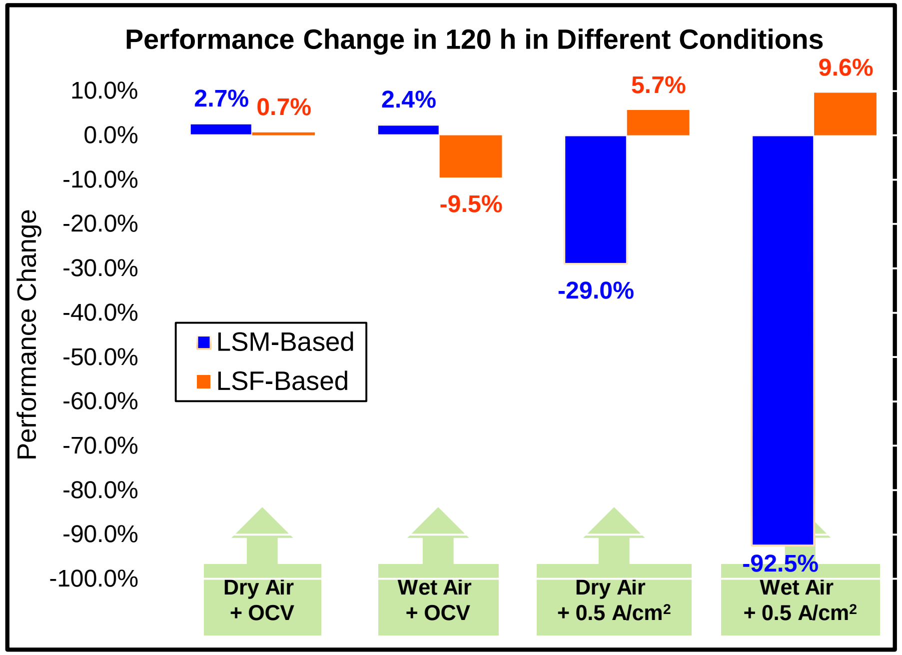
Electrochemical Degradation: V-i

	Condition 1: Dried Air + OCV	Condition 2: 10% Humidified Air + OCV	Condition 3: Dried Air + 0.5 A/cm^2	Condition 4: 10% Humidified Air + 0.5 A/cm^2
LSM-Based cells				
LSF-Based cells				

Electrochemical Degradation: V-i

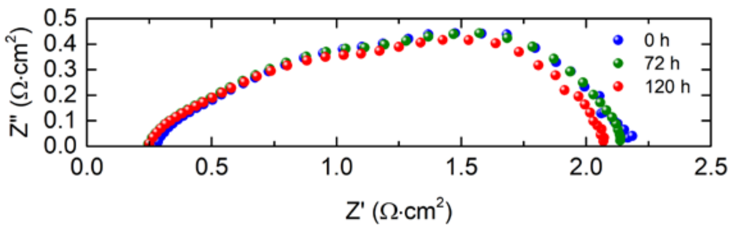
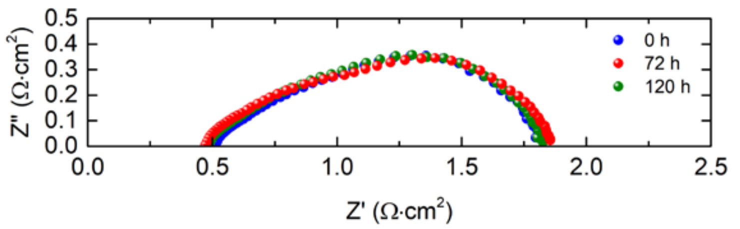
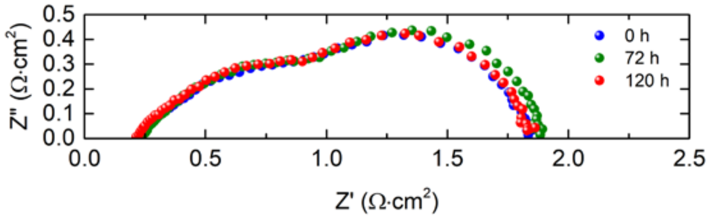
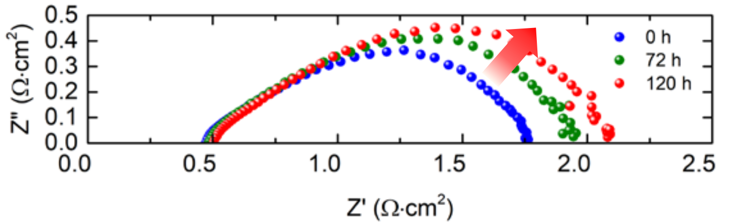
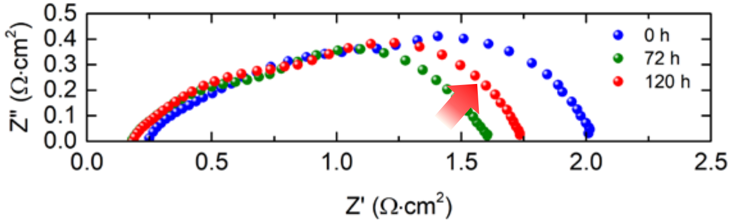
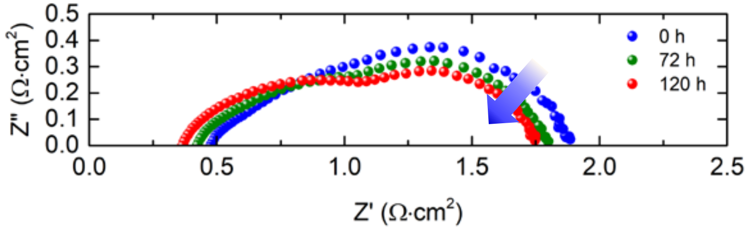
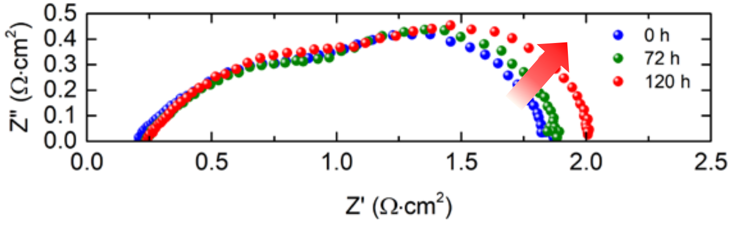
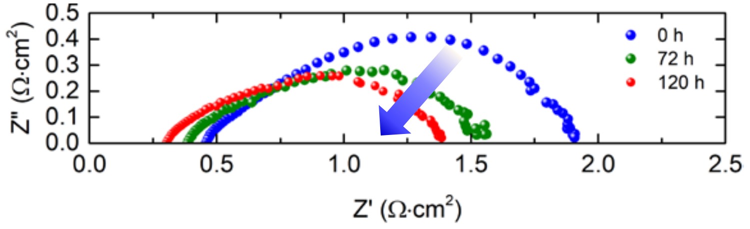




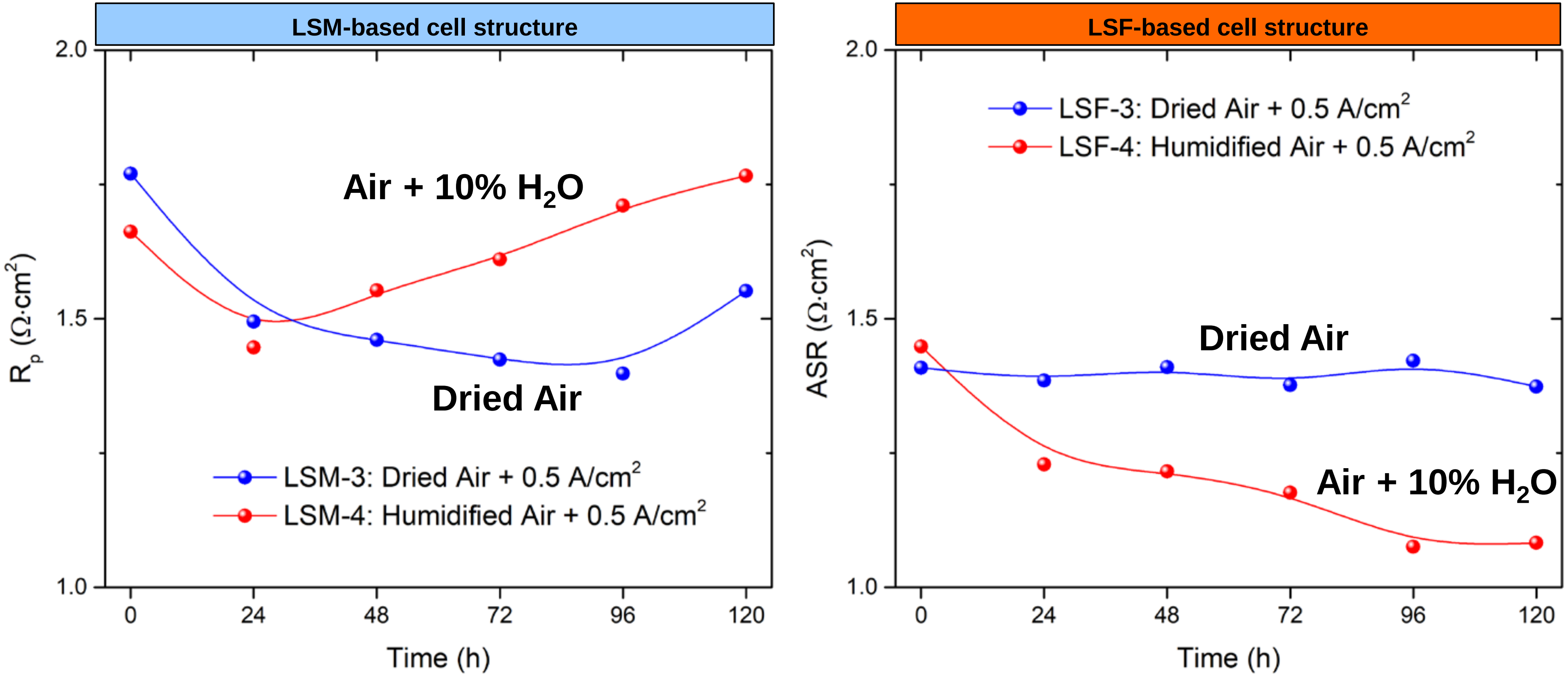


- **Cr-poisoning is more deleterious in LSM-based cell than that in LSF-based cell.**
- **In the case of LSM-based cell:**
  - **Current load (0.5 A/cm²) accelerates the degradation**
  - **Presence of humidity in air promotes degradation under current load**
- **In the case of LSF-based cell:**
  - **Current load (0.5 A/cm²) slightly improved the cell performance (presumably due to cell break-in)**
  - **In humidified air, performance deteriorated under OCV condition but improved under current load**

Electrochemical Degradation: EIS

Conditions	LSM-Based	LSF-Based
Condition 1: **Dried Air** **+ OCV**		
Condition 2: **Humidified Air** **+ OCV**		
Condition 3: **Dried Air** **+ 0.5 A/cm²**		
Condition 4: **Humidified Air** **+ 0.5 A/cm²**		

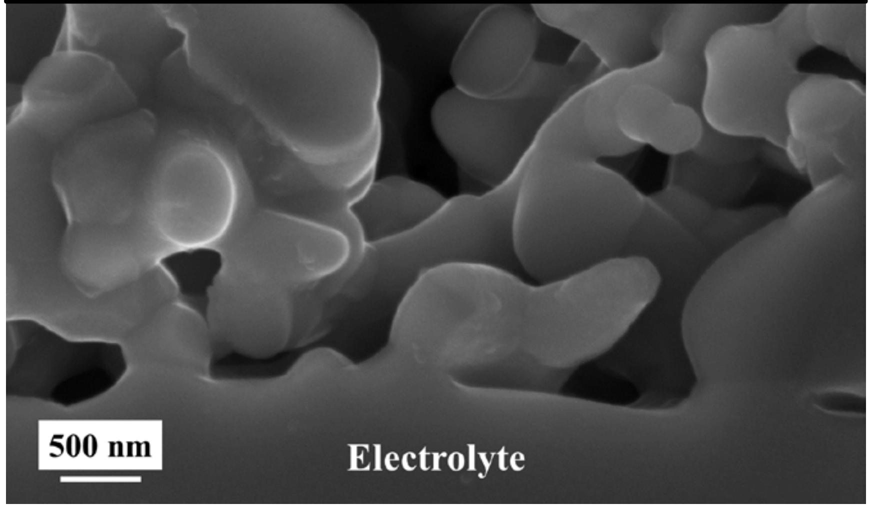
Electrochemical Degradation: EIS



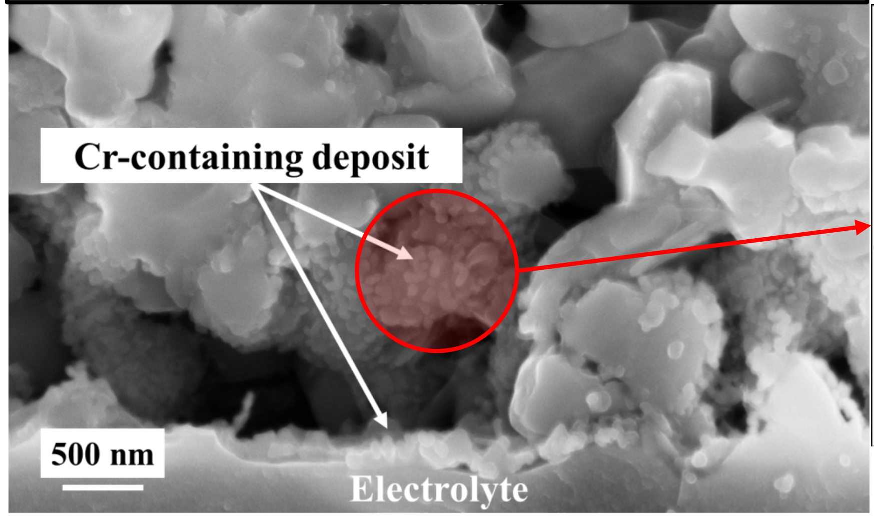
- **EIS consistent with the V-i results. In 10% humidified air, it shows increasing polarization of LSM-based cell and decreasing polarization of LSF-based cell.**

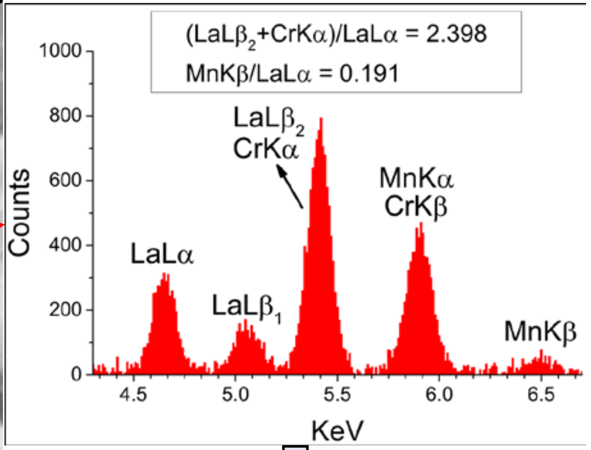
Microstructural Evolution: LSM-Based

LSM-1: Dry Air + OCV

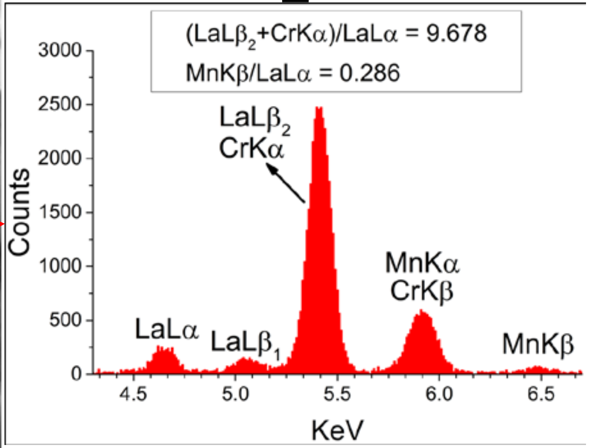


LSM-3: Dry Air + Current

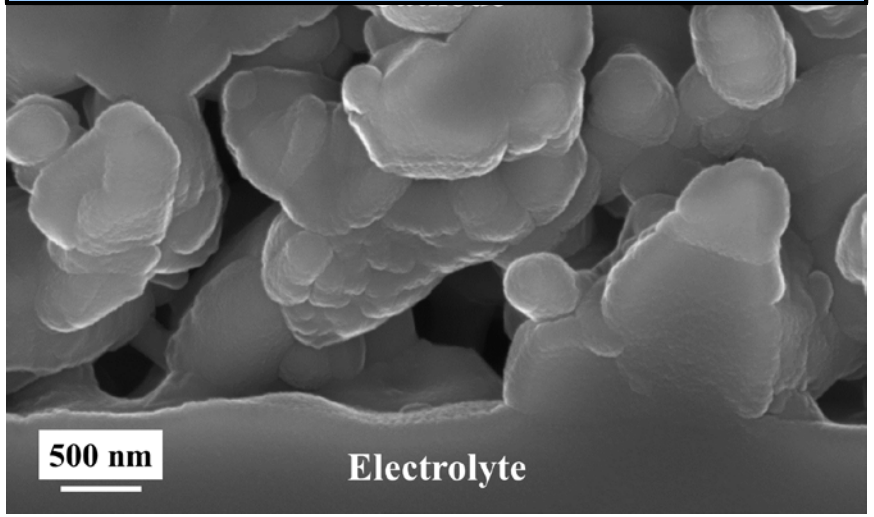




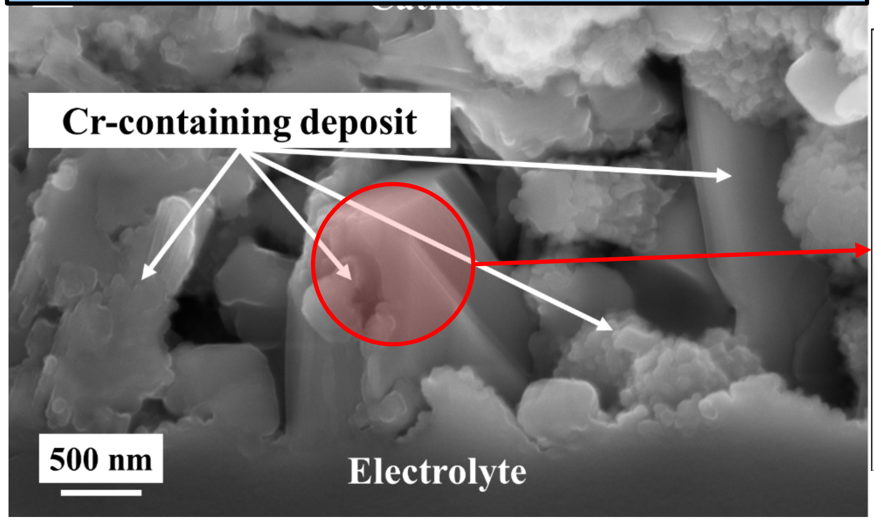
Cr-containing deposits are Cr,Mn-rich, suggesting $(Cr,Mn)_3O_4$ spinel phases



LSM-2: Humidified Air + OCV

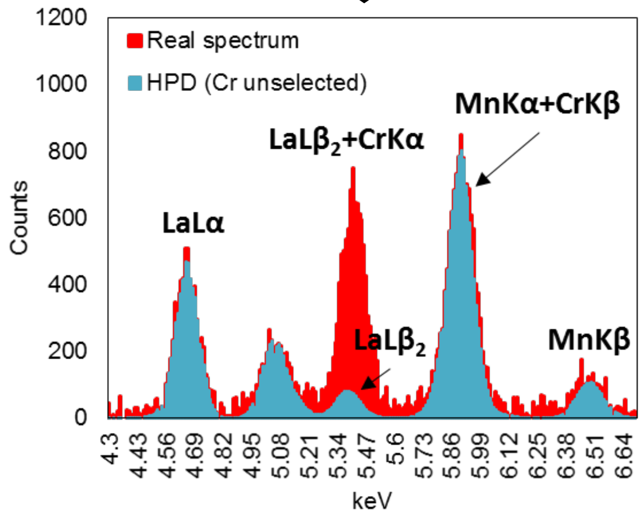


LSM-4: Humidified Air + Current



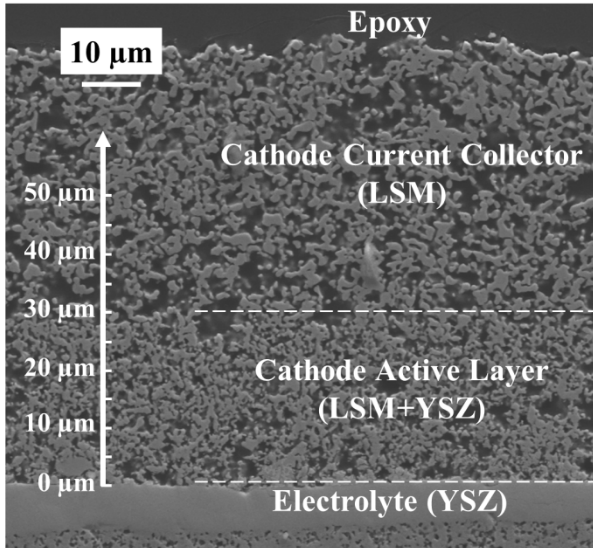
Microstructural Evolution: LSM-Based

Criterion for quantifying Cr distribution in LSM

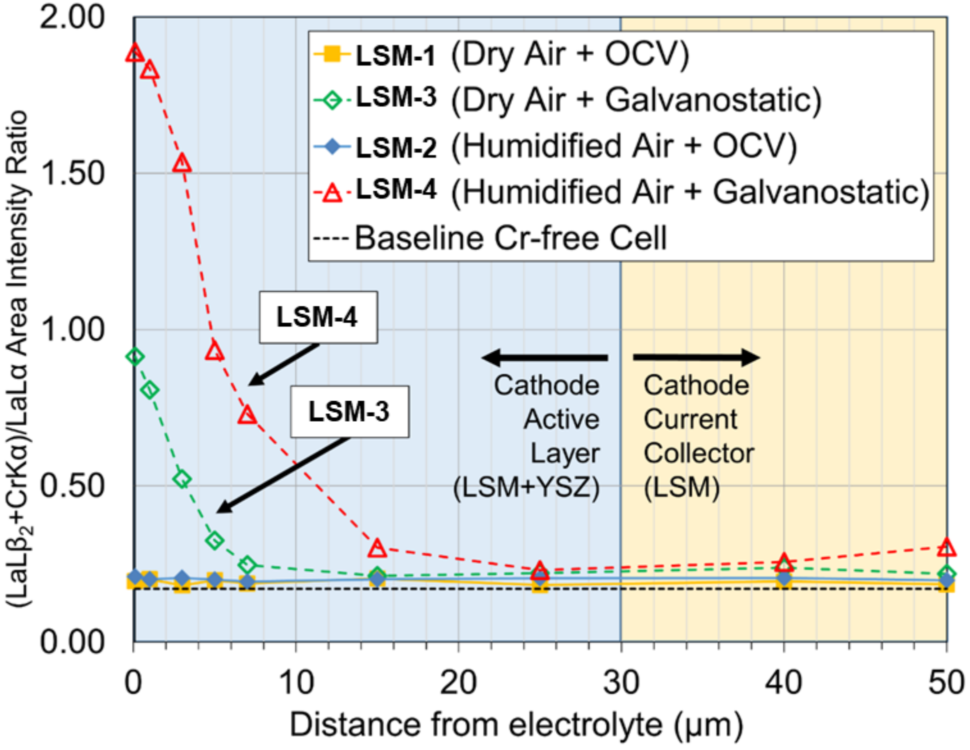


Intensity Ratio: $\frac{LaL_{\beta 2}+CrK_{\alpha}}{LaL_{\alpha}}$

Cross section of LSM-based cathode



Cr-enrichment profile in the LSM-based cathode



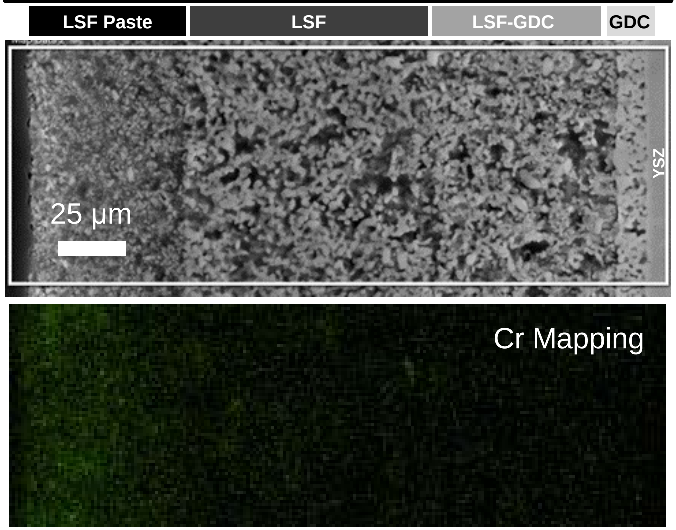
- **Cr intensity at cathode/electrolyte interface: LSM-4 > LSM-3 > LSM-2 ≈ LSM-1**
- **Cr deposition was promoted by current and extended to TPB's away from the cathode/electrolyte interface.**

* Wang, R., Pal, U. B., Gopalan, S., & Basu, S. N. (2017). Journal of The Electrochemical Society, 164(7), F740-F747.

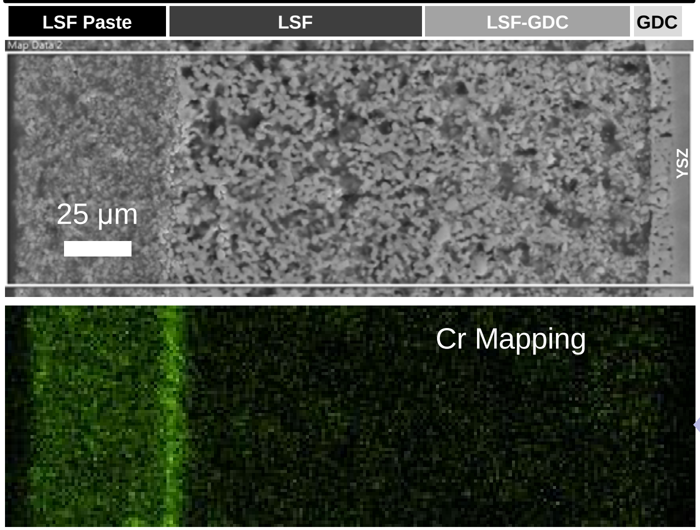
Microstructural Evolution: LSF-Based

OCV condition:
Cr distribution is homogeneous in the bulk of cathode

LSF-1: Dried Air + OCV

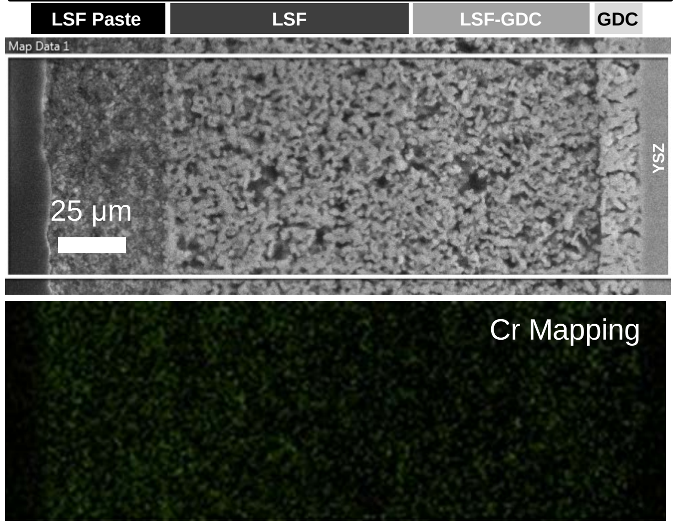


LSF-3: Dried Air + 0.5 A/cm^2

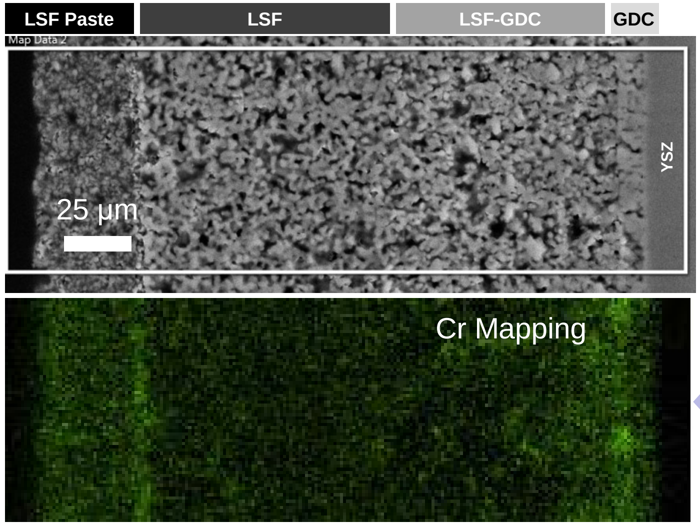


Most of Cr is distributed at the surface of cathode

LSF-2: 10% Humidified Air + OCV



LSF-4: 10% Humidified Air + 0.5 A/cm^2



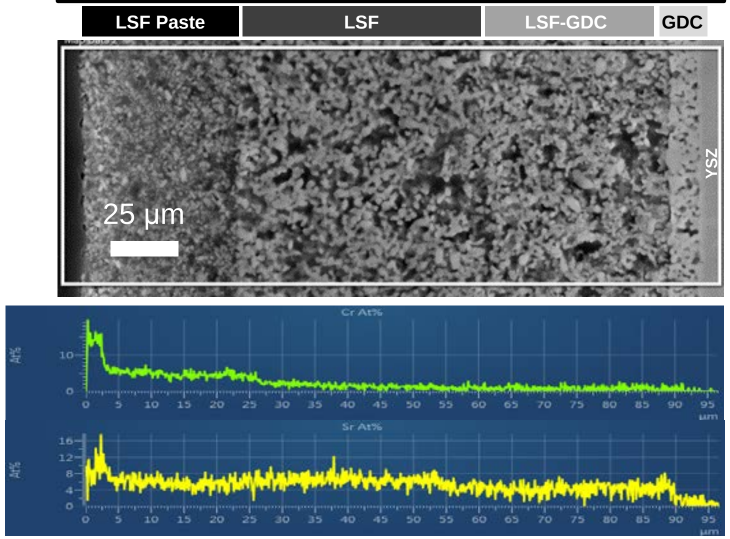
Cr is distributed at the surface of cathode and also cathode/electrolyte interface

Microstructural Evolution: LSF-Based

LSF-1: Dried Air + OCV

Cr Line Scan

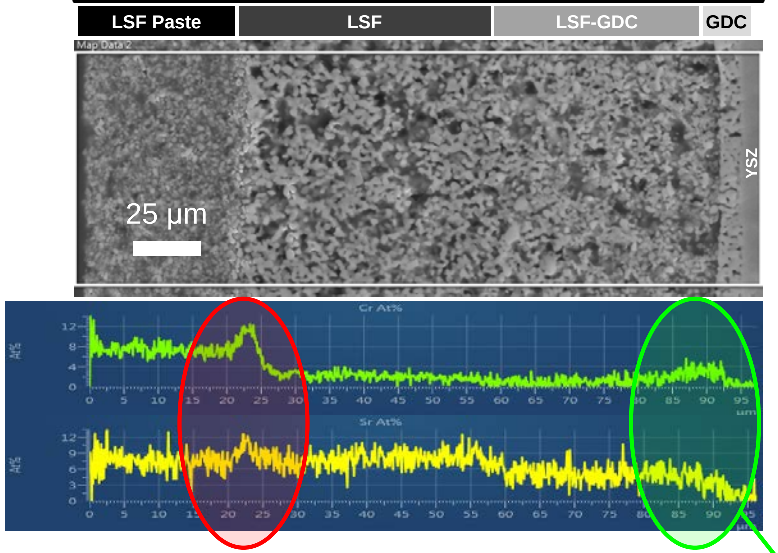
Sr Line Scan



LSF-3: Dried Air + 0.5 A/cm^2

Cr Line Scan

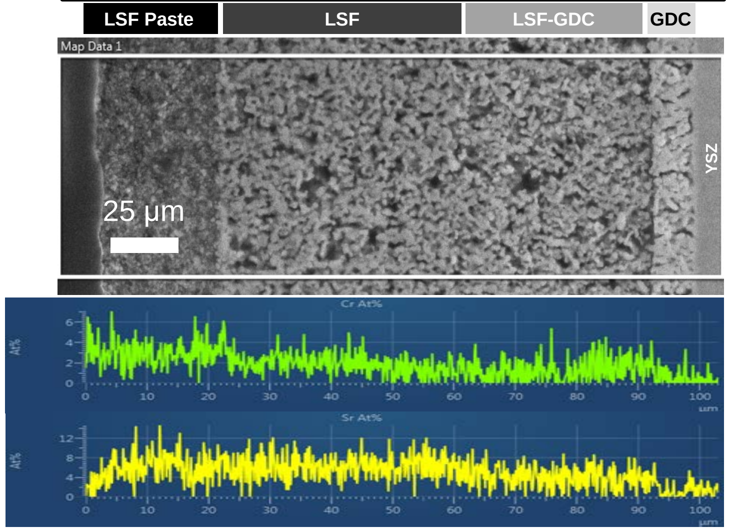
Sr Line Scan



LSF-2: 10% Humidified Air + OCV

Cr Line Scan

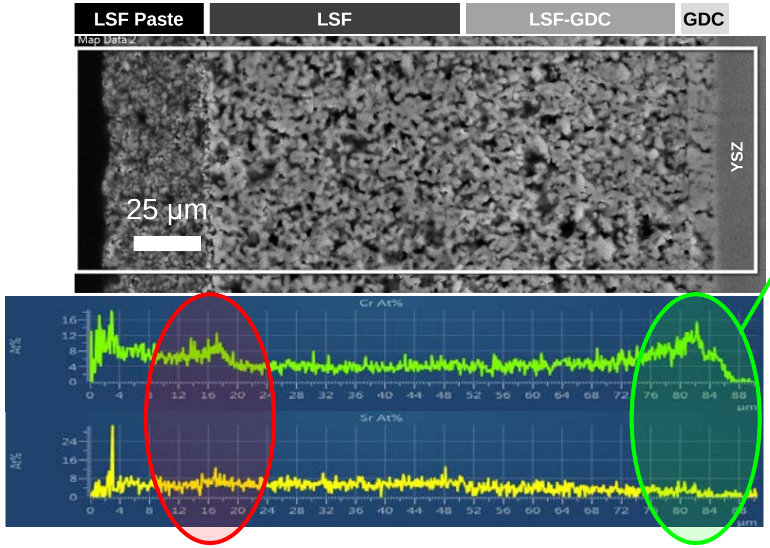
Sr Line Scan



LSF-4: 10% Humidified Air + 0.5 A/cm^2

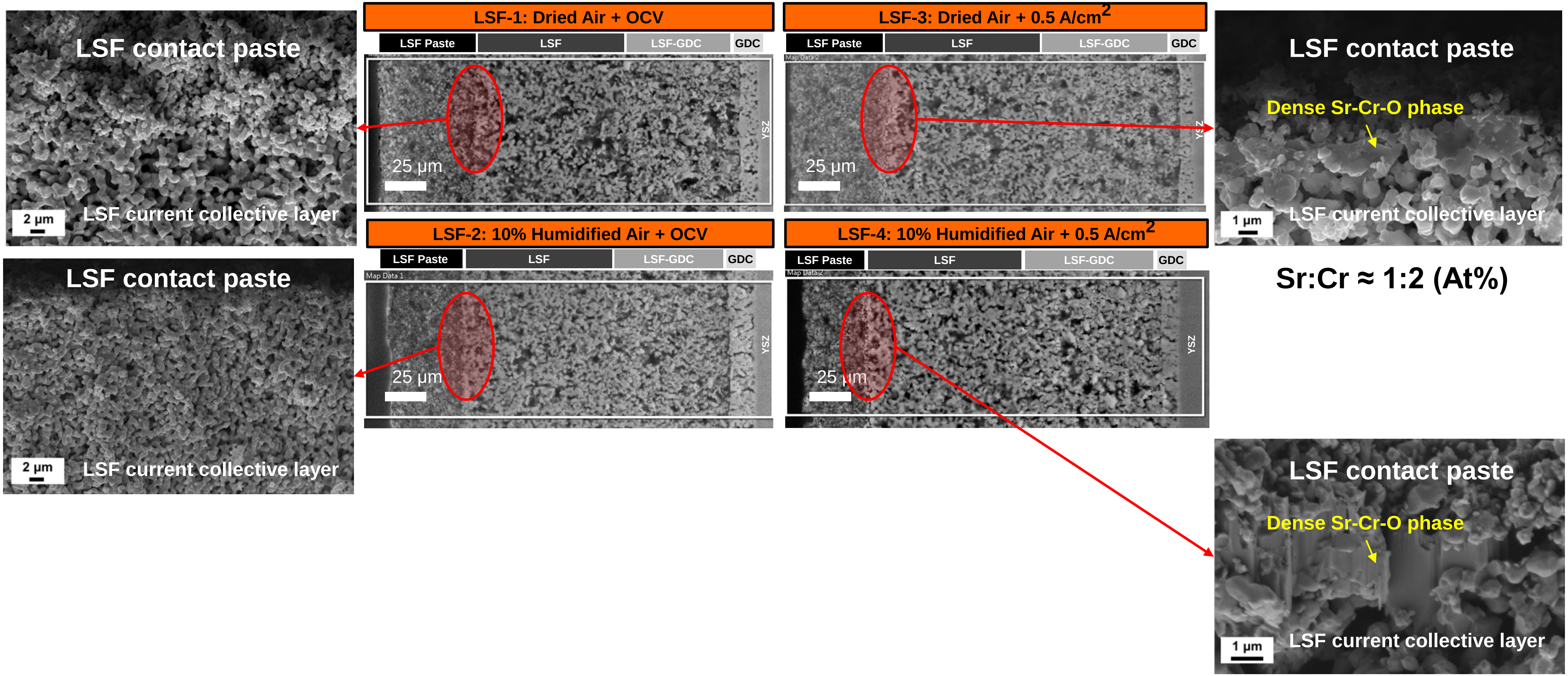
Cr Line Scan

Sr Line Scan



Cr and Sr profiles do not match at the cathode/electrolyte interface

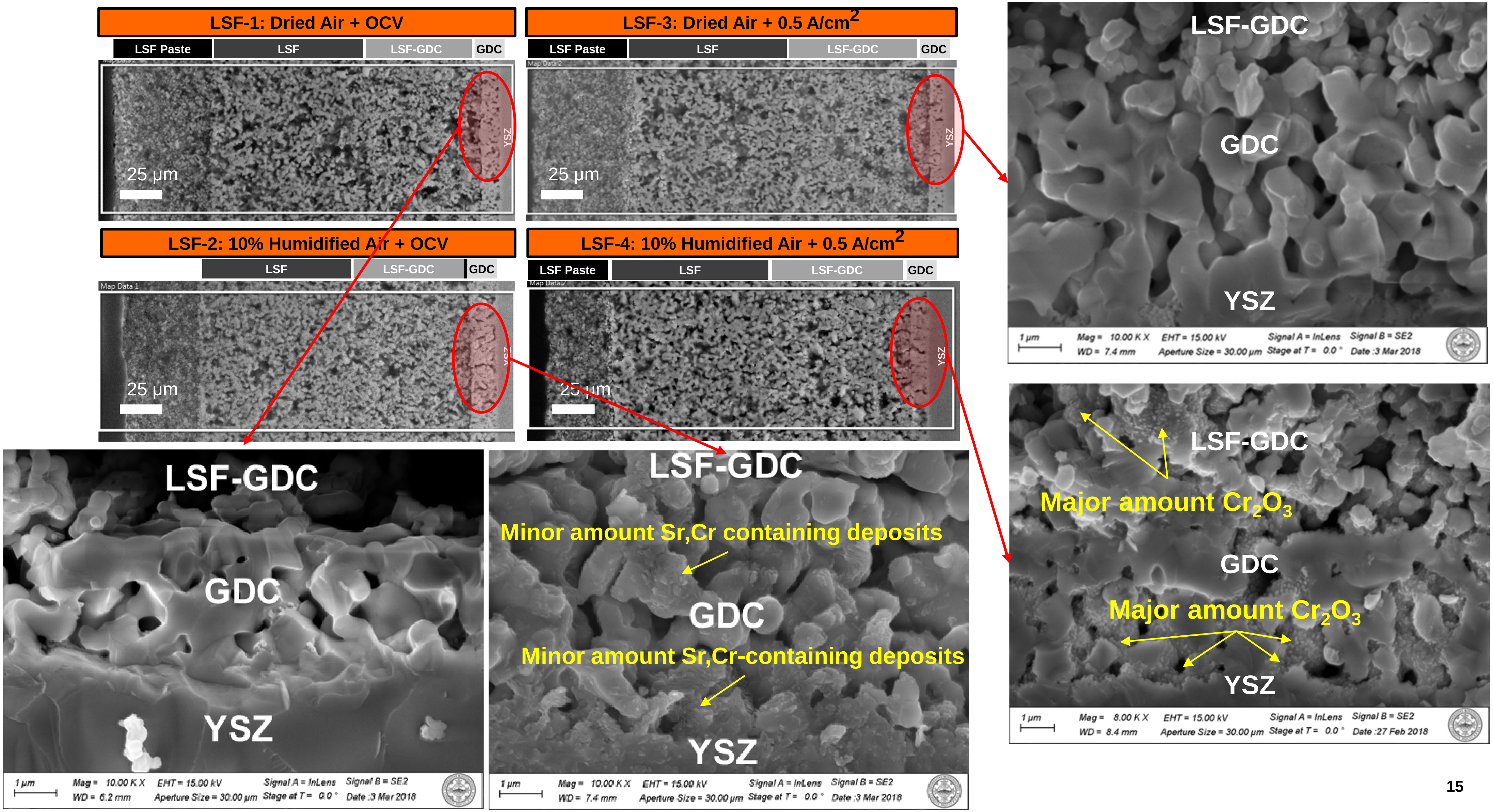
Microstructural Evolution: LSF-Based



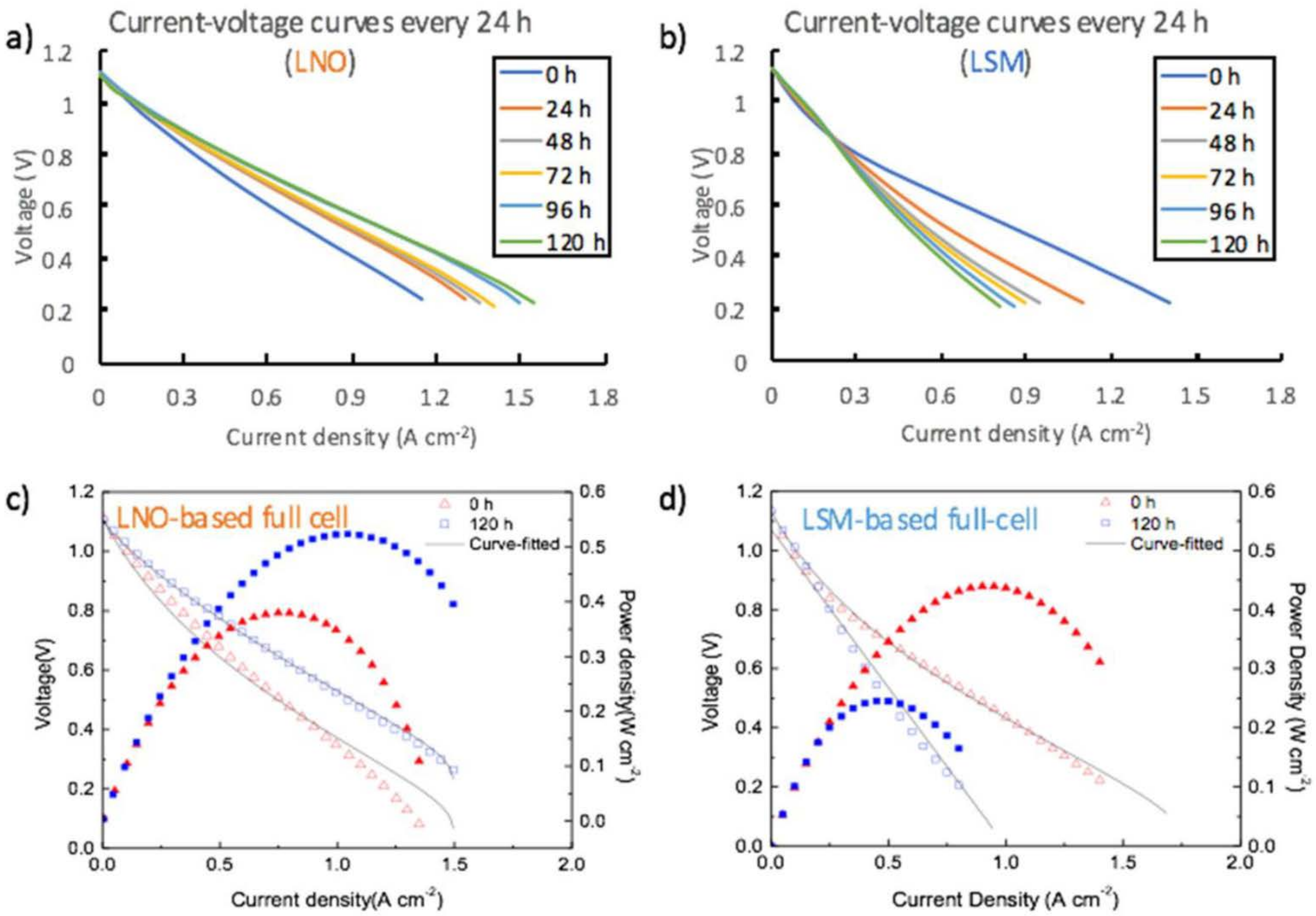
Sr:Cr ≈ 1:2 (At%)

Sr:Cr ≈ 1:1 (At%)

Microstructural Evolution: LSF-Based



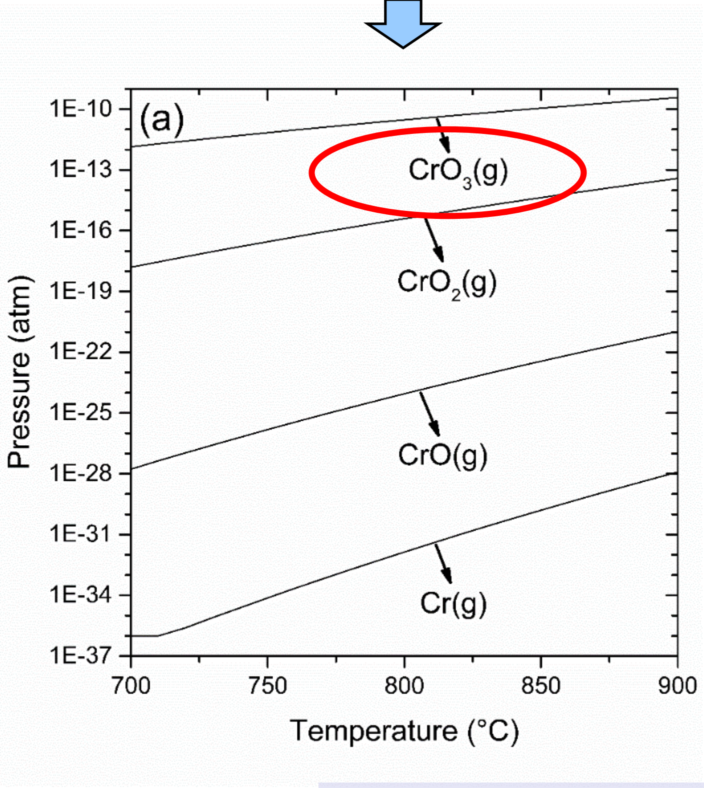
Degradation in LNO Cathodes



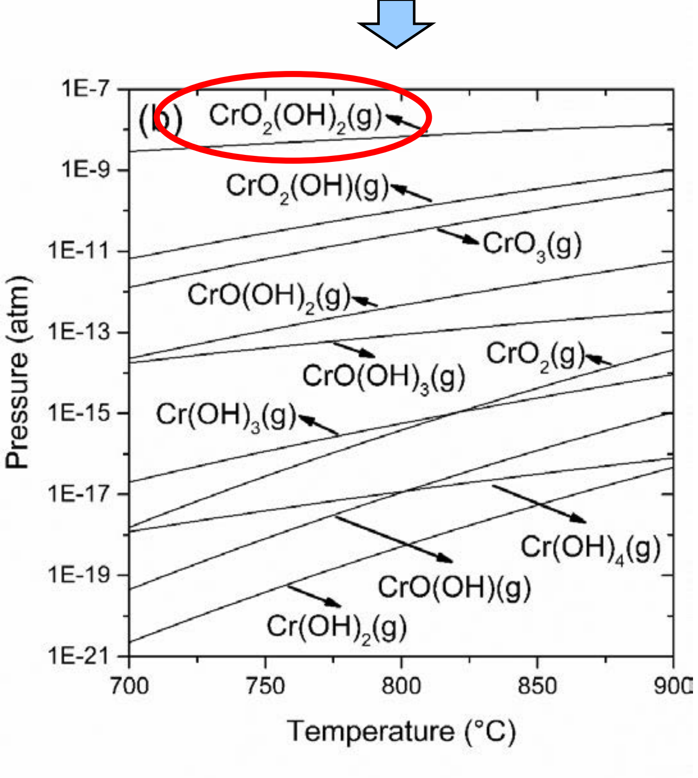
Degradation Mechanisms

- **Effect of humidity on Cr evaporation:**

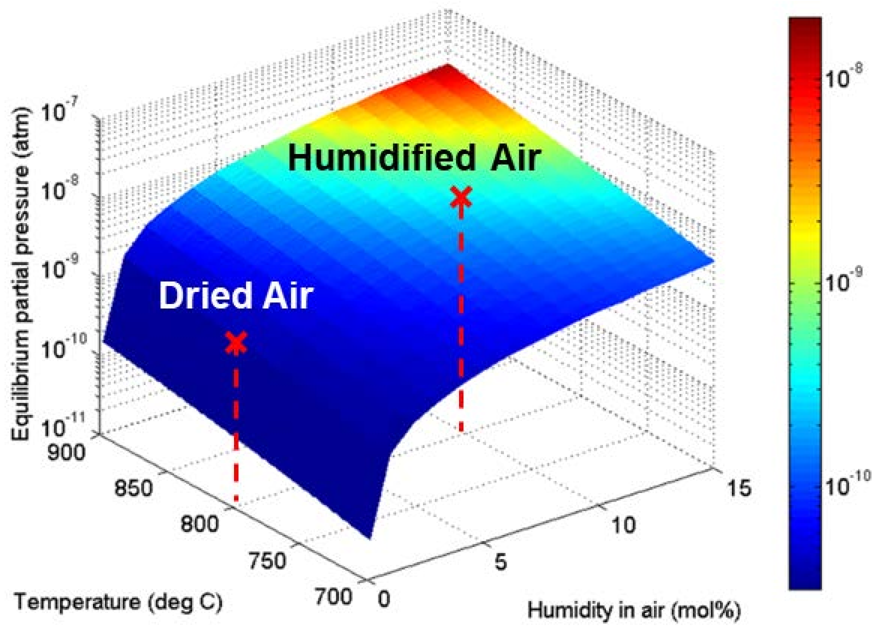
Equilibrium Partial Pressure of Cr in Dry Air



Equilibrium Partial Pressure of Cr in 10% Humidified Air



Equilibrium Partial Pressure of Cr vapor species over Cr_2O_3 scale



- **Cr vapor pressure in 10% humidified air is ~2-order-of-magnitude higher than that in dry air*.**

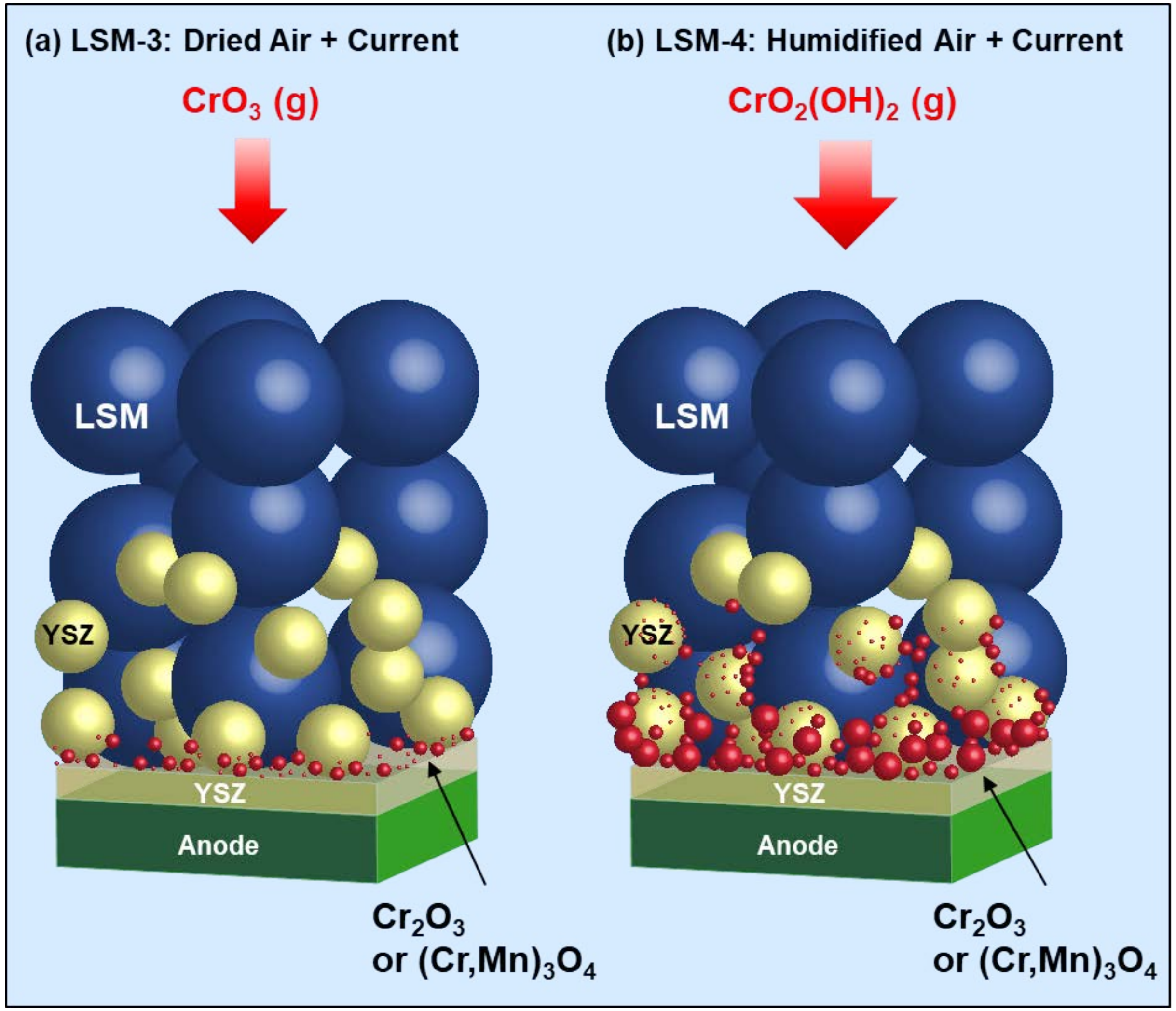
* Wang, R., Würth, M., Pal, U. B., Gopalan, S., & Basu, S. N. (2017). Journal of Power Sources, 360, 87-97.

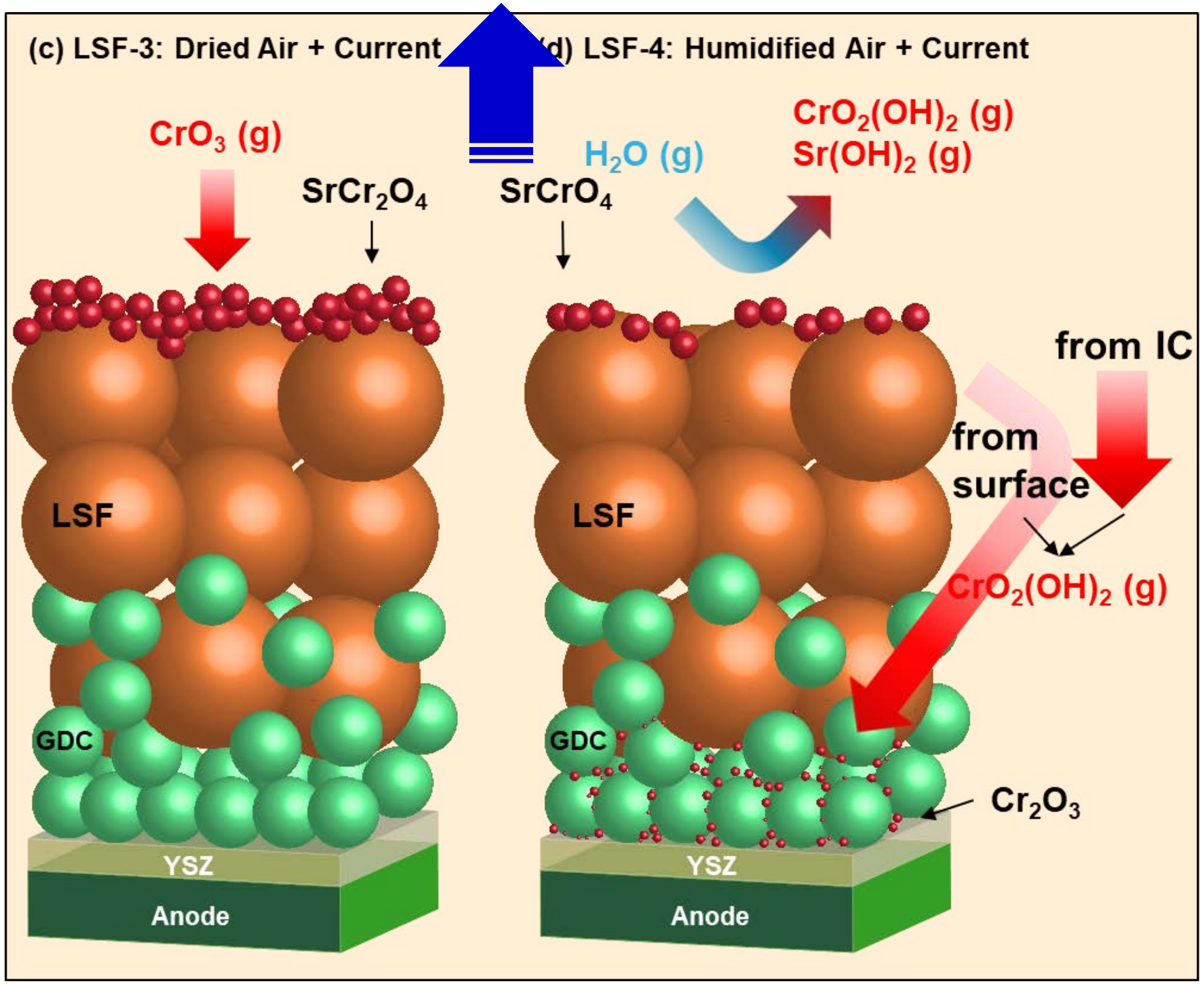
Degradation Mechanisms

- Effect of humidity on Cr distributions:

Evaporation of Cr-deposits on the LSF surface:

$2SrCr_2O_4(s) + 2H_2O(g) + 3O_2(g) = 2SrCrO_4(s) + 2CrO_2(OH)_2(g)$ ----- (1)
or $SrCr_2O_4(s) + 4H_2O(g) + 2O_2(g) = Sr(OH)_4(s) + 2CrO_2(OH)_2(g)$ ----- (2)





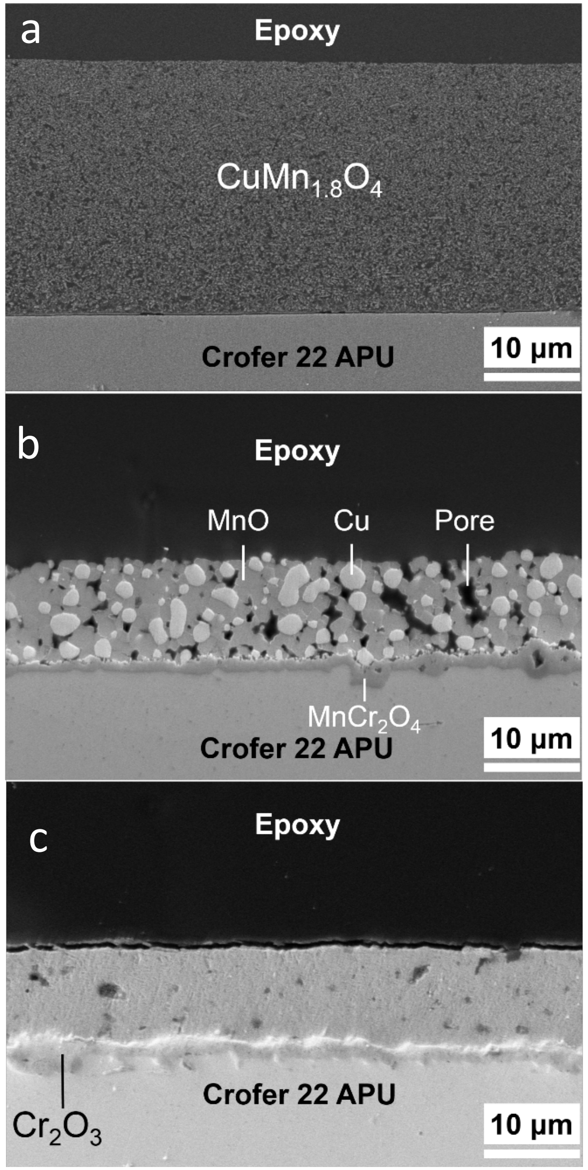
Oxide Protective Coatings

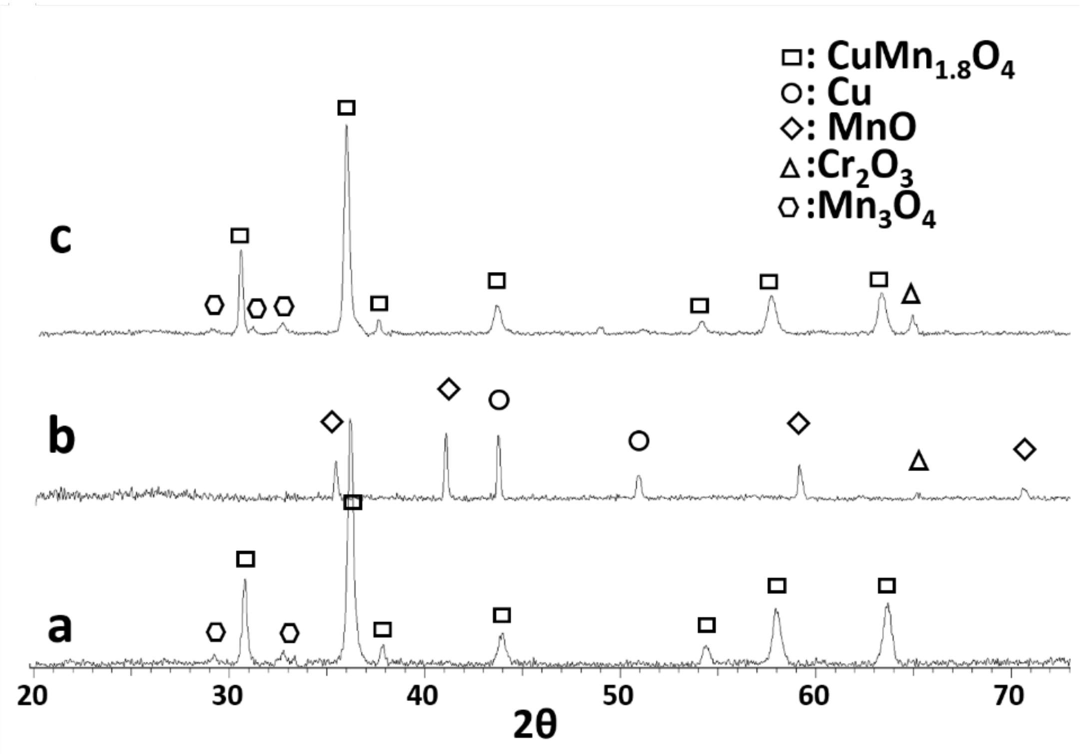
EPD Coating of $CuMn_{1.8}O_4$

EPD

Reduction annealing (1000 °C, 24 h)

Oxidation annealing (850 °C, 1 h)





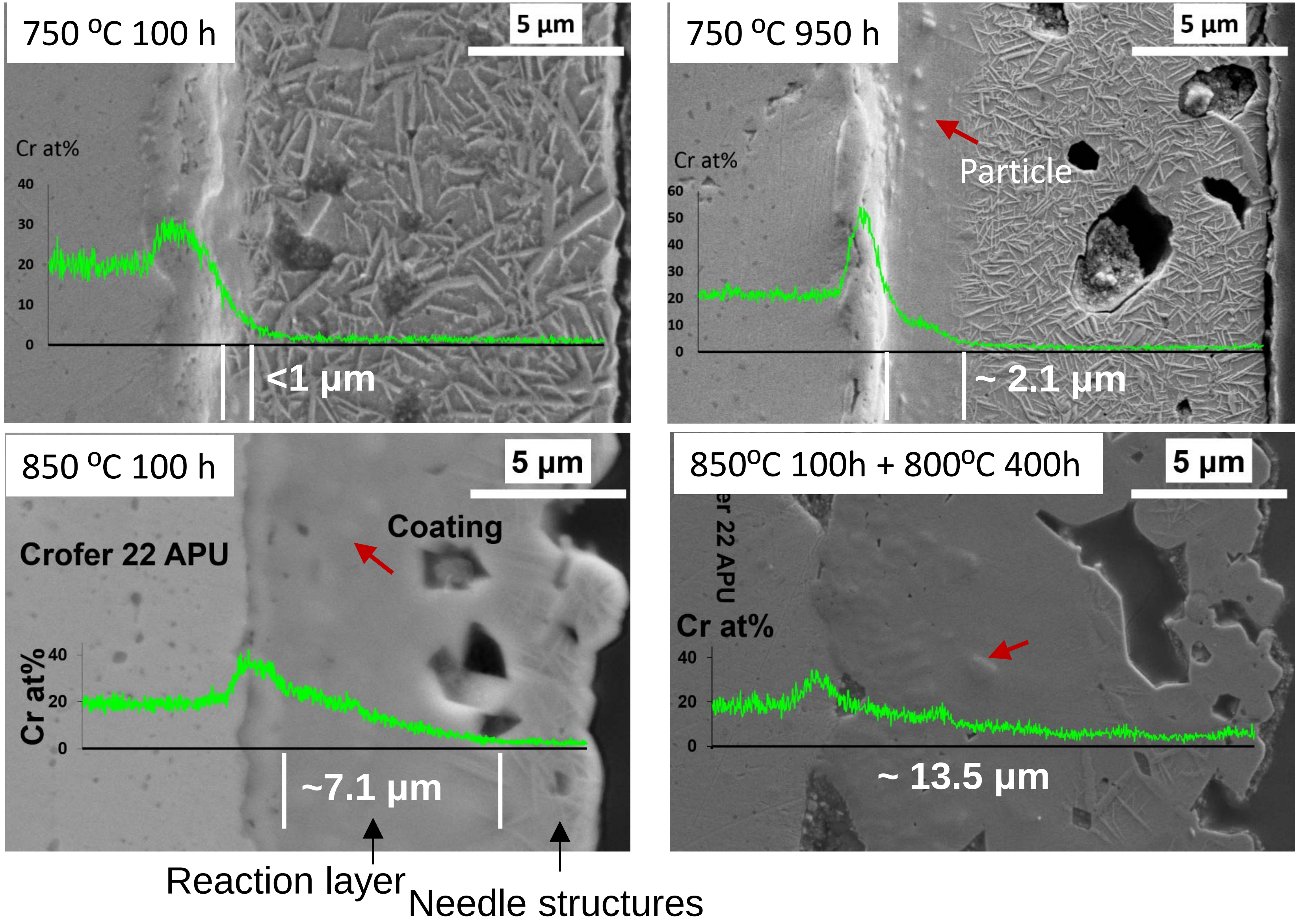
XRD: a) $CuMn_{1.8}O_4$ powders

b) after reduction anneal

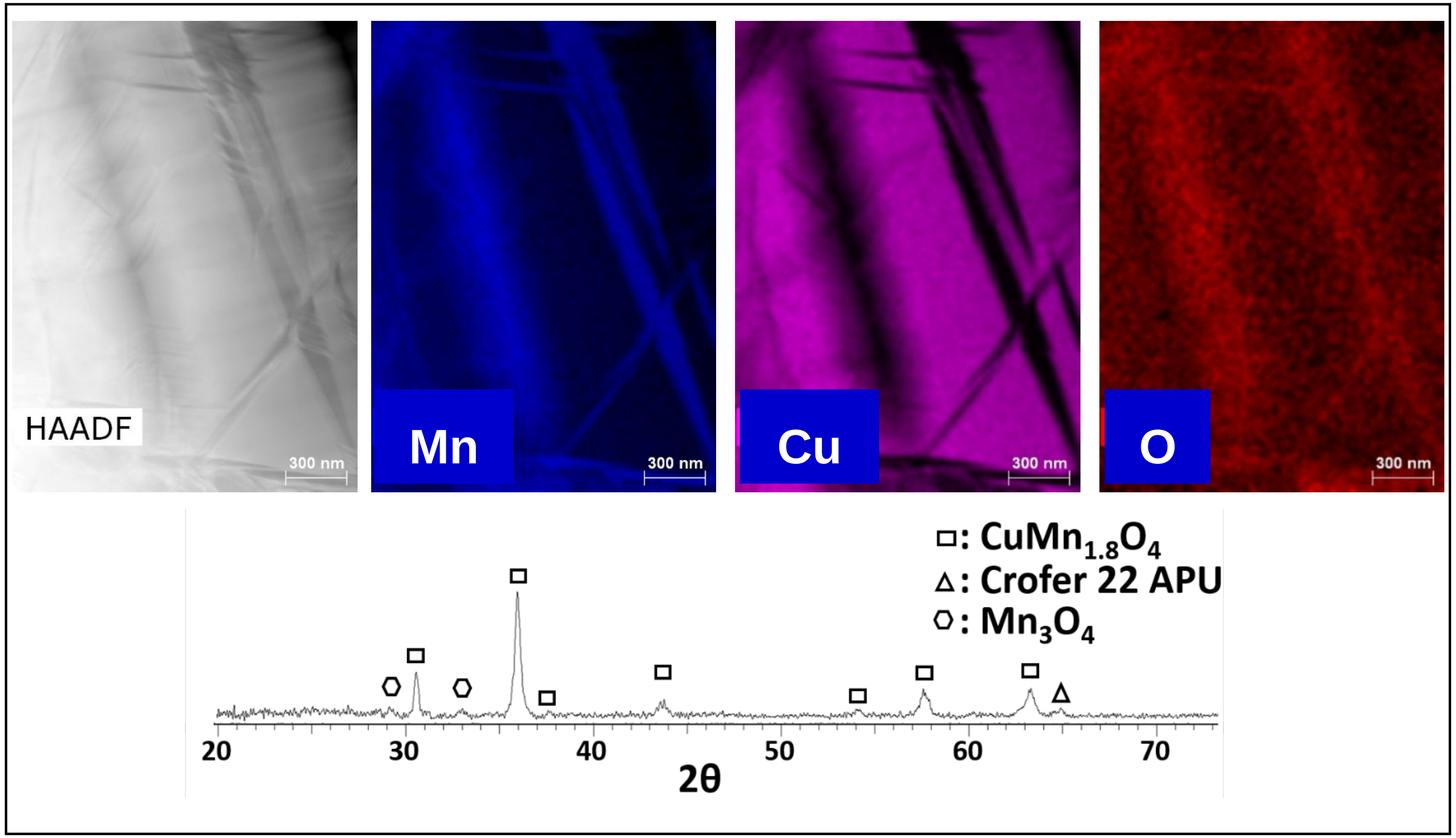
c) after 1h oxidation anneal

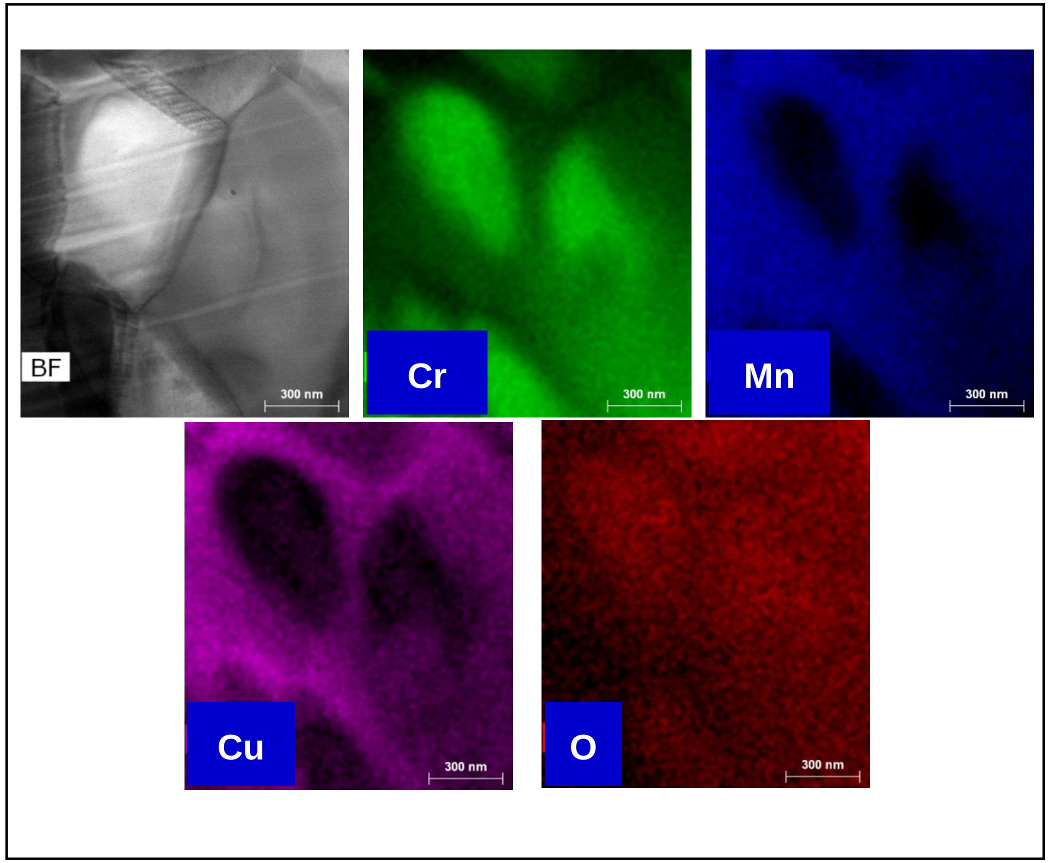
Z. Sun et al, *Journal of Power Sources*, 378 (2018), 125-133.

Cr Diffusion and Microstructure Evolution

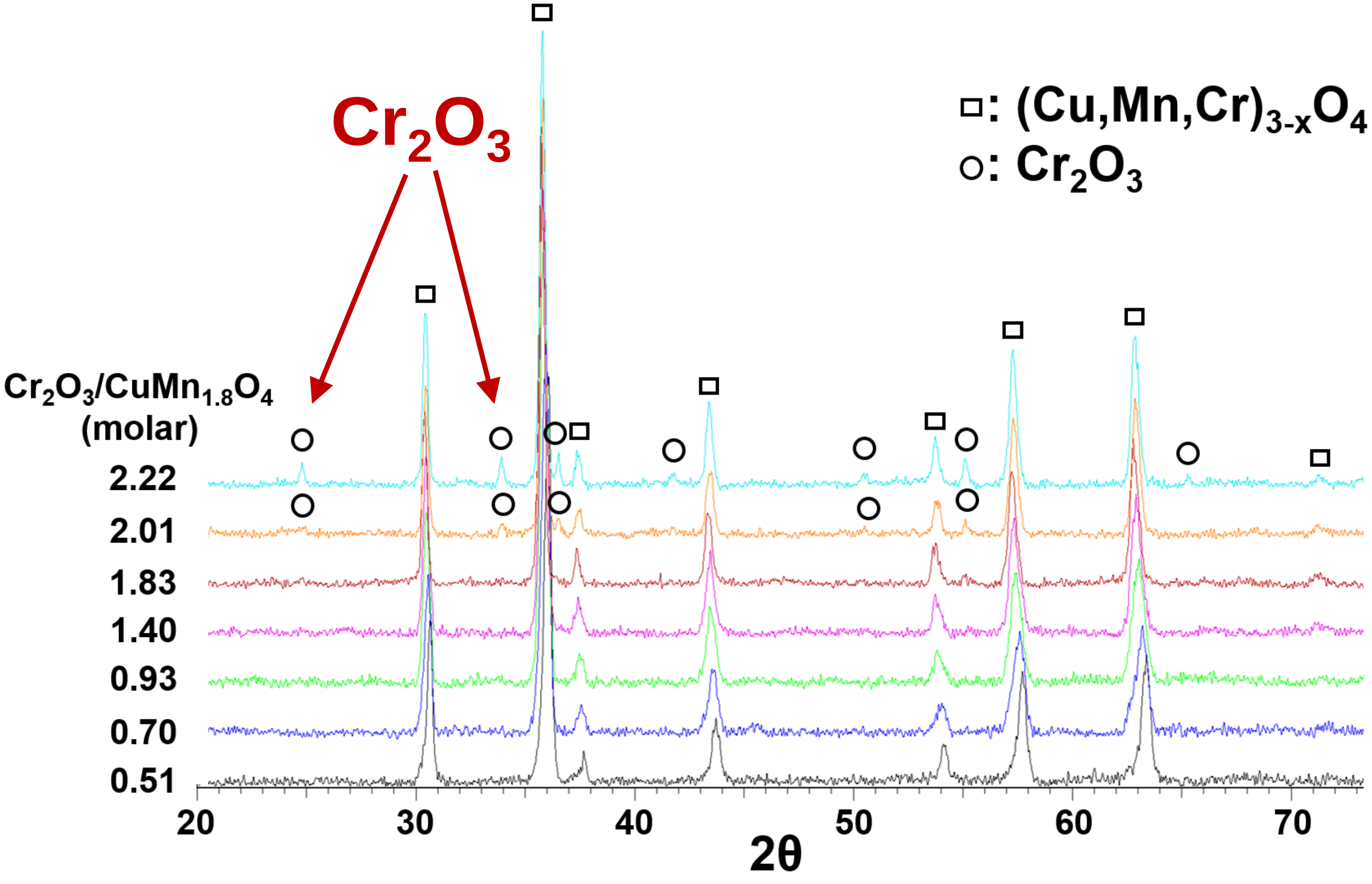


TEM Analaysis of Protective Coatings



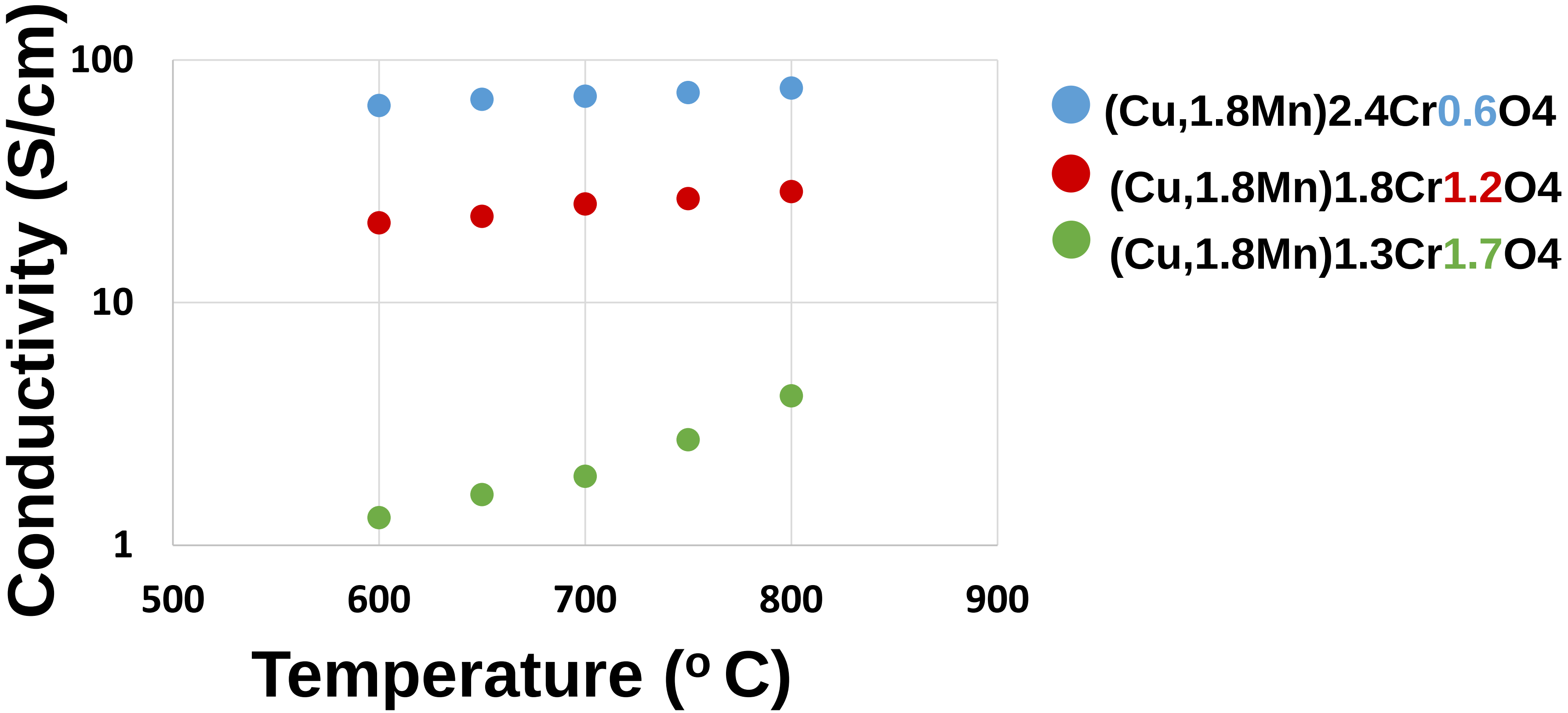


Solubility of Cr_2O_3 in $CuMn_{1.8}O_4$



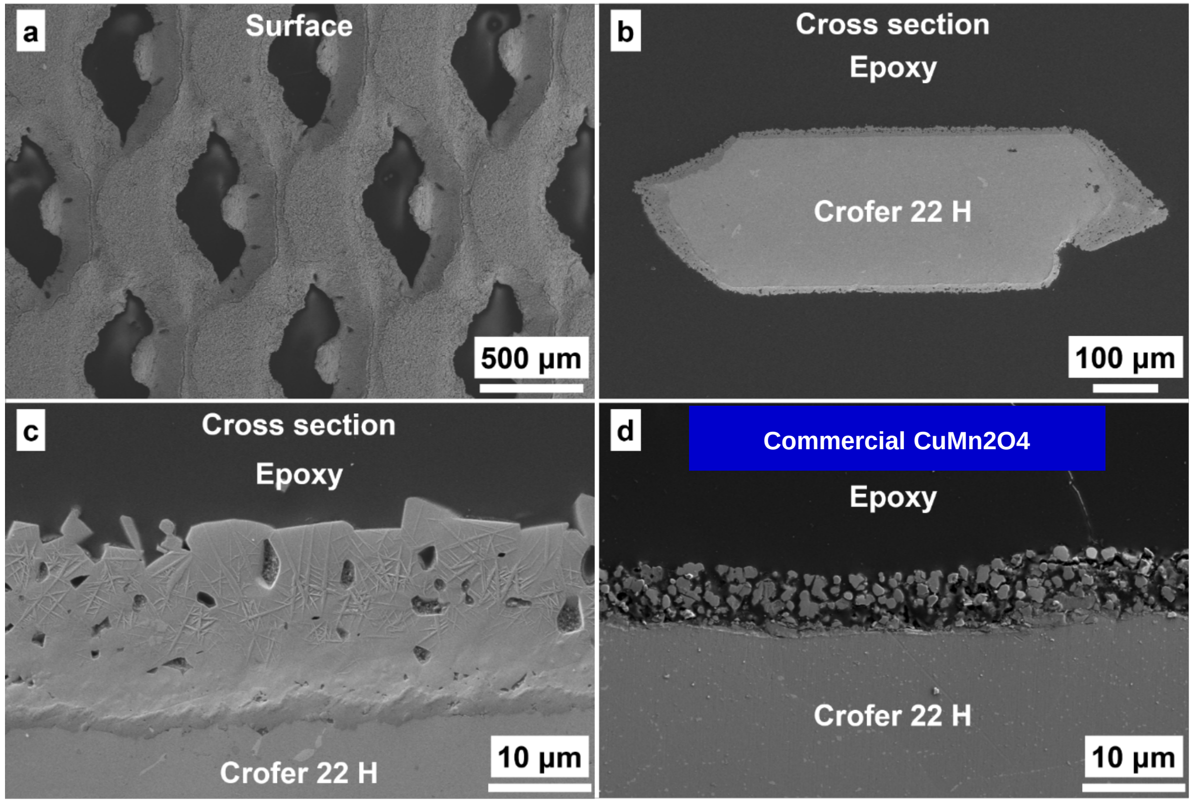
Reaction between Cr_2O_3 and $CuMn_{1.8}O_4$ powders (800 °C, 10 h, in air)

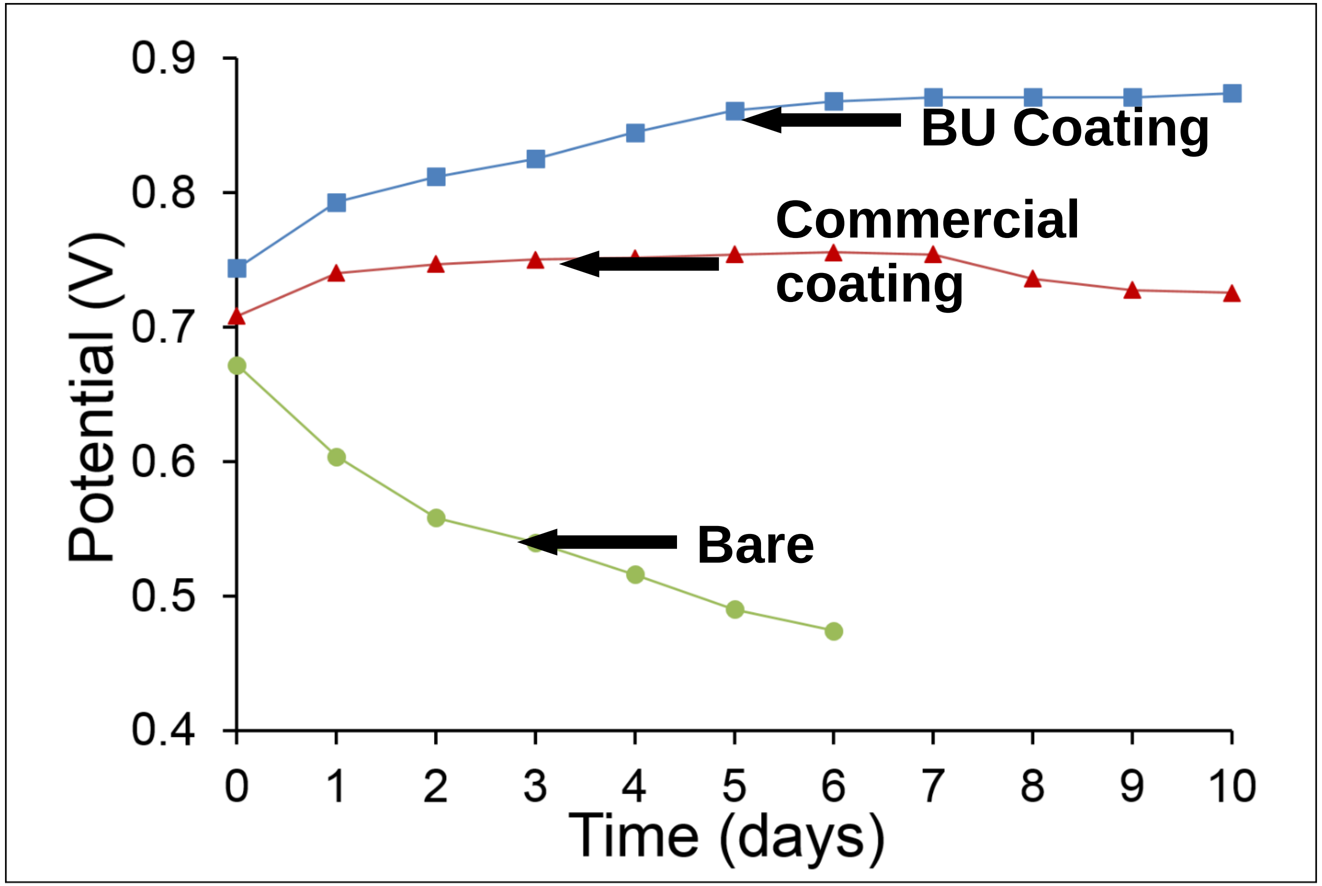
Electrical Conductivity of $(Cu,Mn,Cr)_3O_4$



* Zhu et al, Mater. Sci. Eng. A 348 (2003) 227–243

Coating on complex geometry (mesh) and Electrochemical tests – LSM cells





Summary

- **LSM, LSF-GDC, and LNO-based cathodes have been tested against chromium poisoning under load, and in the presence of 10% humidity**
  - **LSF-GDC and LNO cathodes show excellent tolerance towards chromium poisoning compared to LSM**
  - **The differences in the mechanisms of degradation are still being worked out**

- **High quality CuMn spinels have been applied using EPD to complex geometries of ferritic stainless steel interconnects.**
  - **The coatings are very effective in providing a barrier to Cr attack on LSM cathodes**
  - **The combination of LSF-GDC or LNO with CuMn protective coatings should provide excellent long term stability against Cr poisoning**

Publications

- “Roles of humidity and cathodic current in chromium poisoning of Sr-doped $LaMnO_3$-based cathodes in solid oxide fuel cells,” R Wang, M Würth, UB Pal, S Gopalan, SN Basu, Journal of Power Sources 360, 87–97
- Chromium Poisoning Effects on Performance of $(La,Sr)MnO_3$-Based Cathode in Anode-Supported Solid Oxide Fuel CellsR Wang, UB Pal, S Gopalan, SN Basu, Journal of The Electrochemical Society 164 (7), F740-F747
- Effect of Humidity and Cathodic Current on Chromium Poisoning of Sr-Doped $LaMnO_3$-Based Cathode in Anode-Supported Solid Oxide Fuel Cells, R Wang, M Würth, B Mo, UB Pal, S Gopalan, SN Basu, ECS Transactions 75 (42), 61-67
- Chromium Poisoning of Cathodes in Solid Oxide Fuel Cells and its Mitigation Employing $CuMn_{1.8}O_4$ Spinel Coatings on InterconnectsR Wang, Z Sun, Y Lu, UB Pal, SN Basu, S Gopalan, ECS Transactions 78 (1), 1665-1674
- Mitigation of chromium poisoning of cathodes in solid oxide fuel cells employing $CuMn_{1.8}O_4$ spinel coating on metallic interconnect, R Wang, Z Sun, UB Pal, S Gopalan, SN Basu, Journal of Power Sources 376, 100-110
- $CuMn_{1.8}O_4$ protective coatings on metallic interconnects for prevention of Cr-poisoning in solid oxide fuel cells, Z Sun, R Wang, AY Nikiforov, S Gopalan, UB Pal, SN Basu, Journal of Power Sources 378, 125-133

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Thank you! Questions?

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