Cathode Cleaning for Chromium Poisoning Recovery

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Outline

- **Chromium Poisoning**
- **Mitigation Strategies**
- **Electrochemical Cleaning**
- **Design of Experiments for Process Optimization (LSM Cathodes)**
- **Results**
- **Summary & Future Work on LSF and LSCF Cathodes**

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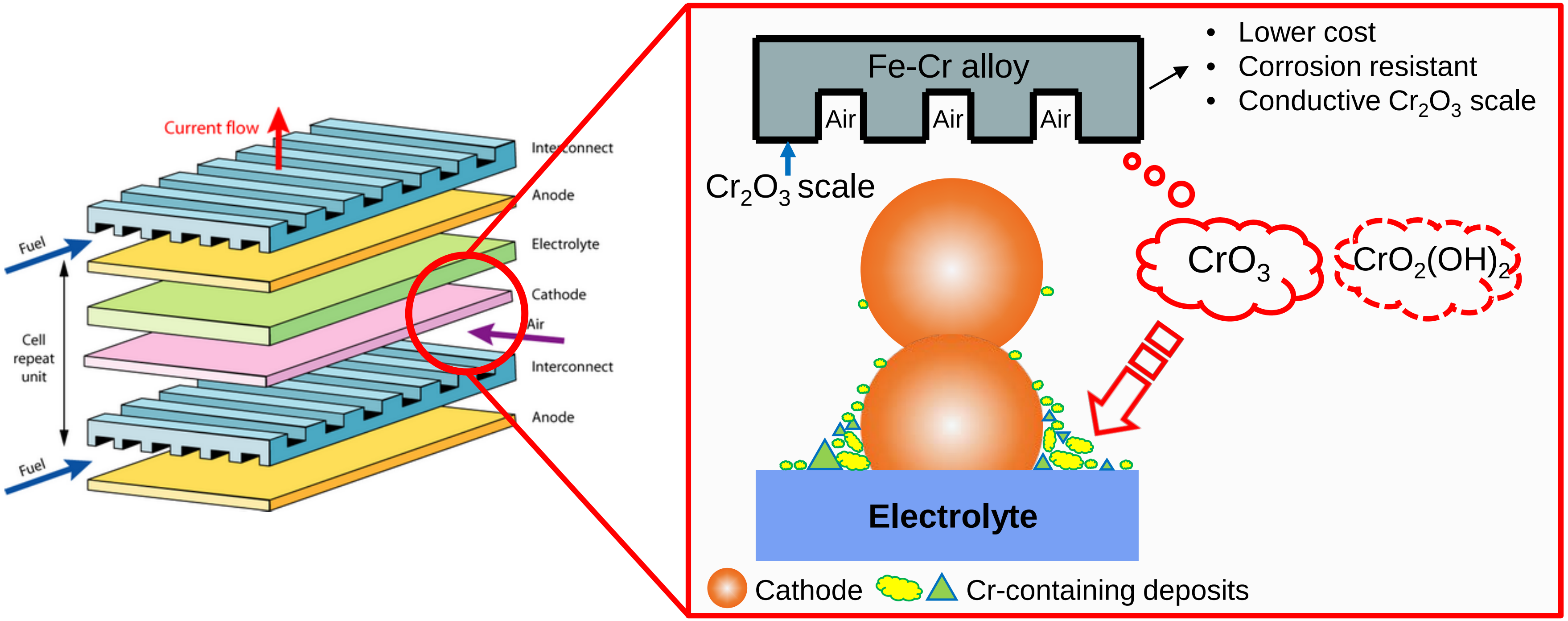
Background

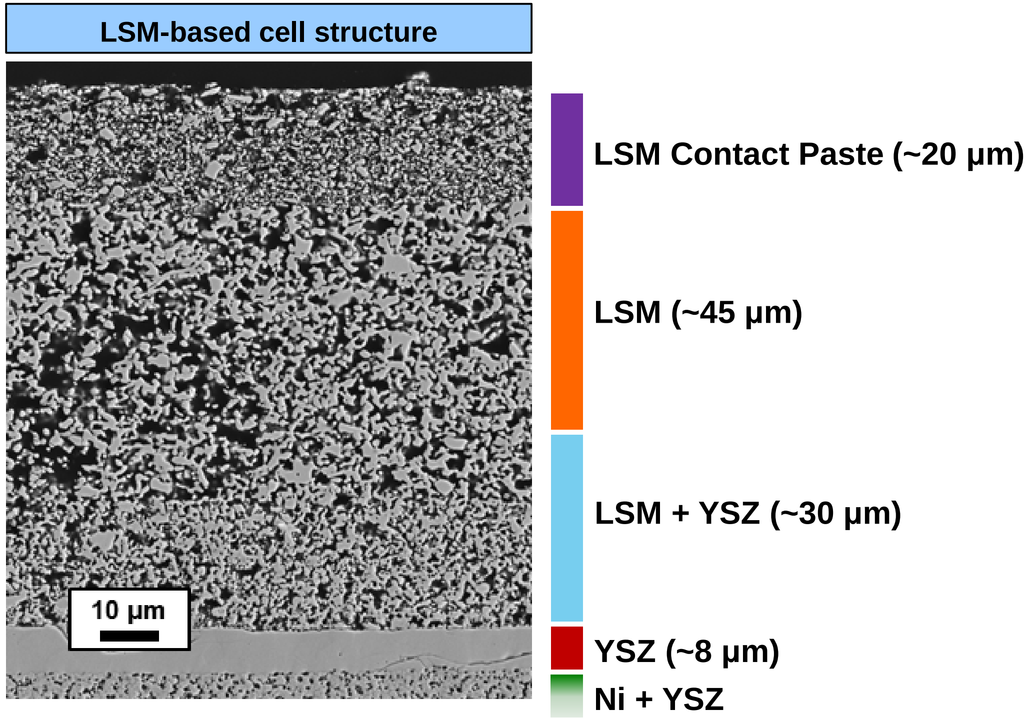
❖ **Cr-Poisoning in SOFC cathodes**

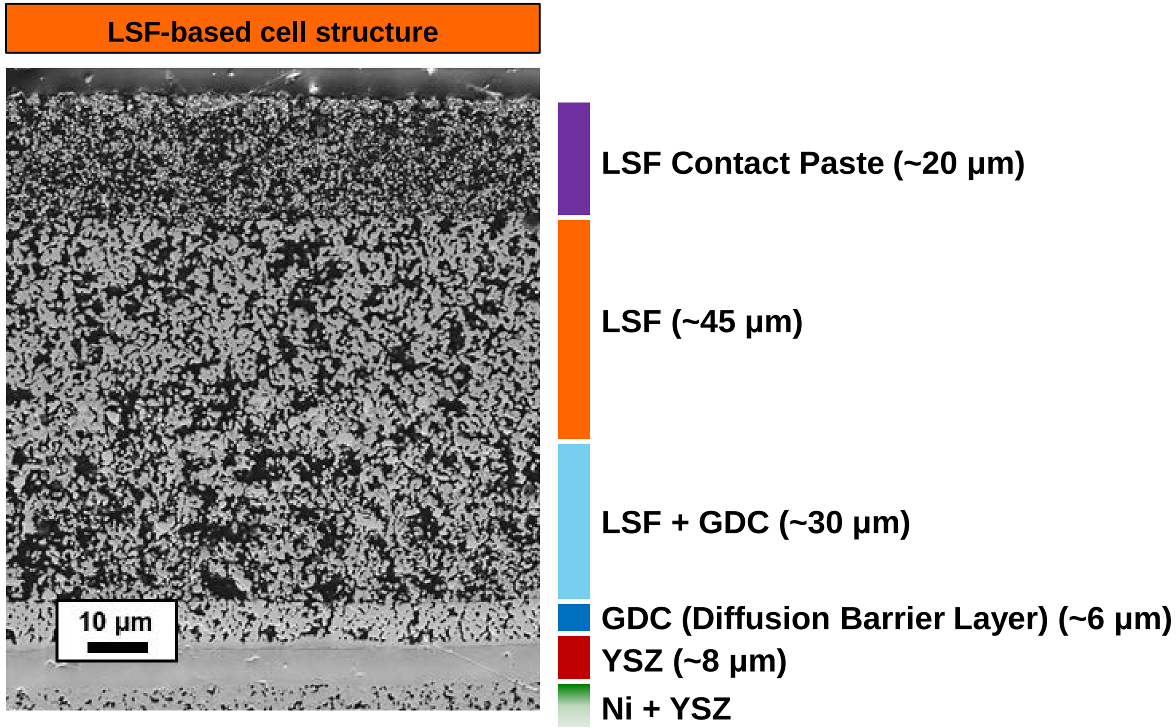


$$CrO_3(g,\ cathode)+\frac{3}{2}H_2(g,\ anode)=\frac{1}{2}Cr_2O_3(s,\ cathode)+\frac{3}{2}H_2O(g,\ anode)$$

$$CrO_2(OH)_2(g,cathode)+\frac{3}{2}H_2(g,anode)=\frac{1}{2}Cr_2O_3(s,cathode)+H_2O(g,cathode)+\frac{3}{2}H_2O(g,anode)$$

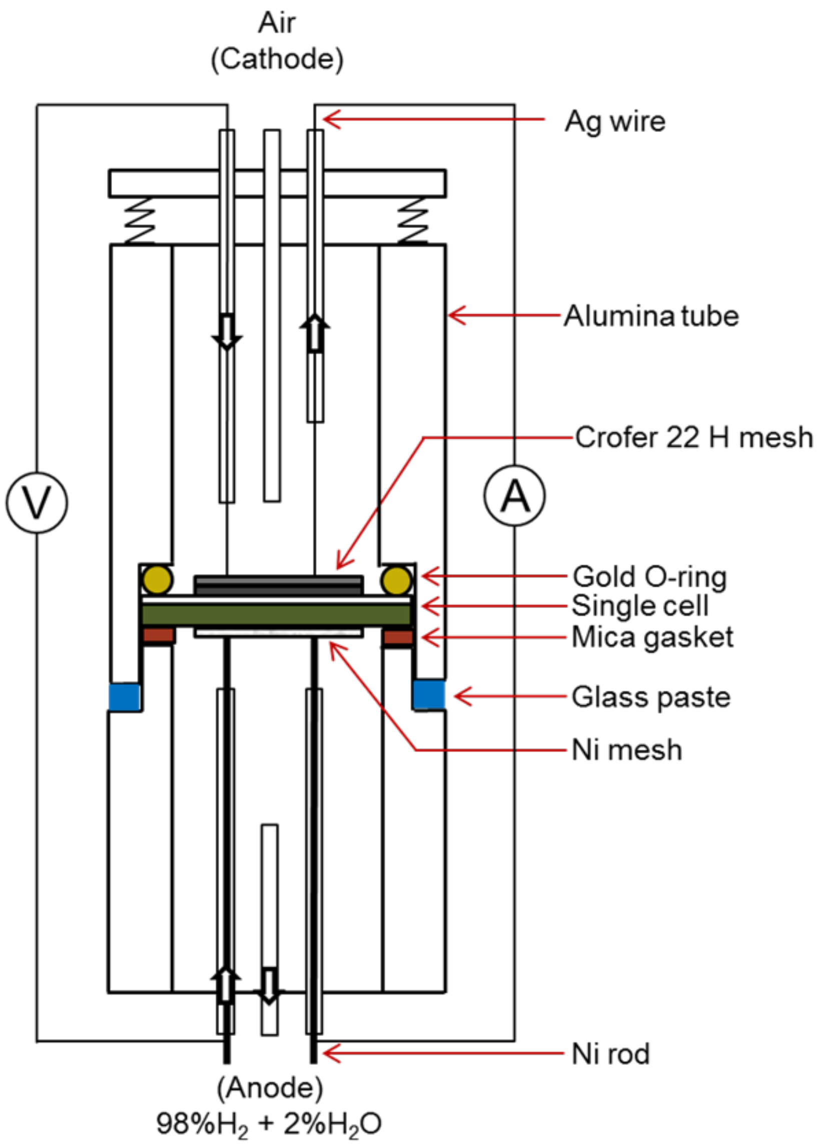
Experimental





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: $(Gd_{0.10}Ce_{0.90})O_{1.95}$

Experimental

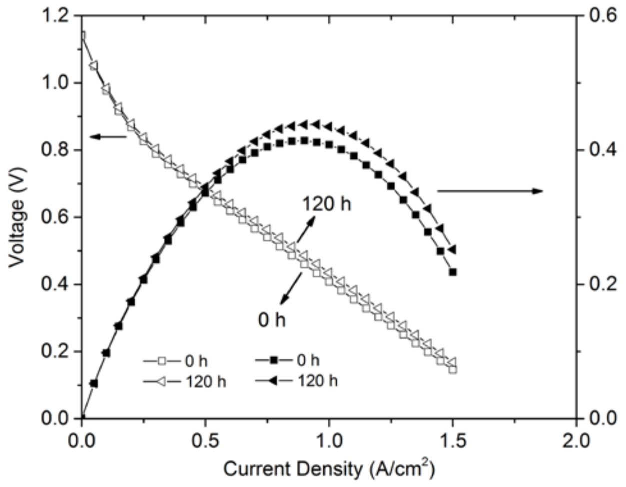
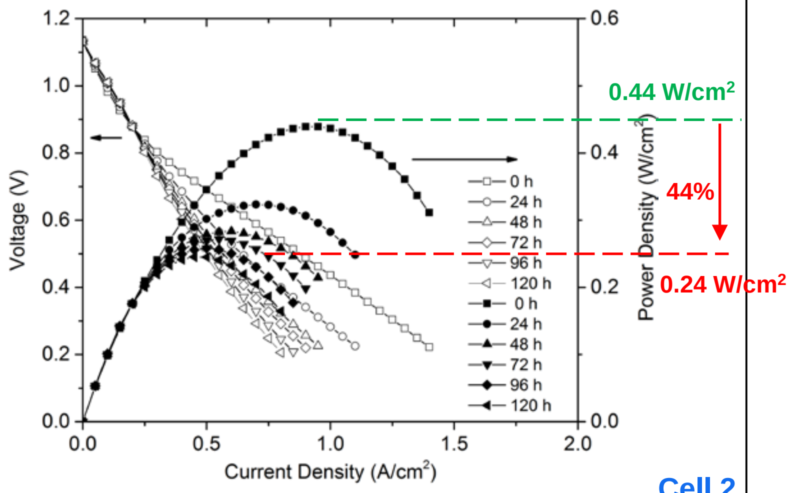
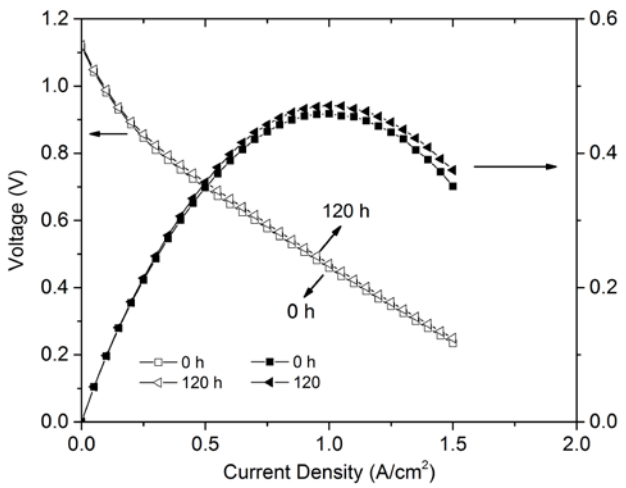
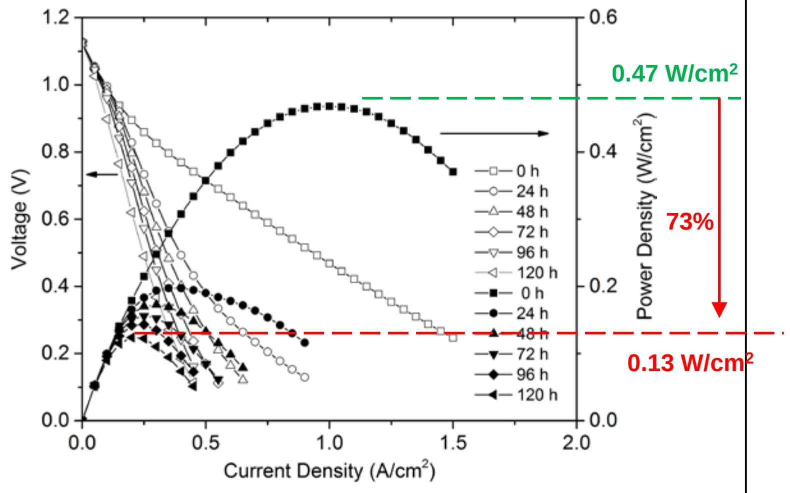


- **General test conditions:**
  - Fuel: 98% H_2+2% H_2O (300 cc/min): Fixed
  - Oxidant: Air (1000 cc/min)
  - Interconnect: Crofer 22 H mesh (used as cathodic current collector in cell tests)
  - 120 hour test
- **Conditions varied in the study:**

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

Cr-Poisoning in LSM-based Cathodes

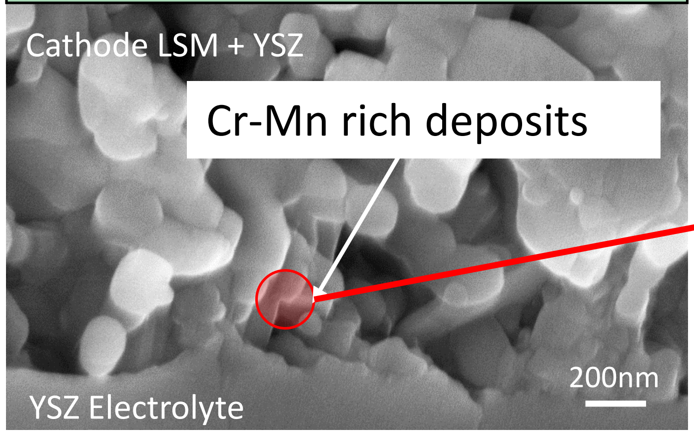
❖ **Current-Voltage Measurements with 4 Test Conditions on 4 Identical Cells (800 °C):**

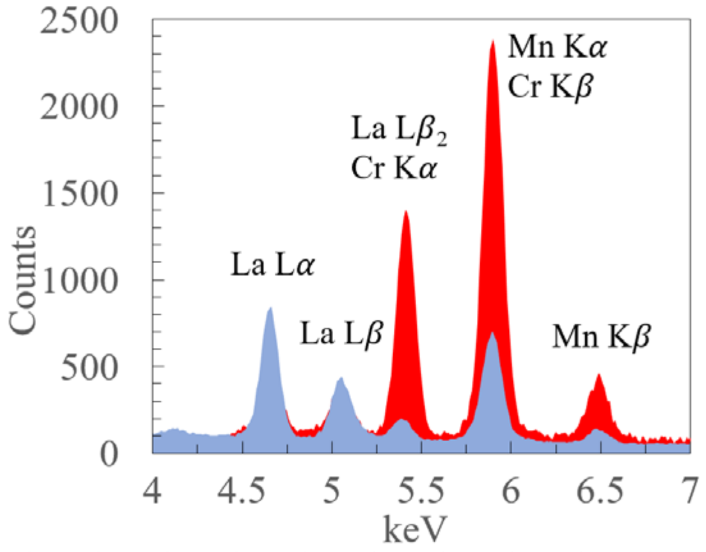
	No Current (OCV)	With Current (0.5 A/cm²)
Dry Air	 Cell 1	 Cell 2
Humidified (10%) Air	 Cell 3	 Cell 4

Two Types of Cr-containing Deposits

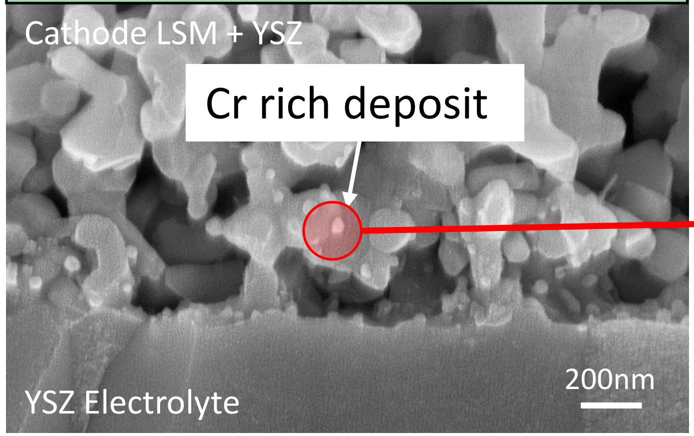
Spectrum for cell after poisoning
Reference spectrum for Cr free cell

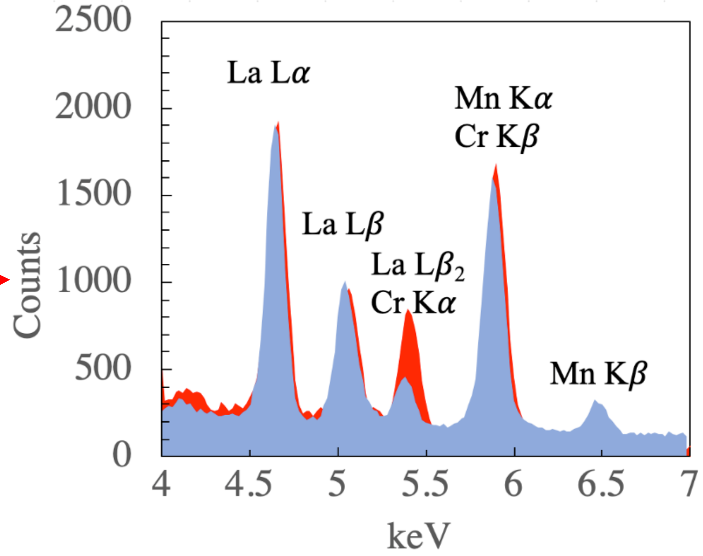
LSM cell after poisoning





LSM cell after poisoning





$$\frac{\text{La L}\beta_2 + \text{Cr K}\alpha}{\text{La L}\alpha} = 1.8$$

$$\frac{\text{Mn K}\beta}{\text{La L}\alpha} = 0.68$$

Increase in Cr and Mn: deposit is Cr-Mn oxide

For as received Cr-free cathodes
The two ratios are fixed

$$\frac{\text{La L}\beta_2 + \text{Cr K}\alpha}{\text{La L}\alpha} = 0.3$$

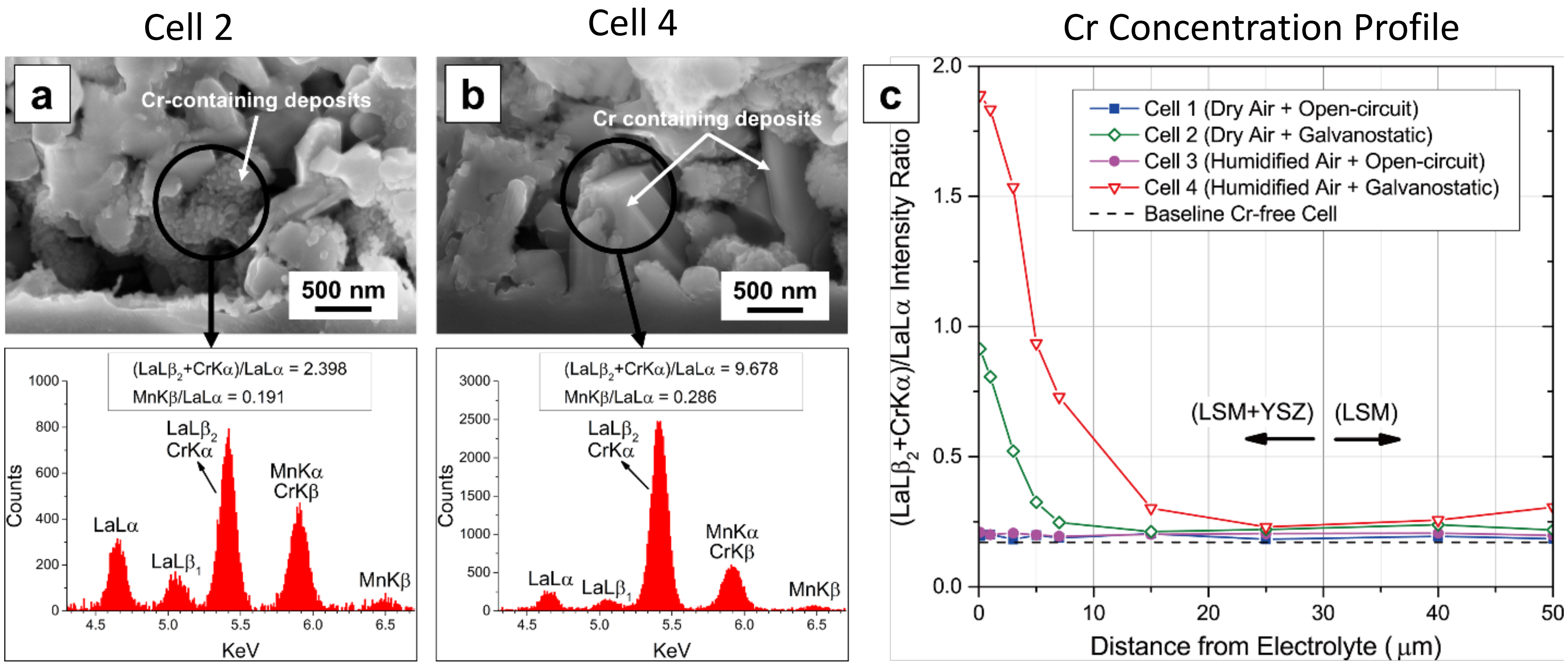
$$\frac{\text{Mn K}\beta}{\text{La L}\alpha} = 0.2$$

$$\frac{\text{La L}\beta_2 + \text{Cr K}\alpha}{\text{La L}\alpha} = 0.5$$

$$\frac{\text{Mn K}\beta}{\text{La L}\alpha} = 0.22$$

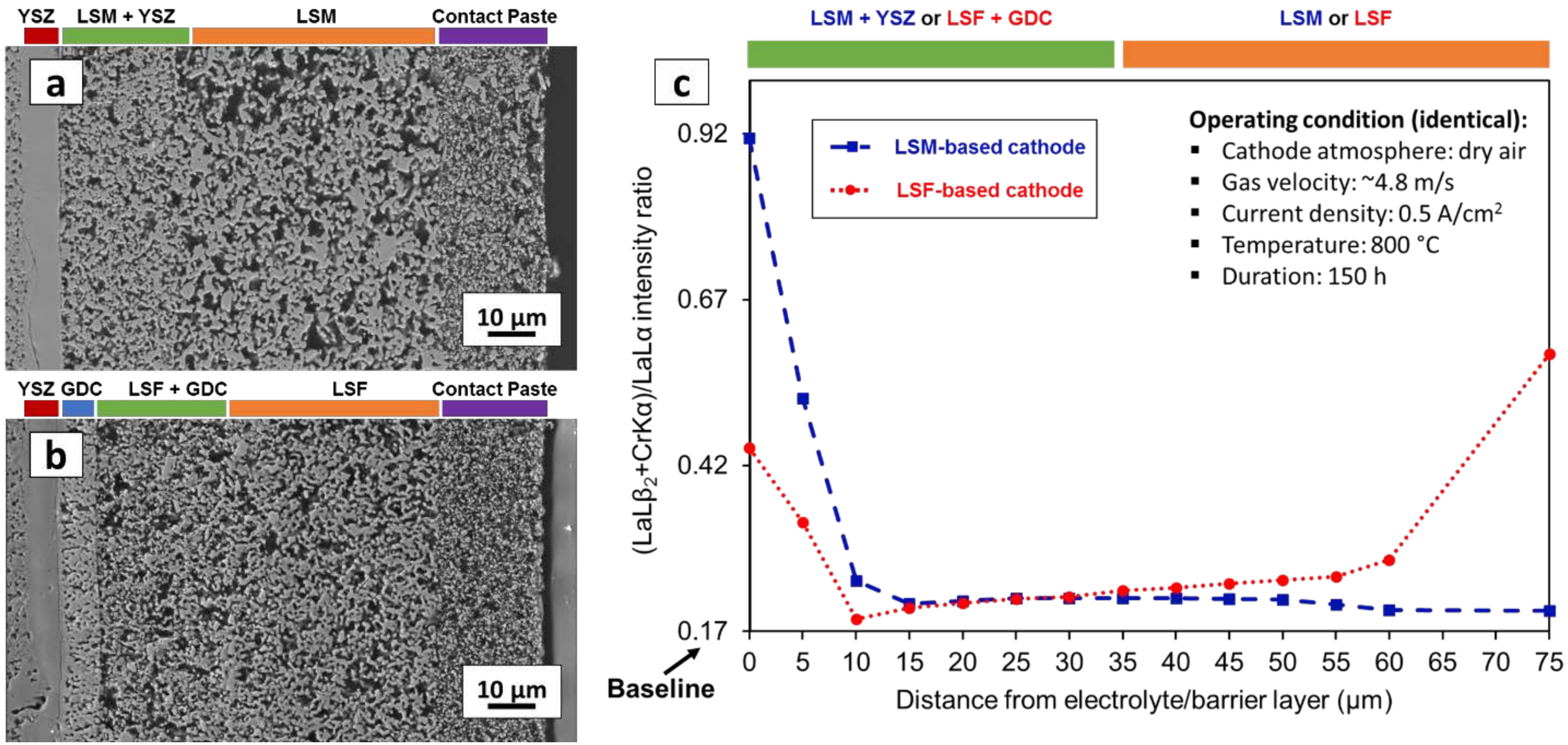
Increase in Cr only: deposit is (Cr-oxide) Cr_2O_3

SEM images and corresponding EDX spectra of Cr-containing deposits at the cathode/electrolyte interfaces in LSM-based cathode



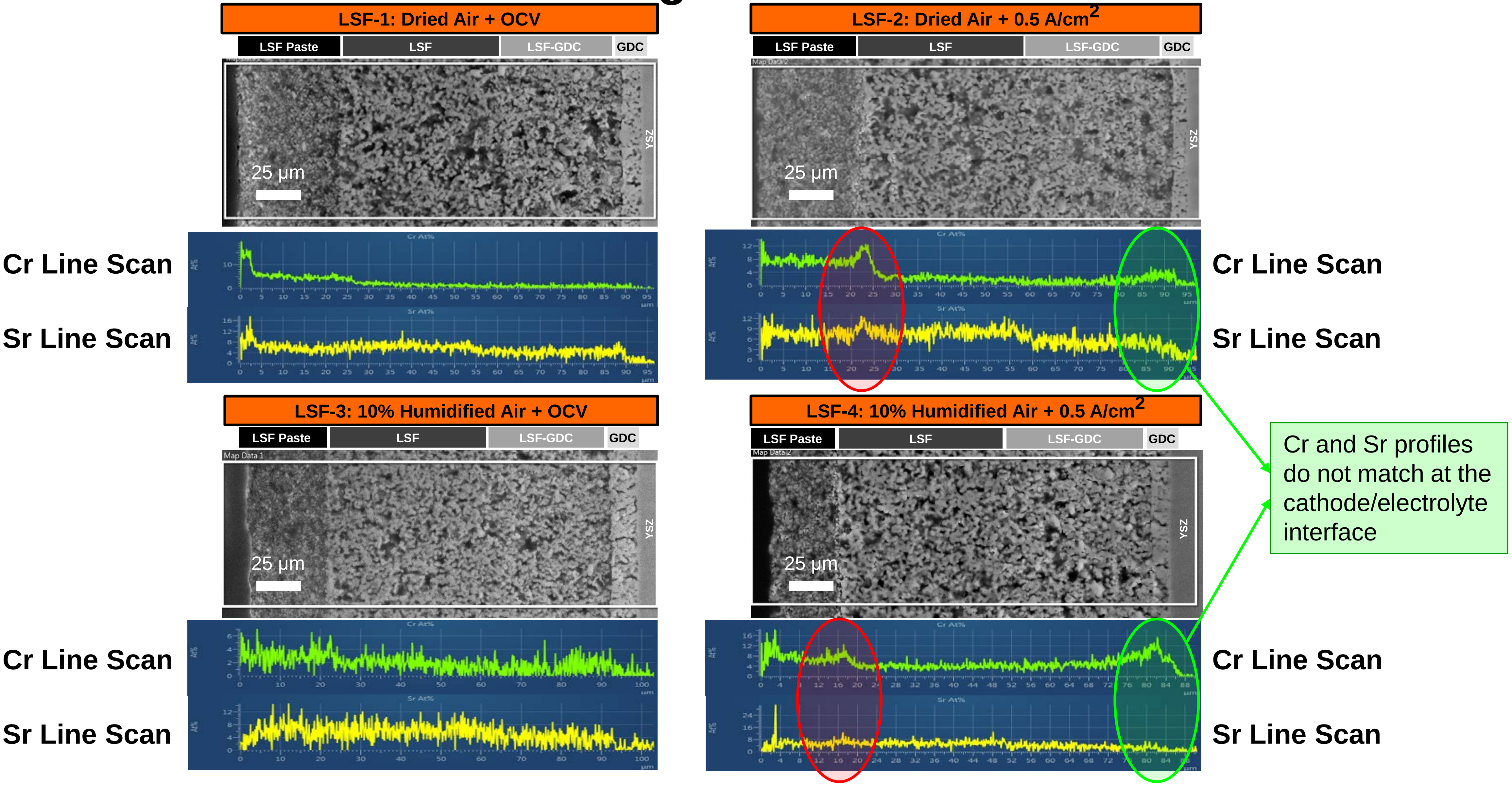
- Cr intensity at cathode/electrolyte interface: LSM-4 > LSM-2 > LSM-3 ≈ LSM-1
- Cr deposition was promoted by current and humidity and extended to TPB’s away from the cathode/electrolyte interface.

Cr-Poisoning Behavior of LSM versus LSF Cathodes



LSF cathodes are more tolerant to chromium poisoning than LSM cathodes

Microstructural Degradation: LSF-Based



Deposits at the electrode surface and electrode/electrolyte interface are Sr-Cr oxide and Cr-oxide

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Cr-Poisoning

- **Complexity and Impact of Chromium Poisoning Phenomena**
  - Cr-poisoning depends on current density, humidity, temperature and type of cathode material
  - Cr-poisoning is one of the major reasons for long-term performance degradation of state-of-the-art SOFCs

- **State-of-the-art mitigation strategies**
  - Use of Cr diffusion resistant coatings on interconnects
  - Use of cathode materials more tolerant to Cr poisoning
  - Use of materials to getter Cr-vapors
  - Use of alumina forming alloys for balance of plant (BOP) components

- **Limitations of the current mitigation strategies**
  - Protective coating and the alternate chromium resistant cathode compositions merely postpone the onset of catastrophic degradation due to Cr poisoning.
  - Cr Gettering requires change out of the getter after its capacity is exhausted
  - Not sufficient to ensure stable reliable SOFC performance for 5 years or more

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Our Technical Approach

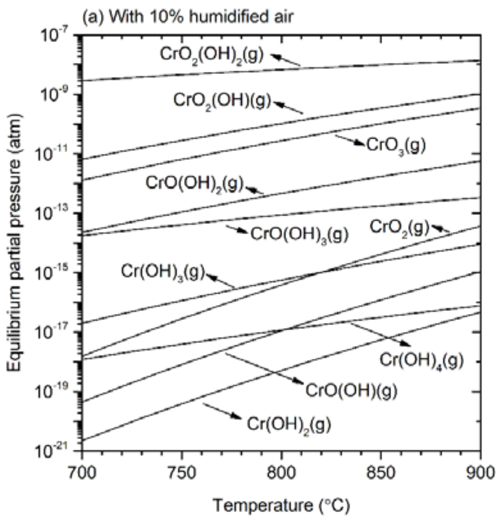
Our approach is to electrochemically reverse the effects of Cr-poisoning by removing the chromium oxide-containing deposits in the cathode as higher valent oxide and oxy-hydroxide vapor species and restore the cathode to its original state.

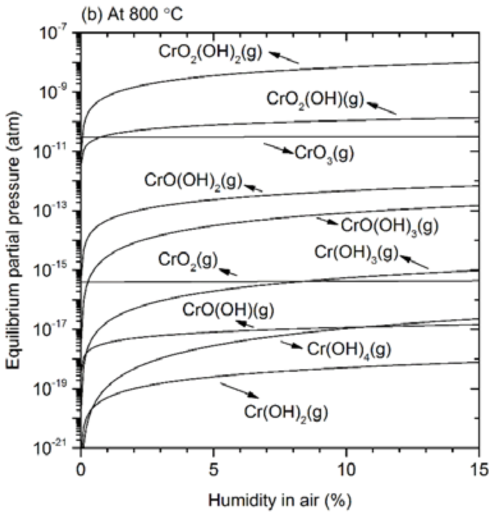
The specific advantages of our technique are:

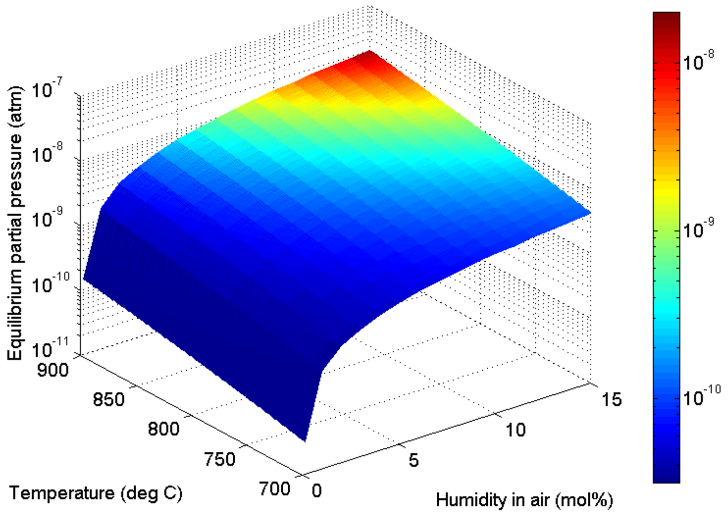
- No modification to any SOFC component from its current state is required and therefore there is no extra capital cost.
- No need to cool down the system, so there is no thermal shock or mechanical damage.
- Relatively quick process.
- No exposure to gas phases that the system does not already see.

Electrochemical Cleaning Procedure

50-100°C above the operating temperature, place the cell under a small electrolytic bias with humidified air containing 5-15% water vapor flowing through the air electrode (chemical cleaning) and introduce 20-40% water vapor in the fuel electrode







Electrochemical Cleaning

- Run cell in electrolysis mode to reverse deposition reaction.

Air electrode reactions

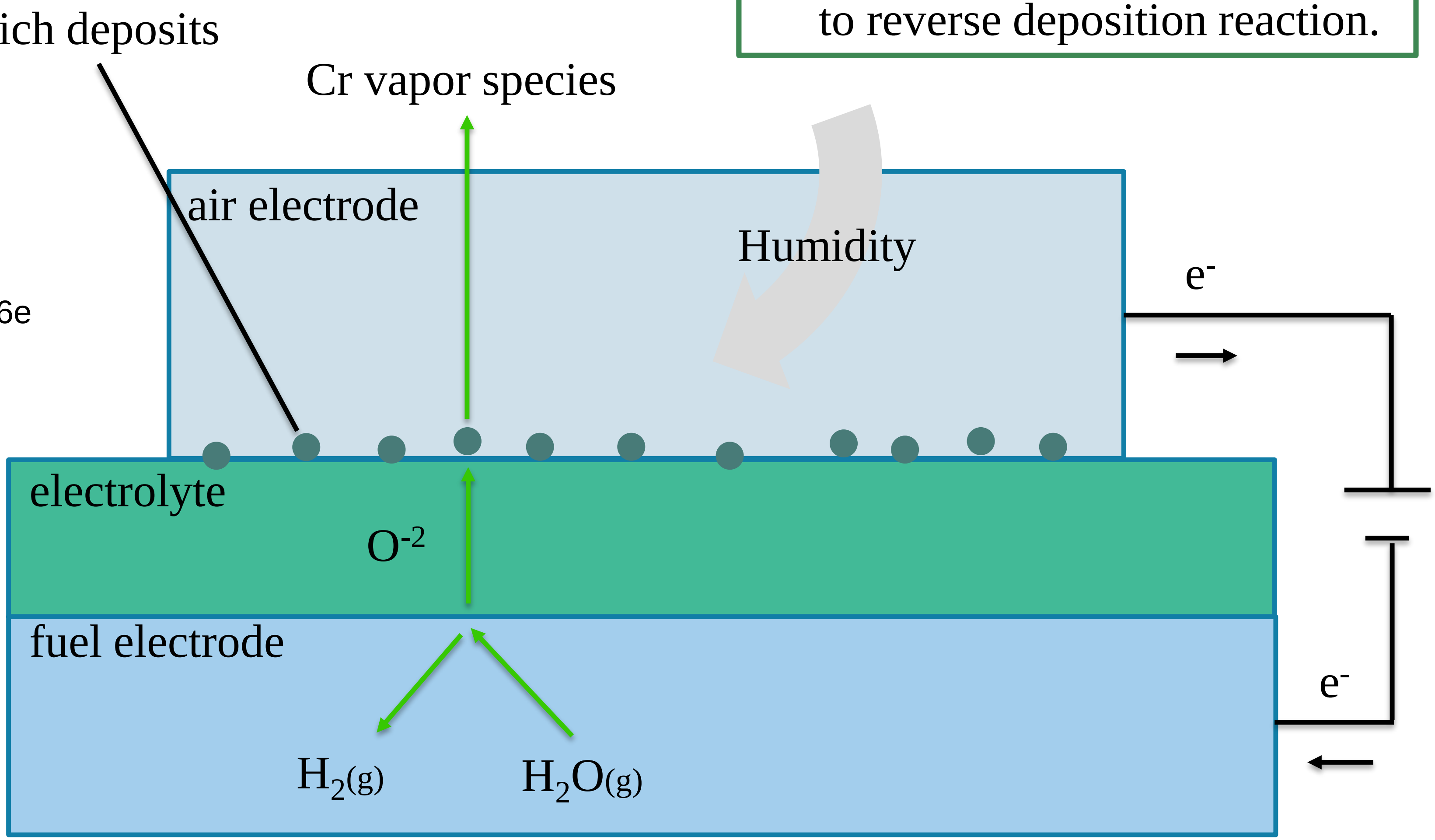
$Cr_2O_3(s) + 3O^{2-} + 2H_2O(g) = 2CrO_2(OH)_2(g) + 6e$

$1.5Cr_2O_3(s) + 3O^{2-} + 1.5H_2O(g) = 3CrO_2(OH)(g) + 6e$

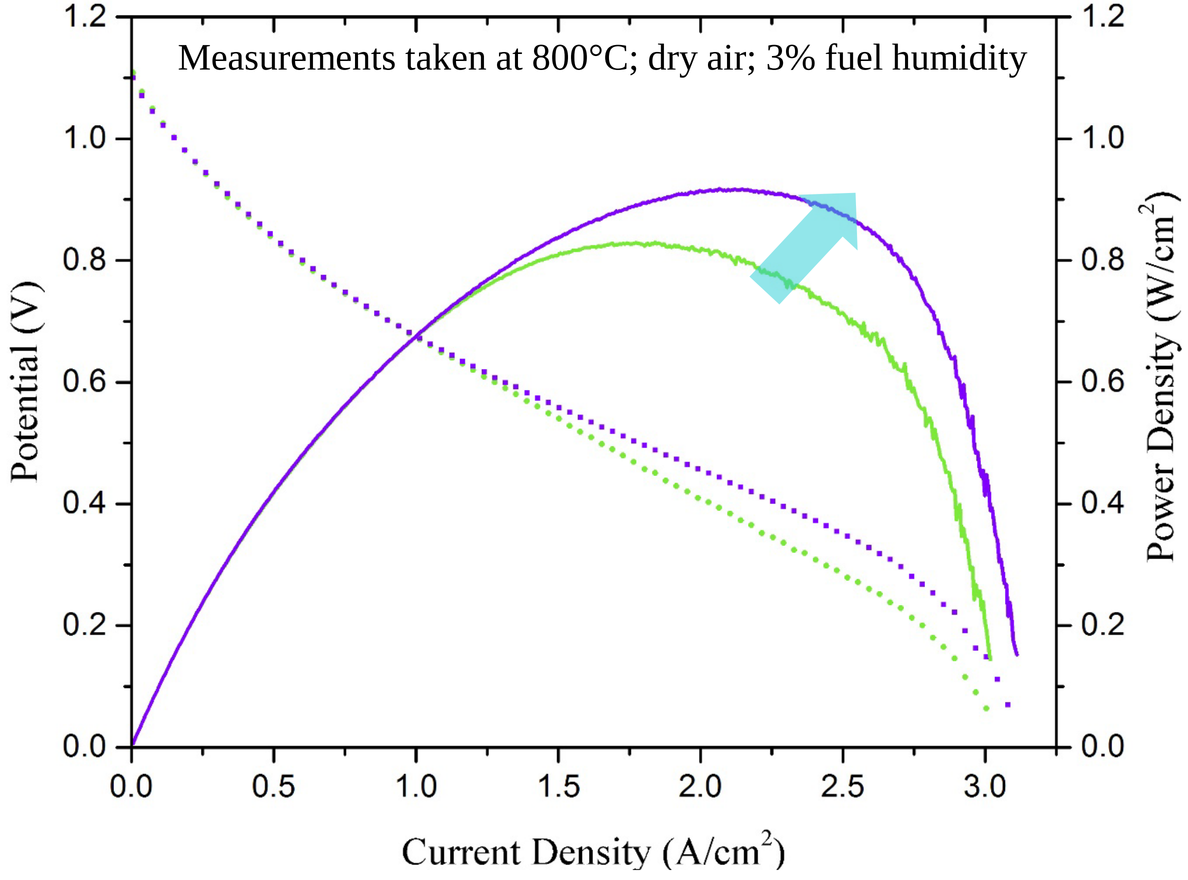
$Cr_2O_3(s) + 3O^{2-} = 2CrO_3(g) + 6e$

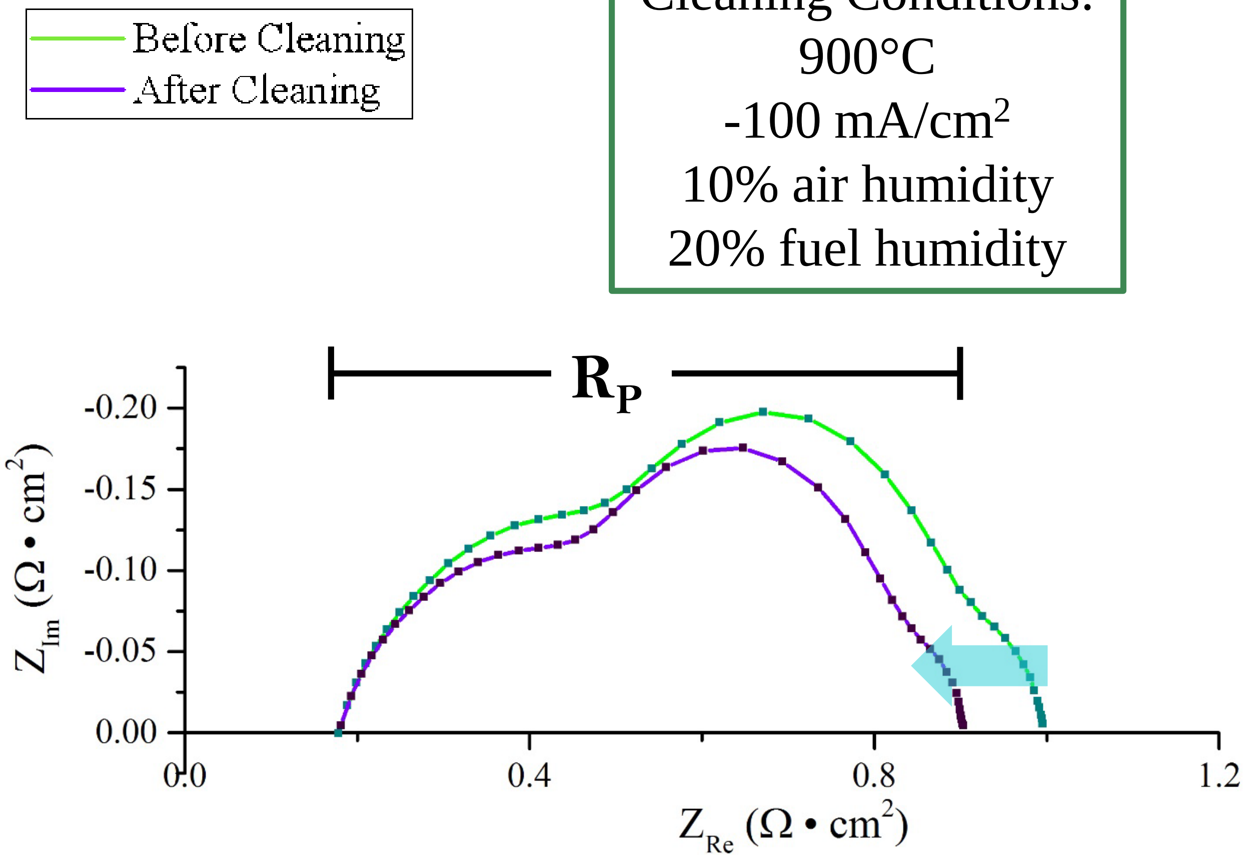
Fuel electrode reactions

$3H_2O(g) + 6e = 3H_2(g) + 3O^{2-}$



Evidence for Electrochemical Cleaning: I-V & EIS



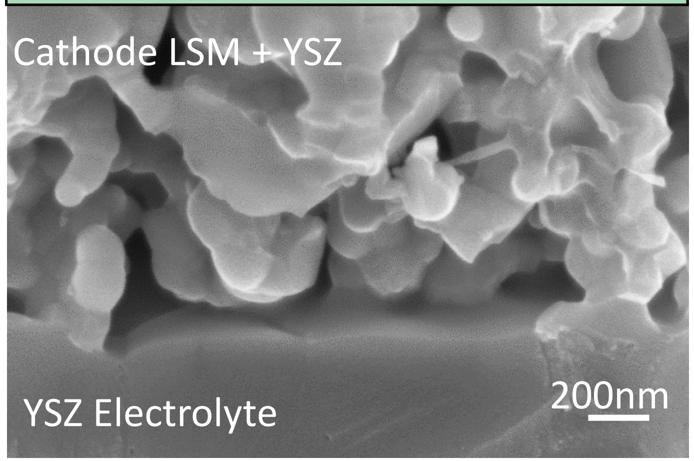


Cleaning Conditions:
900°C
-100 mA/cm^2
10% air humidity
20% fuel humidity

- Max power density and polarization resistance measurements demonstrate an increase in performance due to cleaning.

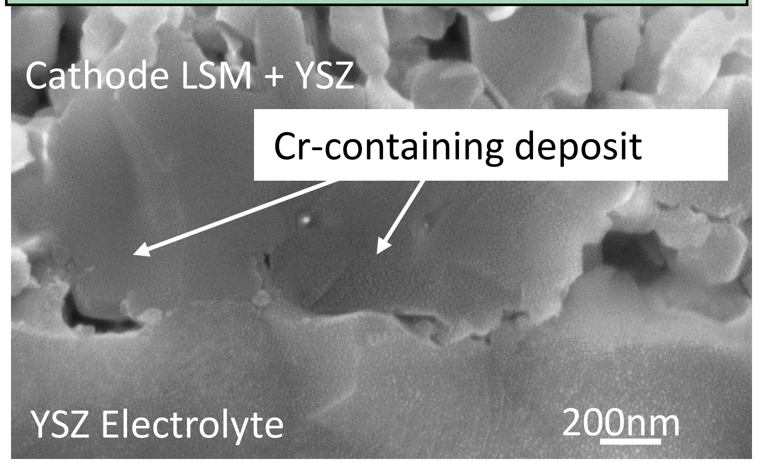
Physical Nature of Cathode Electrolyte Interface

LSM cell without poisoning



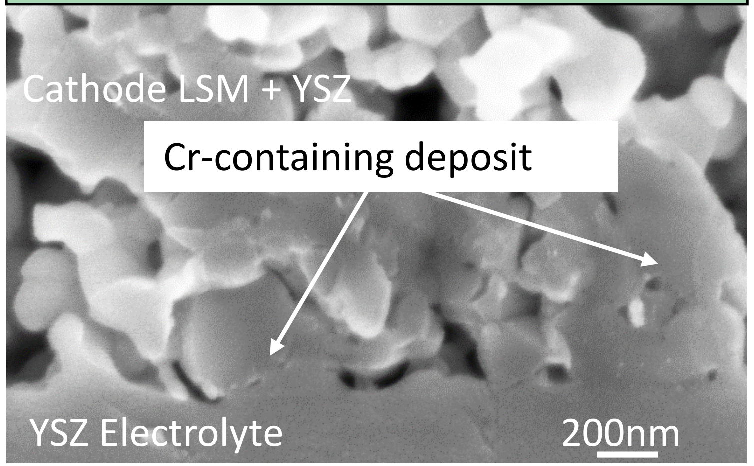
No deposits at cathode/electrolyte interface.

LSM cell after poisoning



Large Cr-containing particles at cathode/electrolyte interface.

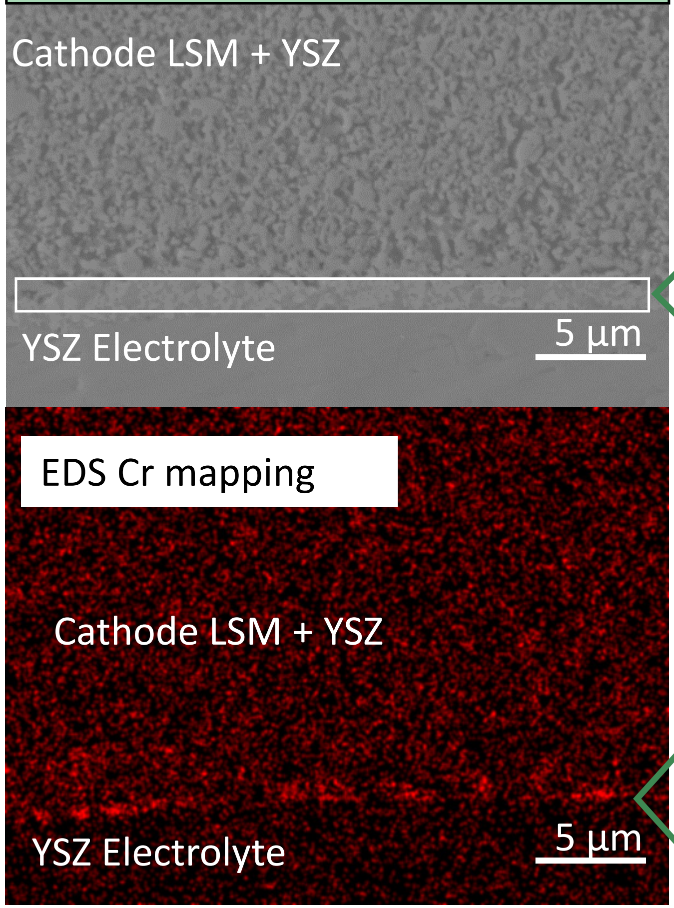
LSM cell after poisoning and cleaning



The cathode/electrolyte interface becomes cleaner.

Cr Mapping Comparison: Before and After Cleaning

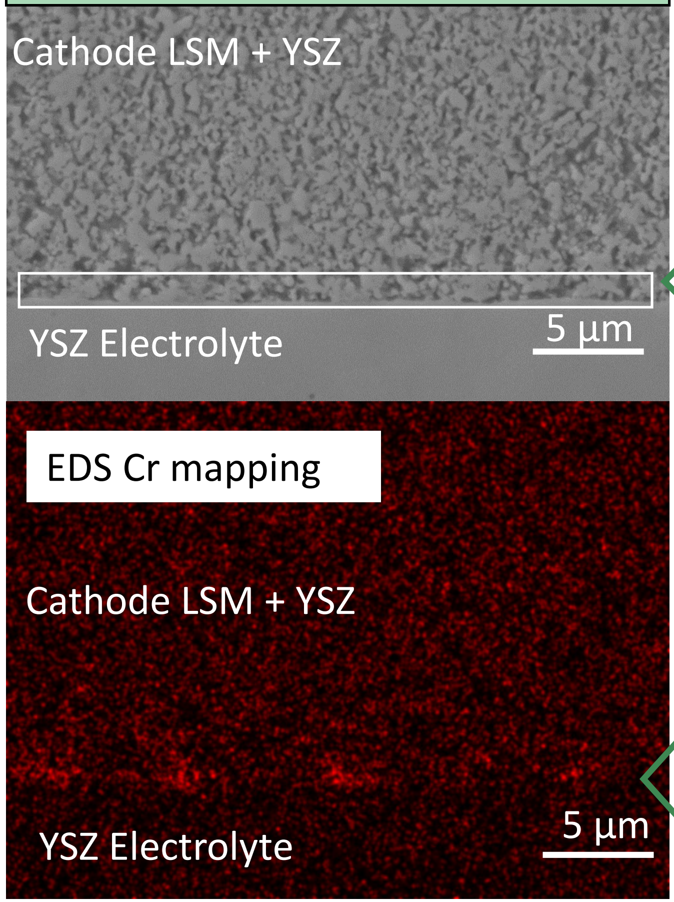
LSM cell after poisoning



Visibly filled pores.

Cr-containing particles found continuously at cathode/electrolyte interface.

LSM cell after poisoning and cleaning



Much cleaner interface.

Cr-containing particles found only periodically at cathode/electrolyte interface.

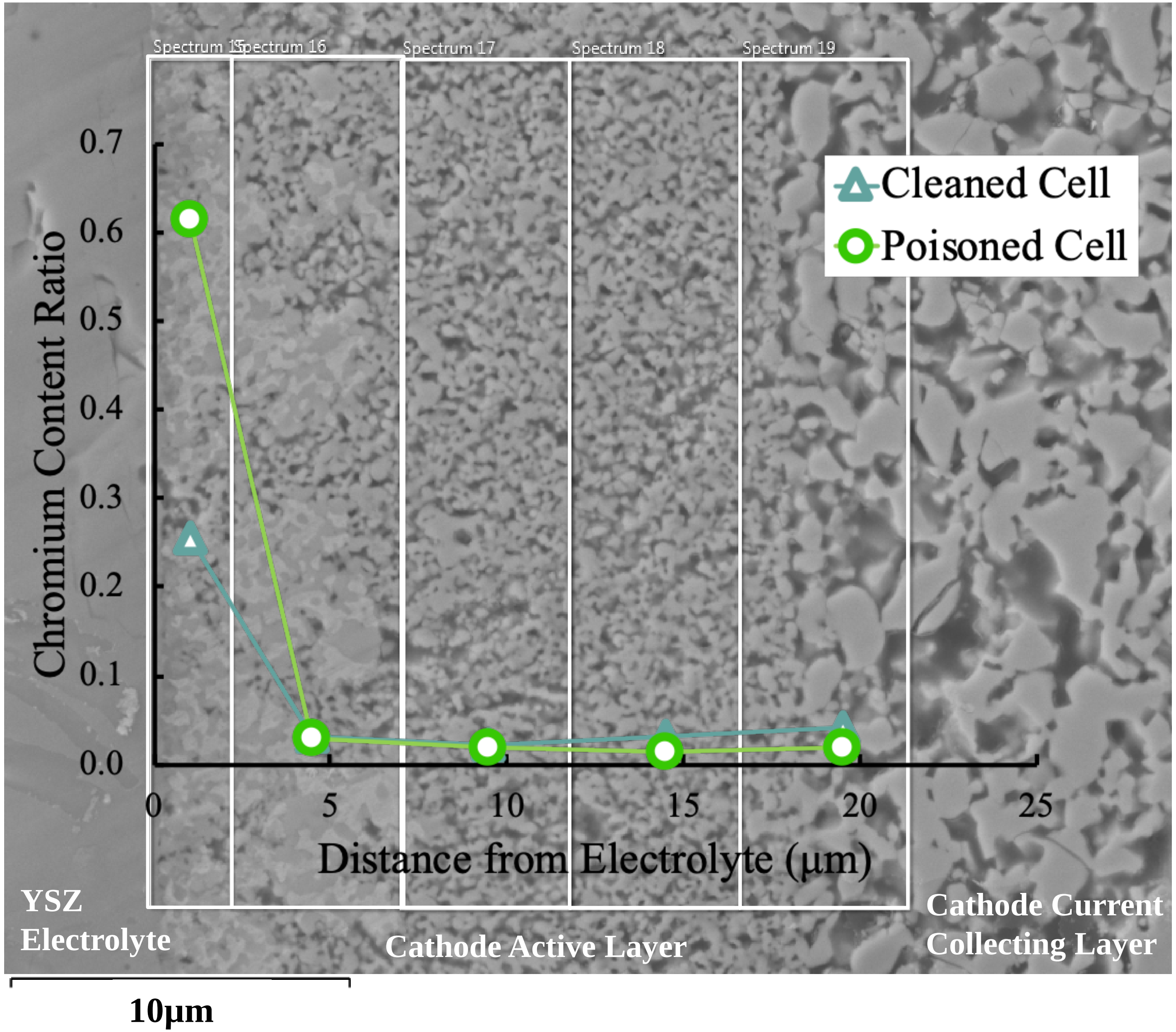
Evidence for Electrochemical Cleaning: Cr Quantification

Cleaning Conditions:
800°C
-100 mA/cm^2
10% air humidity
40% fuel humidity

Chromium Content Ratio:

$$\frac{\textit{Atomic \% of Cr}}{\textit{Atomic \% of La}}$$

- Cr preferentially deposits near the cathode/electrolyte interface.
- Cleaned Cell demonstrates significant decrease in chromium content.



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Design of Experiments for Cleaning Optimization

Five parameters affecting cleaning:

- Temperature
- Current density
- Air humidity
- Fuel humidity
- Cleaning duration

Using high and low level for each parameter yields $2^5 = 32$ possible experiments.

Can be reduced to $2^4 = 16$ unbiased experiments.

Still too many experiments! → limit to four parameters

Fractional Factorial Design of Experiments for Cleaning Optimization (2 hr duration)

Four Variables

Each variable has lower and upper bound

Total possible experiments 2^4

↓

Reduced number of unbiased experiments 2^3

Experiment	(A) Temperature (°C)	(B) Current (mA/cm^2)	(C) Air Humidity (%)	(D) Fuel Humidity (%)	(y) Performance Metric
1	800	-25	10	20	#
2	900	-25	10	40	#
3	800	-100	10	40	#
4	900	-100	10	20	#
5	800	-25	15	40	#
6	900	-25	15	20	#
7	800	-100	15	20	#
8	900	-100	15	40	#

Regression Analysis: $y = \mu + \beta_1 \cdot A + \beta_2 \cdot B + \beta_3 \cdot C + \beta_4 \cdot D$

Performance Metrics

Current-Voltage Curves

- Increase in maximum power density

EDS quantification

- Lower Cr content compared to poisoned cell

Testing Procedure

Poisoned Cell (Activation, Poisoning)

Cleaned Cells (Activation, Poisoning, Cleaning)

	Duration (h)	Furnace Temperature (°C)	Current Density (mA/cm^2)	Air Humidity (%)	Fuel Humidity (%)
ACTIVATION	60	800	500	0	3
POISONING	90	800	500	5	3
CLEANING	2	800 / 900	-25 / -100	10 / 15	20 / 40

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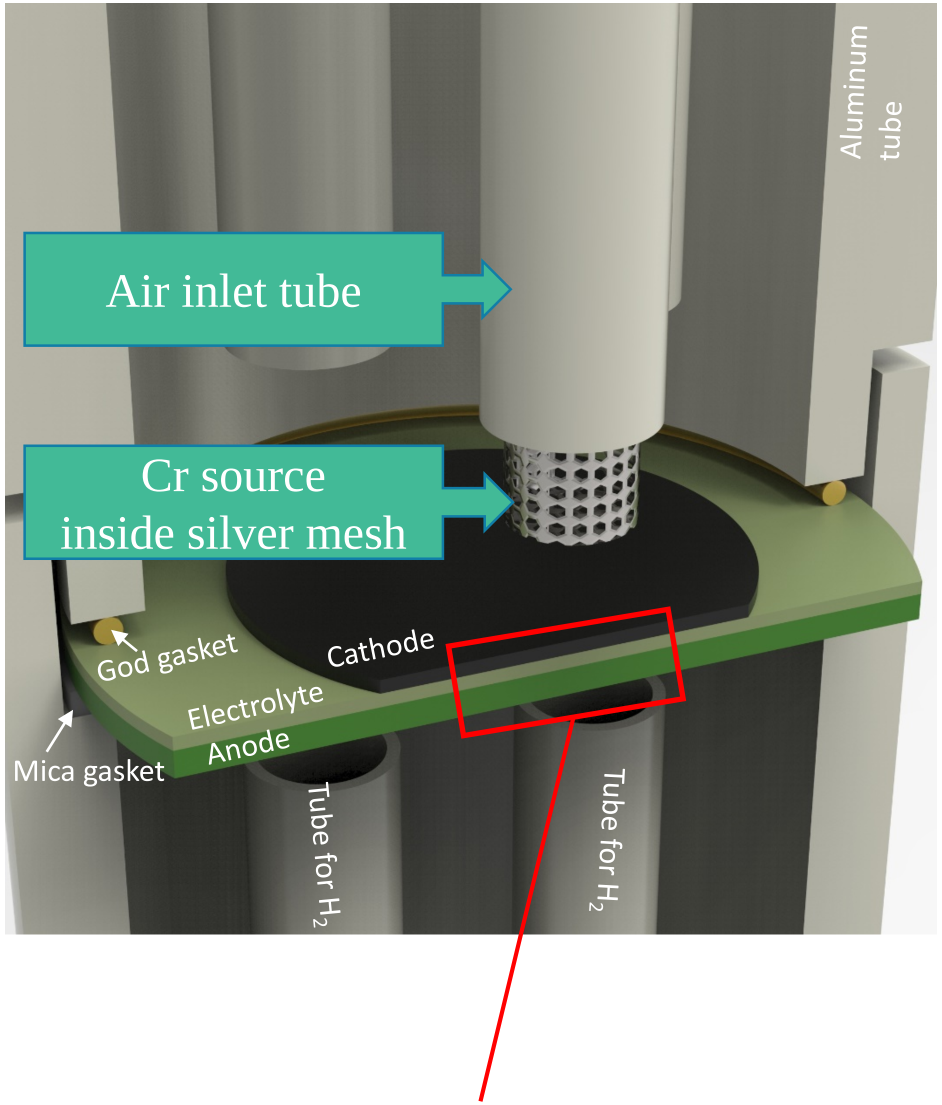
Experimental Matrix

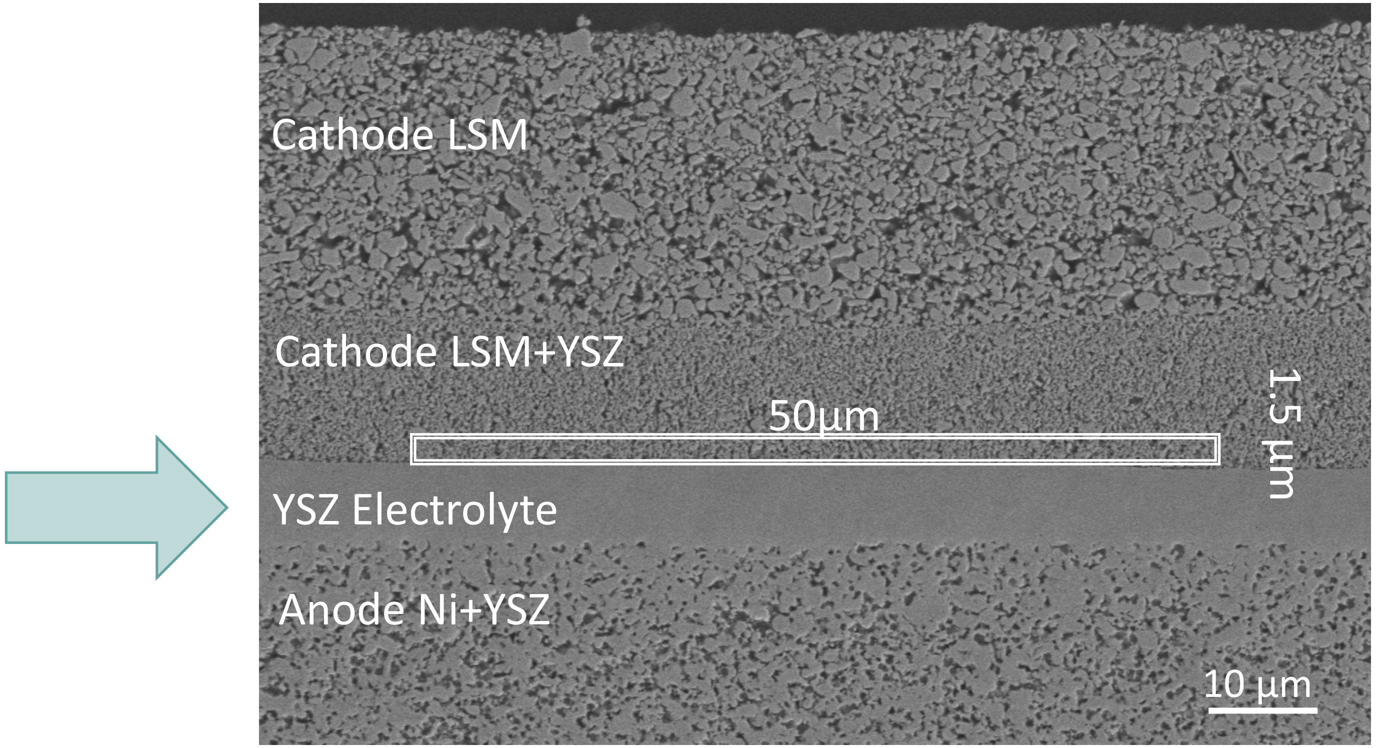
Experiment	(A) Temperature (°C)	(B) Current (mA/cm^2)	(C) Air Humidity (%)	(D) Fuel Humidity (%)
1	800	-25	10	20
2	900	-25	10	40
3	800	-100	10	40
4	900	-100	10	20
5	800	-25	15	40
6	900	-25	15	20
7	800	-100	15	20
8	900	-100	15	40

Poisoning Baseline

EDS Cr Quantification Method



Area investigated using EDS

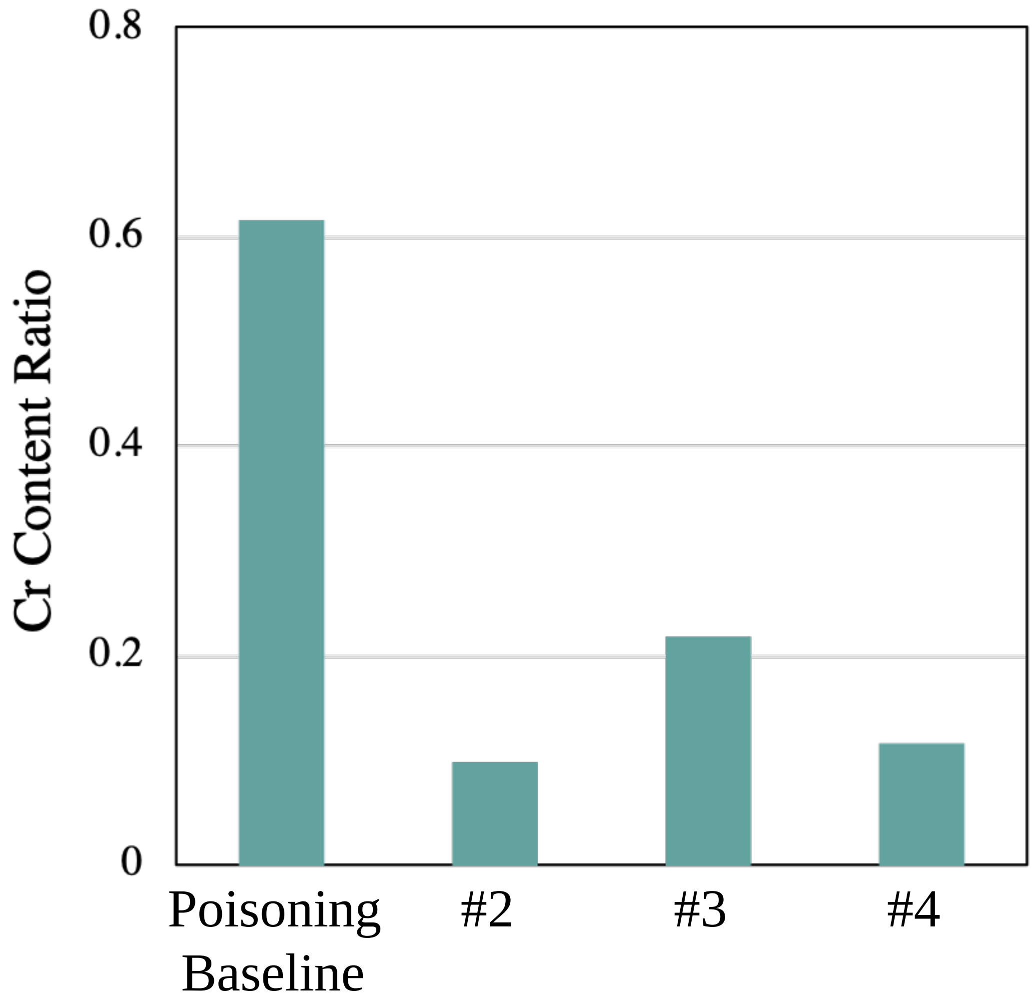


Repeat area scan 30 times across the 5mm cathode/electrolyte interface under Cr source.

Chromium Content Ratio:

$$\frac{Atomic\ \%\ of\ Cr}{Atomic\ \%\ of\ La}$$

EDS Cr Quantification Results



Cleaning parameters:

Experiment	Temperature (°C)	Current (mA/cm²)	Air Humidity (%)	Fuel Humidity (%)
2	900	-25	10	40
3	800	-100	10	40
4	900	-100	10	20

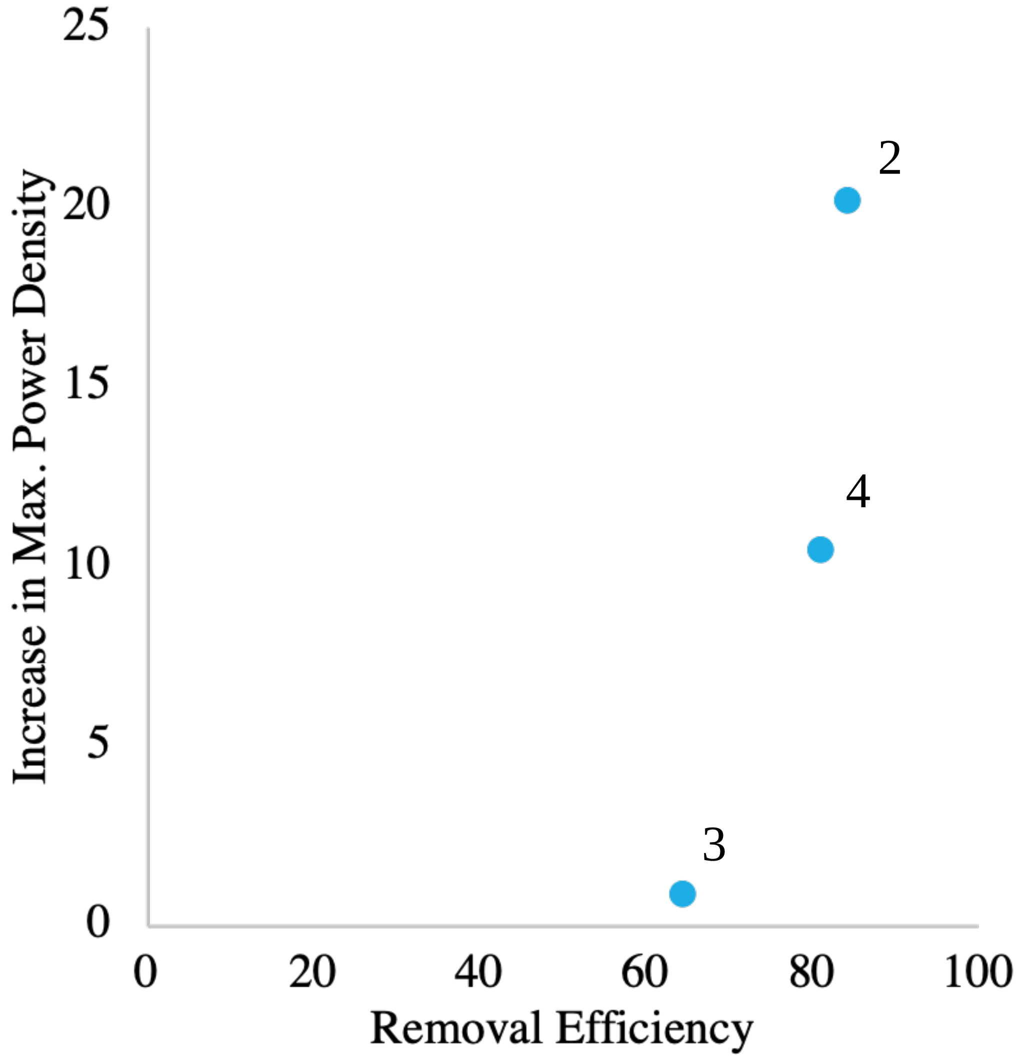
After electrochemical cleaning, lower amounts of chromium are found at the cathode/electrolyte interface.

Cr Removal and Performance Improvement

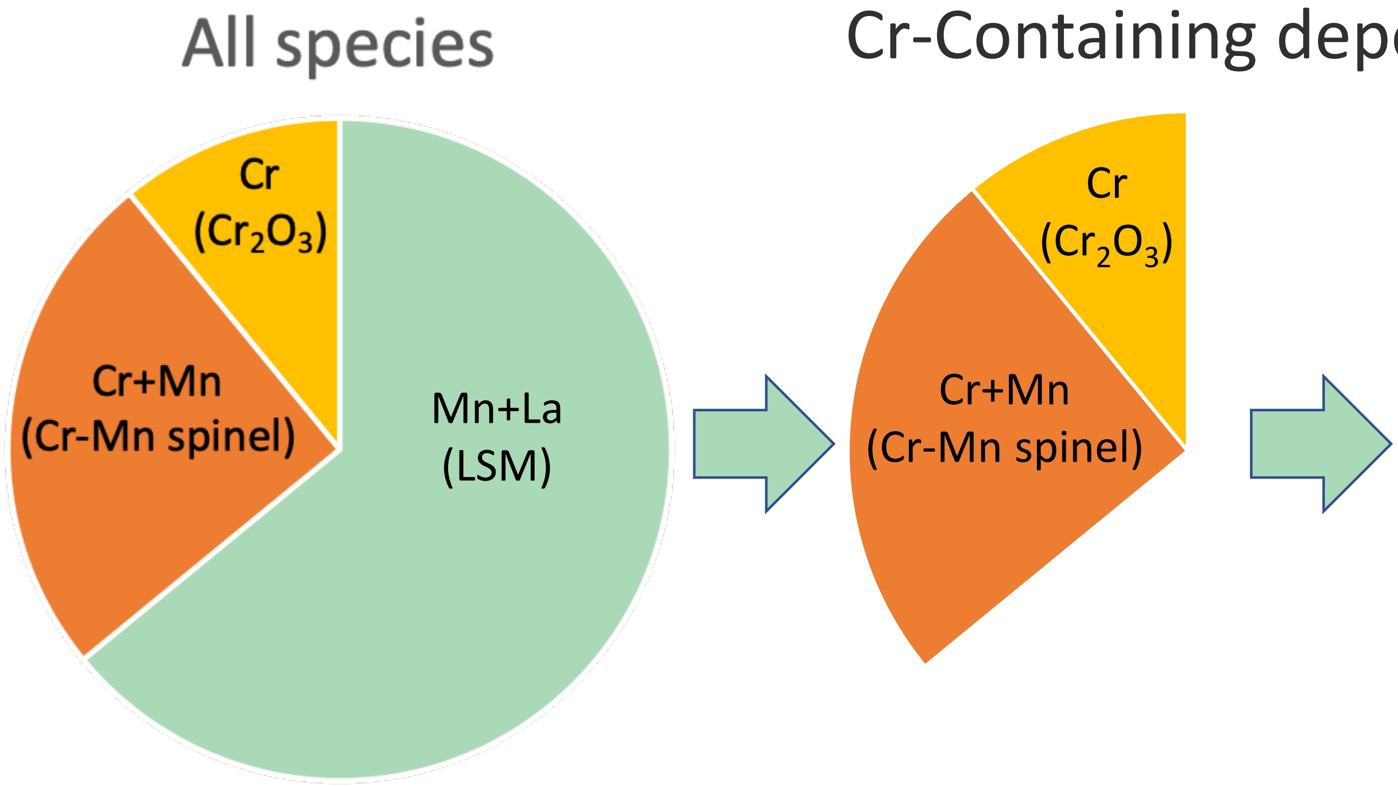
Experiment	Increase in Max. Power Density	Removal Efficiency*
2	20.2%	84.0%
4	10.5%	81.0%
3	0.9%	64.4%

*Comparing Cr Content Ratio to that of Poisoning Baseline

Increased chromium deposit removal correlates with greater max power density recovery.



Quantification of Cr-containing Deposits



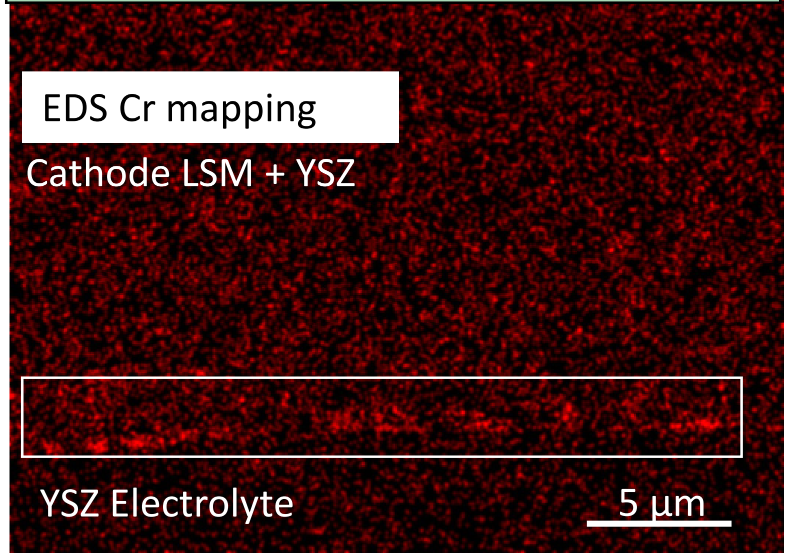
Measure Mn to Cr ratio in deposit

Part of Mn signal from background LSM

$$\text{Mn/Cr ratio in deposit} = \frac{\text{Measured atomic\%Mn} - \text{Known atomic\%Mn in LSM}}{\text{Measured atomic\%Cr}}$$

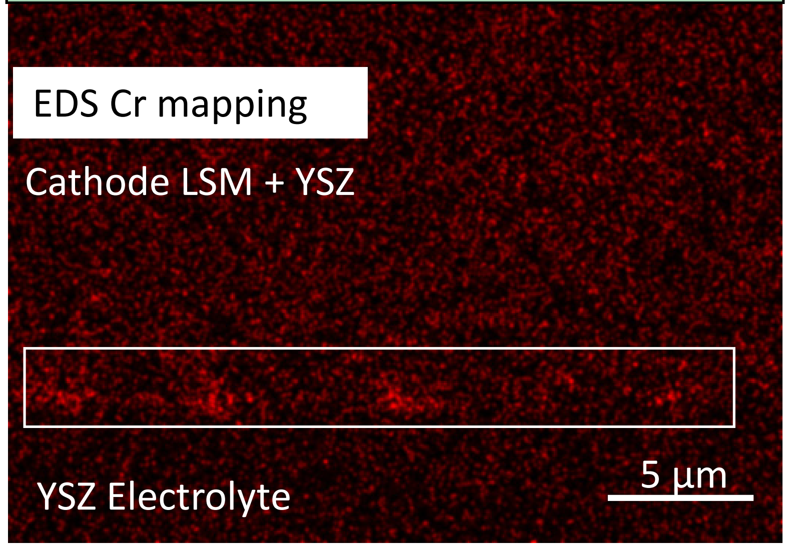
Mn/Cr Ratio in Deposits: Before and After Cleaning

LSM cell after poisoning



Mn/Cr ratio in deposits: 0.53

LSM cell after poisoning and cleaning

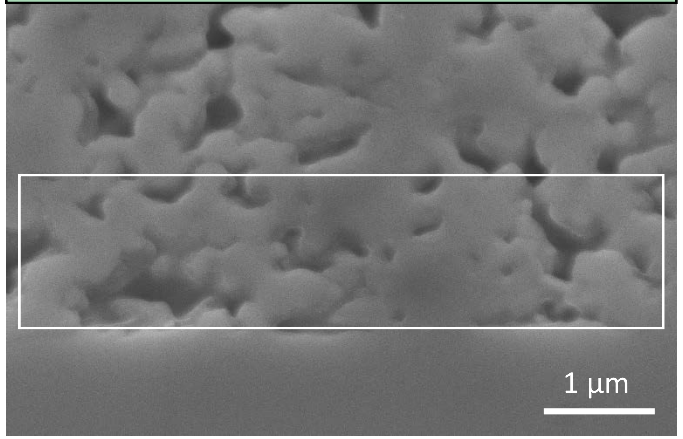


Mn/Cr ratio in deposits: 0.80

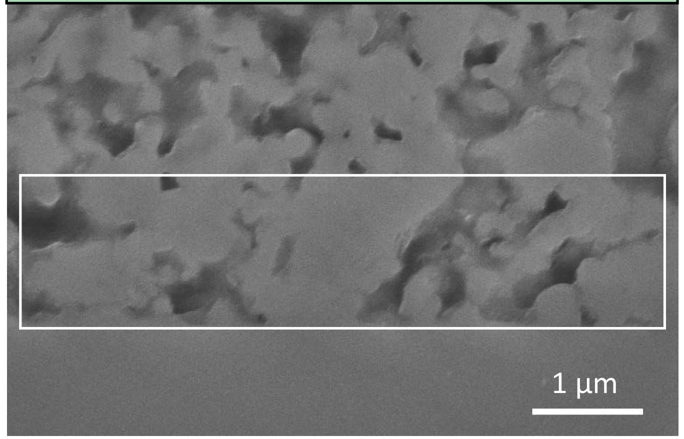
Higher Mn/Cr Ratio in Deposits after cleaning compared to after poisoning shows that **Cr_2O_3 is the major phase being removed during the cleaning process**.

Mn/Cr Ratio in Deposits VS Removal Efficiency

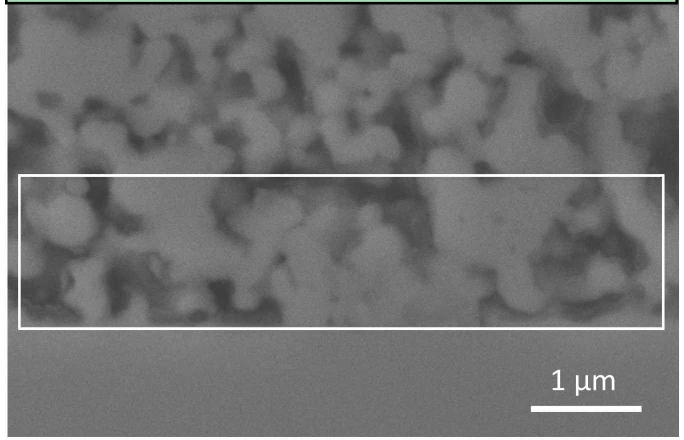
Cleaning Experiment #2



Cleaning Experiment #3



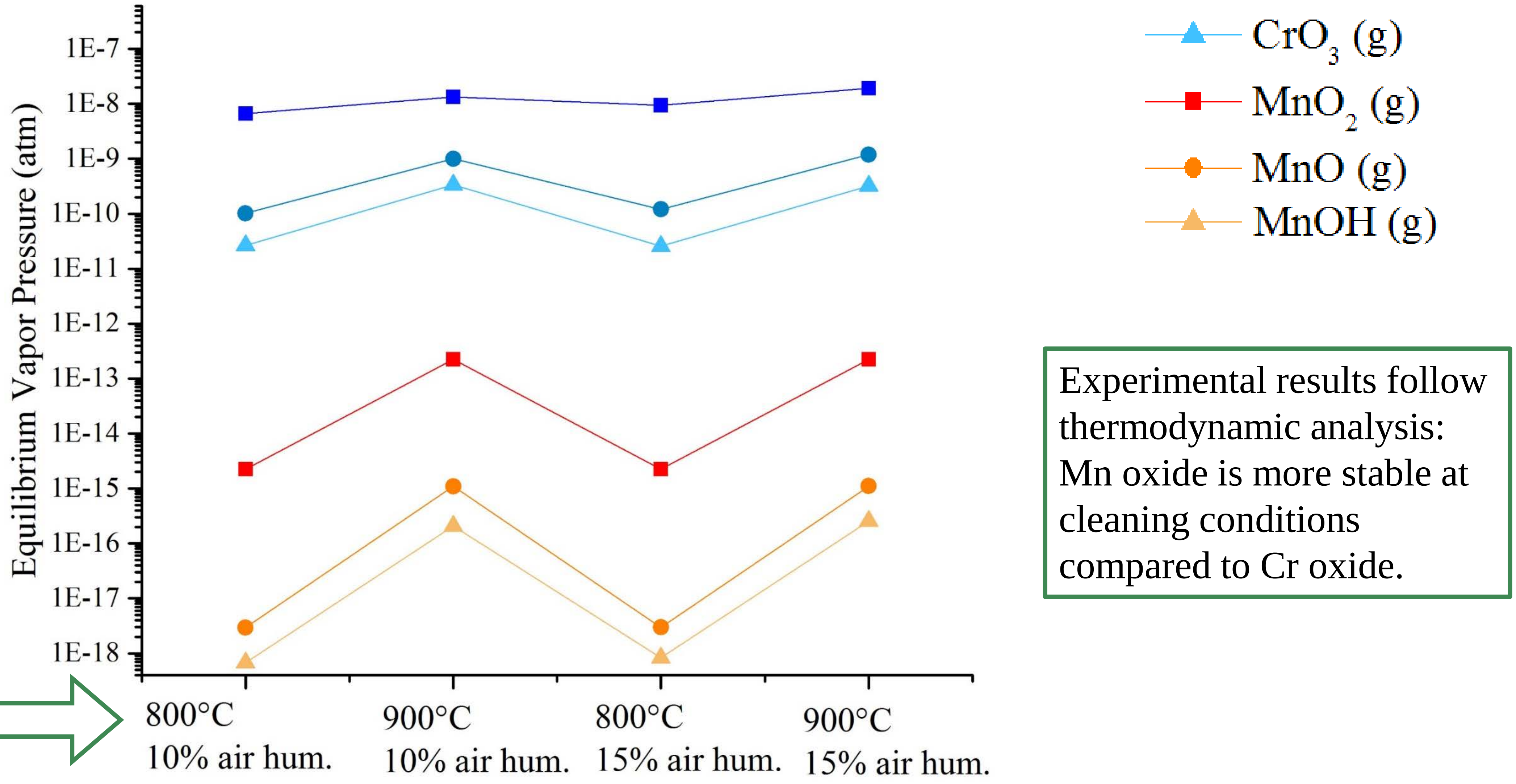
Cleaning Experiment #4



Experiment	Cr Removal Efficiency	Mn/Cr Ratio in Deposits
Poisoning Baseline	/	0.44
#2	84.0%	0.86
#3	64.4%	0.62
#4	81.0%	0.73

Increased removal efficiency is related to the removal of Cr as opposed to Mn in the oxide deposits.

Cr, Mn Oxide Removal Thermodynamics



Four different atmospheres on air side in cleaning experiments.

Experimental results follow thermodynamic analysis: Mn oxide is more stable at cleaning conditions compared to Cr oxide.

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Summary

- For LSM cathodes I-V and EDS analyses supports chromium removal via electrochemical cleaning method.
- For LSM cathodes, EDS analysis reveals two types of Cr deposits, Cr-oxide and Cr-Mn oxide, and that the electrochemical cleaning is more effective in removing Cr-oxide deposits.

Ongoing

- For LSM cathodes, complete the factorial design of experiments and perform analysis to obtain optimal cleaning conditions.
- Test cleaning/poisoning cyclability.
- Conduct chromium cleaning test in larger cells at Fuel Cell Energy, Inc.

Future Work: Test Electrochemical Cleaning on LSF/LSCF Cathodes

LSCF and LSF cathodes are more tolerant to chromium poisoning compared to LSM.

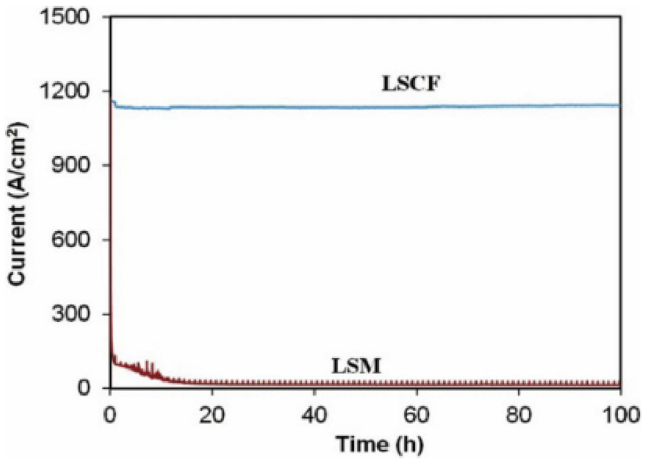

Fig. 2 — I–t curves of LSM/YSZ/Pt and LSCF/GDC/Pt half cells. Tests were conducted at 1023 K with 150 sccm of 3% H_2O/air flowing through a Cr_2O_3 powder bed and an applied bias of 0.5 V.

Rather than Cr-Mn oxide deposits, Cr-Sr oxide deposits form in LSCF & LSF.

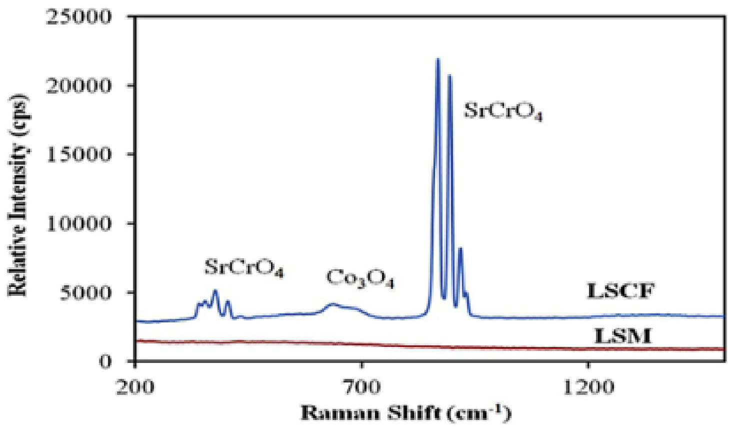

Fig. 6 — Raman spectra of post tested LSM and LSCF cathodes at 1023 K for 100-h tests in presence of chromium vapor.

Hu B et al., Experimental and thermodynamic evaluation of La1-xSrxMnO3±d and La1-xSrxCo1-yFeyO3-d cathodes in Cr-containing humidified air, International Journal of Hydrogen Energy (2017), http://dx.doi.org/ 10.1016/j.ijhydene.2017.01.040

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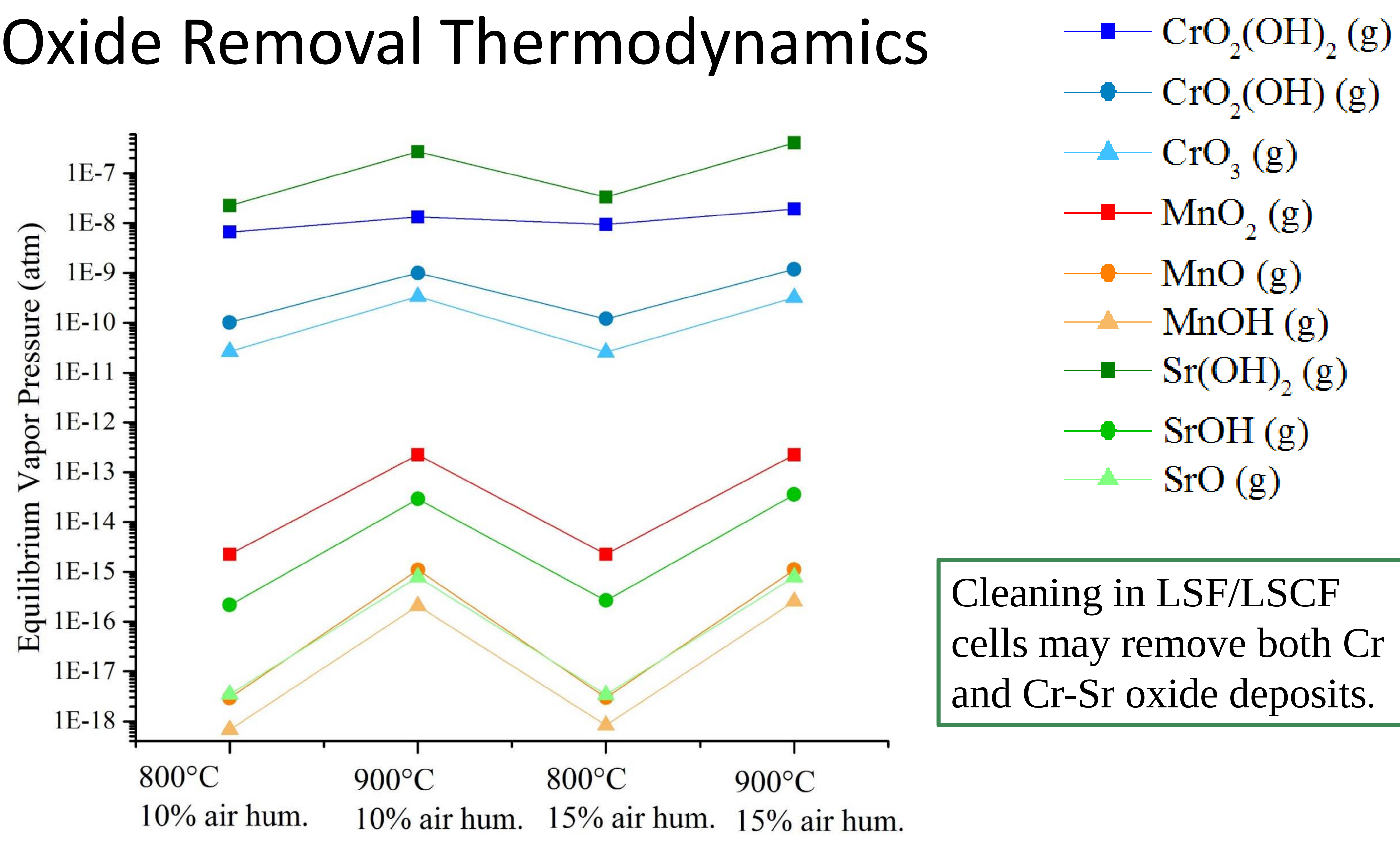

Cleaning in LSF/LSCF cells may remove both Cr and Cr-Sr oxide deposits.

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