Chromium Tolerant, Highly Active and Stable Electrocatalytic Internal Surface Coating for Cathode of Commercial SOFCs

Xueyan Song, Ph.D.
George B. Berry Chair Professor of Engineering
Department of Mechanical and Aerospace Engineering, West Virginia University

National Energy Technology Laboratory
DOE Award – FE0031665

Program Manager: Sarah Michalik
Technology Manager: Dr. Shailesh Vora

Atomic Layer Deposition (ALD) of Solid Oxide Fuel Cells (SOFC)

Overview

- **Project Background & Technical Challenges**
  - Alternative to an interconnect coating: Cr-resistant cathode through infiltration
  - ALD & technical challenges for the development of an ALD coated Cr-resistant cathode

- **ALD-Enabled, Chromium Tolerant Air Electrode**

  LSM/YSZ Cathode

  - LSM/YSZ: Baseline Performance & nanostructure degradation induced by Cr poisoning
  - Cell power density & longevity increased by ALD coating
  - ALD-enabled Significantly increased power density & durability against contamination

  LSCF/SDC Cathode

  - Baseline nanostructure degradation induced by Cr poisoning

- **Summary**

Overview

- **Project Background & Technical Challenges**
  - **Alternative to an interconnect coating: Cr-resistant cathode through infiltration**
  - **ALD & technical challenges for the development of an ALD coated Cr-resistant cathode**
- **ALD Enabled- Chromium Tolerant Air Electrode**

  LSM/YSZ Cathode
  - LSM/YSZ: Baseline Performance & nanostructure degradation induced by Cr poisoning
  - Cell power density & longevity increase introduced by ALD coating
  - ALD-enabled Significant increased power density & durability against contamination

  LSCF/SDC Cathode
  - Baseline nanostructure degradation induced by Cr poisoning
- **Summary**

Cr-Poisoning SOFC Cathode & Interconnect Coating

Commonly used metallic interconnect materials:

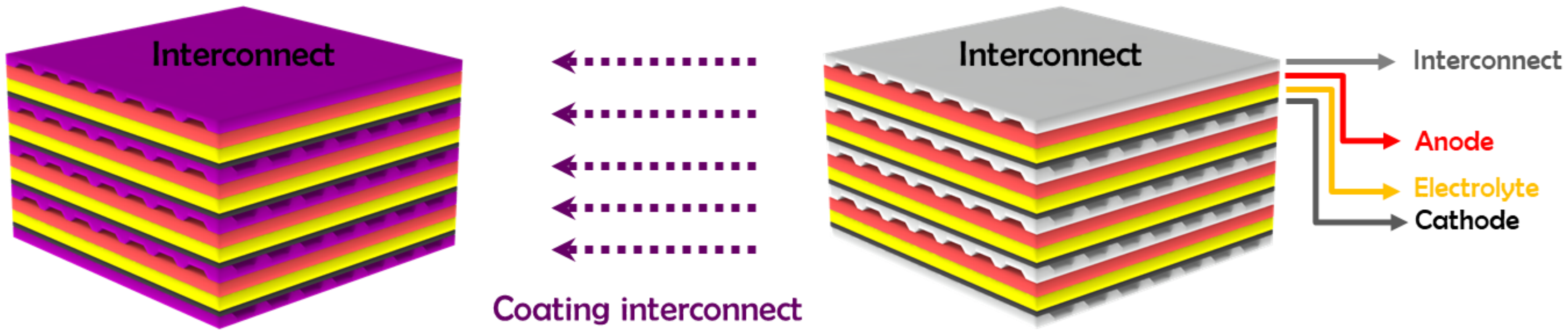
- Ni(Fe)-Cr based heat resistant alloys, Cr-based alloys, and chromia-forming ferric stainless steels.
- Contain Cr to form a protective chromium oxide scale Cr_2O_3.

Volatilization of Cr species strongly depends on oxygen partial pressure.

Vaporization of Cr species on the SOFC fuel side anode could be neglected.

Cr deposition & poisoning of SOFC cathode:

- Volatile Cr species, such as CrO_3 and $Cr(OH)_2O_2$, are generated in oxidizing atmospheres.
- Volatile Cr species react with the cathodes, causing rapid cell degradation.



- Badwal, S.; Deller, R.; Foger, K.; Ramprakash, Y.; Zhang, J., Interaction between chromia forming alloy interconnects and air electrode of solid oxide fuel cells. *Solid State Ionics* 1997, *99* (3-4), 297-310.
- Chen, X.; Zhen, Y.; Li, J.; Jiang, S. P., Chromium deposition and poisoning in dry and humidified air at (La0. 8Sr0. 2) 0.9 MnO3+ δ cathodes of solid oxide fuel cells. *international journal of hydrogen energy* 2010, *35* (6), 2477-2485.
- Jiang, S. P.; Chen, X., Chromium deposition and poisoning of cathodes of solid oxide fuel cells–a review. *International Journal of Hydrogen Energy* 2014, *39* (1), 505-531.
- Park, E.; Taniguchi, S.; Daio, T.; Chou, J. T.; Sasaki, K., Influence of cathode polarization on the chromium deposition near the cathode/electrolyte interface of SOFC. *International Journal of Hydrogen Energy* 2014, *39* (3), 1463-1475.

Development of Cr Tolerant Cathode via Infiltration or Coating

For commercial SOFCs with well-developed materials sets, Cathode Cr-resistance can be improved through solution-based infiltration or cathode surface coating.

Structural requirements of Cr-tolerant surface coating layer on SOFC cathode:

- Deeply penetrating into the active layer of the cathode.
- Uniform and conformal on the internal surface of the cathode active layer that possess complex three-dimensional topographies with high aspect ratio, and the TPBs.
- Intimate adhesion and bonding to the cathode surface at atomic scale without spallation.

Coating Film deposition to facilitate the Cr-tolerant cathode through coating:

Magnetron sputtering, sol-gel dip-coating, and electro-deposition techniques used for applying protective coating on ferritic stainless steel interconnects:

- Involving physical vapor deposition or liquid solutions.
- Having the limitation of not deeply penetrating into the cathode active layer or not providing the conformal coating on cathode surface.
- Not ideal for infiltrating and coating the internal surface of porous cathode.

Atomic Layer Deposition: Chemical vapor deposition technique that sequentially applied atomic mono-layers to a substrate, typically alternating compounds to produce a locally balanced atomic distribution of target material.

ALD is uniquely suitable for coating uniform and conformal films on complex three-dimensional topographies with high aspect ratio.

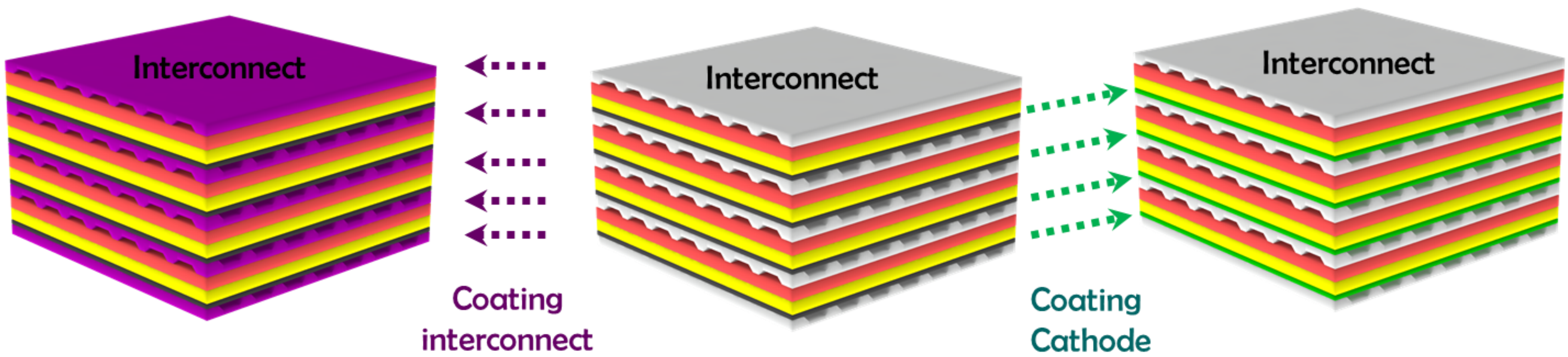
Jiang, S. P. & Chen, X. Chromium deposition and poisoning of cathodes of solid oxide fuel cells – a review. Int. J. Hydrog. Energy 39, 505–531 (2014).

Development of Cr Tolerant Cathode Through ALD Coating

For a commercial SOFC with well-developed materials set, Cathode Cr-resistance can be improved through ALD coating.

ALD is uniquely suitable for depositing uniform and conformal films on complex three-dimensional topographies with high aspect ratio.

Two Alternative Approaches to Mitigate Cr Poisoning



Approach I	Approach II
Interconnect Coating	**ALD Coating of Cathode**

Technical challenges for ALD coating of Cr resistance layers

Structure requirement of Cr-tolerant surface coating could be satisfied by ALD:

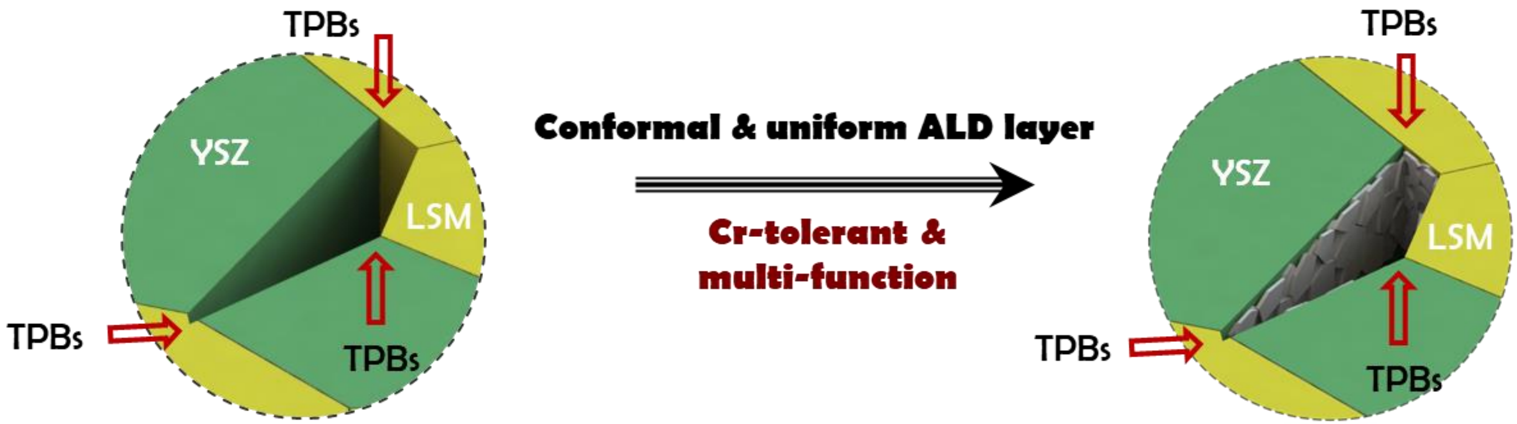
- ☑ Deeply penetrating into the active layer of the cathode.
- ☑ Uniform and conformal on the internal surface of the cathode active layer, that possess complex three-dimensional topographies with high aspect ratio, and the TPBs.
- ☑ Intimate adhesion and bonding to the cathode surface at atomic scale without spallation.

Functional requirement of Cr-tolerant surface coating layer on SOFC cathode:

- Cr-inert ALD coating layer should not impair the electrochemical reactions taking place on the cathode surface.

Ideal Cr-inert ALD coating layer should possess the multiple functions of:

- Conformal on internal surfaces of backbones, prevent Sr out diffusion and Cr inward diffusion.
- Highly active towards electrochemical reactions.
- Super stable upon the long term electrochemical operation at high temperatures.



Overview

- Project Background & Technical Challenges
  - Alternate to interconnect coating: Cr-resistant cathode through infiltration
  - ALD & technical challenges for the development of ALD coated Cr-resistant cathode
- **ALD-Enabled Chromium Tolerant Air Electrode**

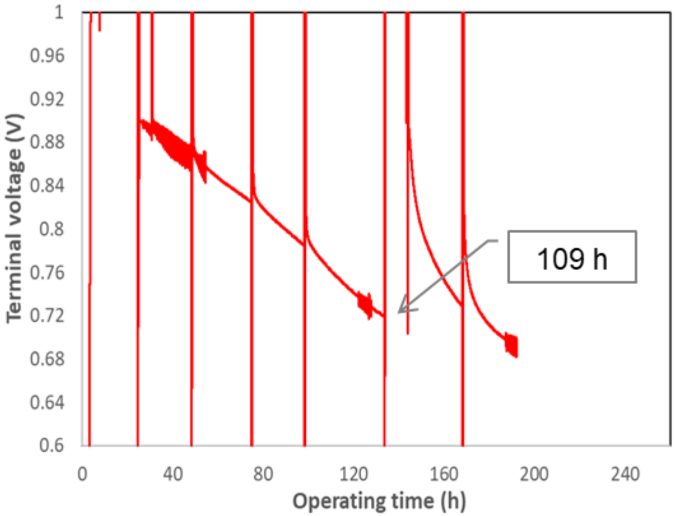
  LSM/YSZ Cathode

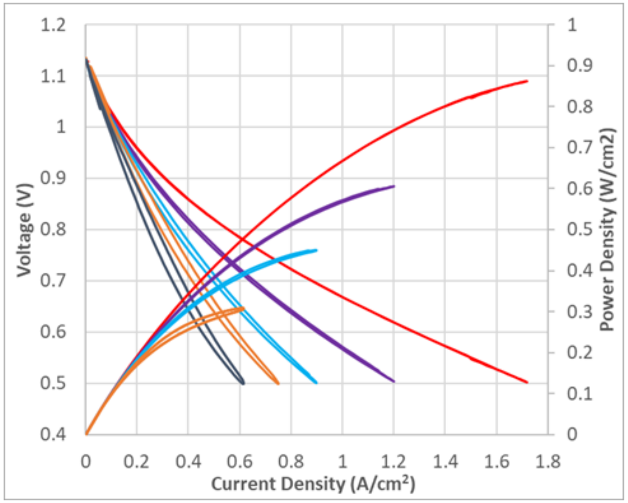
  - **LSM/YSZ: Baseline Performance & nanostructure degradation induced by Cr poisoning**
  - Cell power density & longevity increase introduced by ALD coating
  - ALD-enabled Significant increased power density & durability against contamination

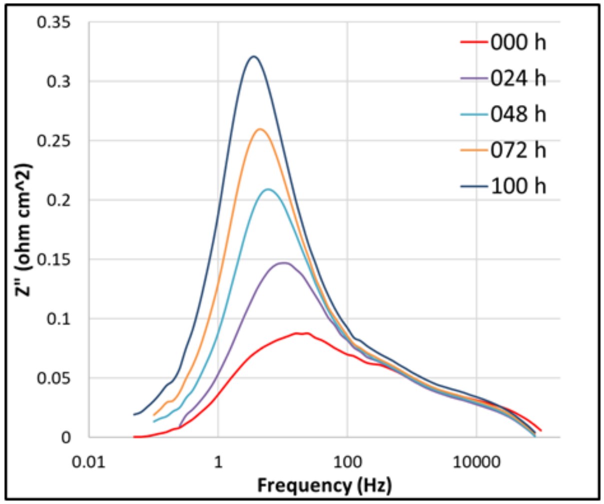
  LSCF/SDC Cathode

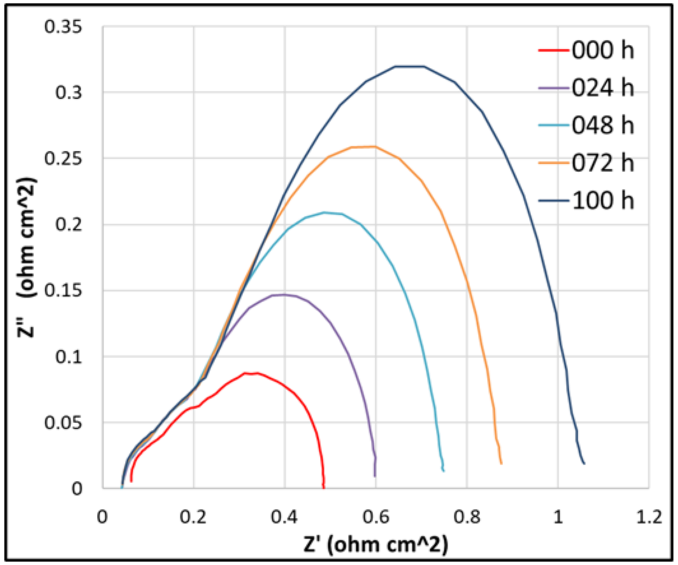
  - Baseline nanostructure degradation induced by Cr poisoning
- Summary

Severe Degradation of LSM/SSZ Baseline Cell Upon Cr Contamination









Operating time (h)	Peak power density (W/cm^2)	Percentage degradation (%)
0	0.862	-
24	0.605	29.8 %
50	0.45	47.8 %
74	0.375	56.5 %
109	0.307	64.4 %

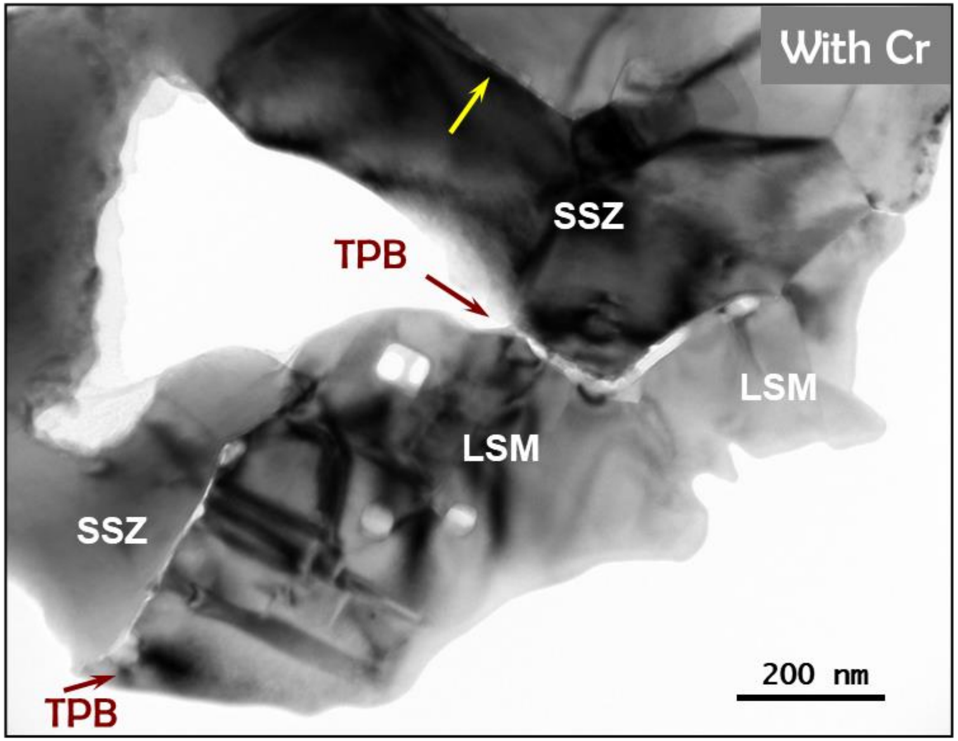
100 h operation, the terminal voltage dropped ~ 190 mV.

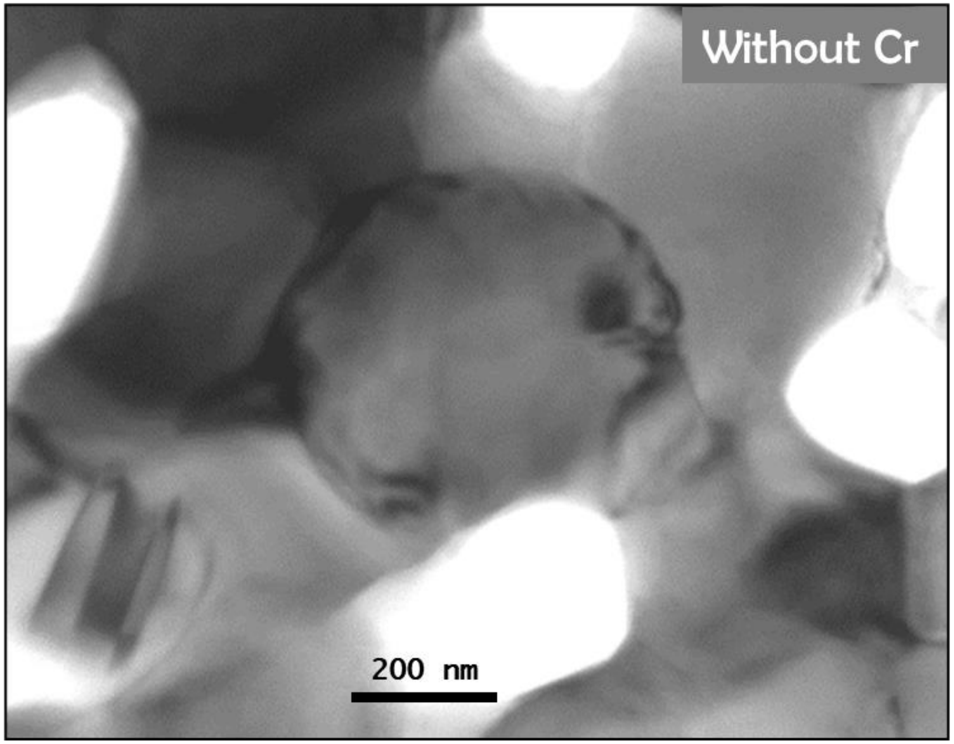
At 0.3 A/cm^2: Degradation rate is 1.68 V per 1000 h

Severe Degradation of LSM-based Baseline Cell

- Little change of series resistance R_s.
- Large increase of the polarization resistance R_p.
- R_p increase could be related to activity loss of oxygen reduction reaction at TPB.

As-Received LSM Baseline Cell Cathode: Typical Nanostructure





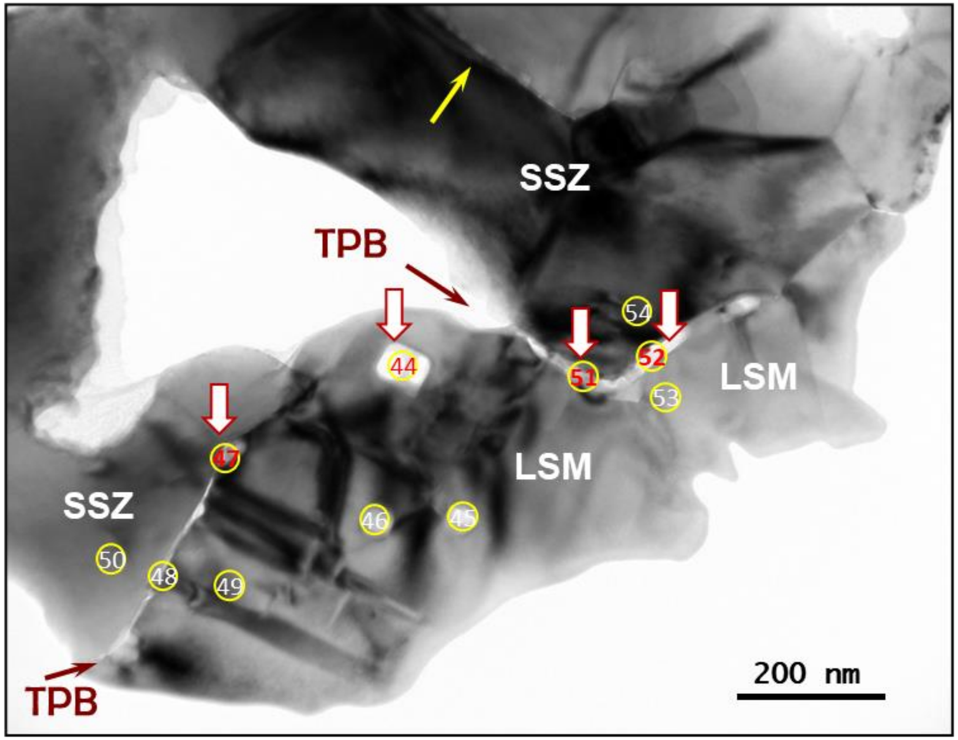
Baseline without Cr contamination.

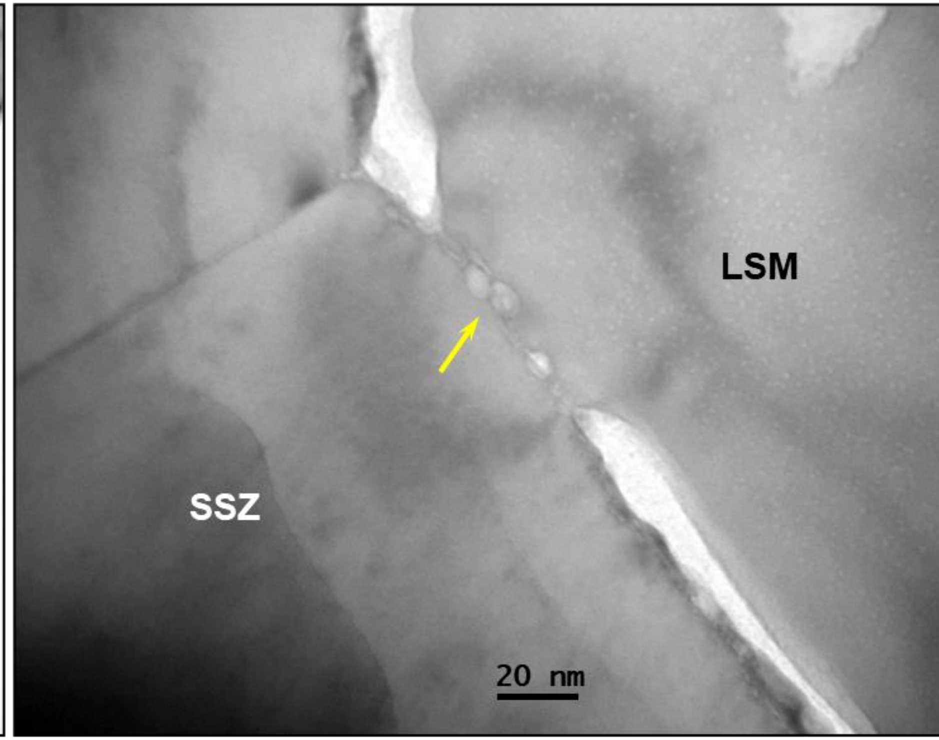
- Intact clean LSM/YSZ interface.
- No formation of the nano-scale MnO_x, SrO_x, or La_2O_3 phases.

Baseline with Cr contamination: Original TPB and LSM/SSZ Interface Degradation.

- Internal cracking initiated from the original triple phase boundary (TPB) and propagated along the internal interface between Sc-stabilized ZrO_2 (SSZ) and LSM.
- In the local SSZ/LSM interface region that there is no apparent internal cracking, there are internal nano-pores that are elongated along the SSZ/LSM interface.
- Intragranular structure has spherical nano-pores, while the SSZ grains remained to be intact.

Cr Contamination: Nanostructure Degradation of LSM/SSZ Baseline Cell





Atomic%	O	La	Sr	Mn	Zr	Sc	Cr	Formulation
44	66.37	12	3.1	15.14			**3.39**	$La_{0.79}Sr_{0.21}MnCr_{0.22}O_x$
45	71.89	10.37	2.53	14.76			0.46	$La_{0.8}Sr_{0.2}Mn_{1.14}Cr_{0.04}O_x$
46	68.01	11.99	3.23	16.65			0.12	$LaSrMn_{0.97}Cr_{1.06}O_x$
47	73.06	7.35		7.15	3.85	0.79	**7.8**	$LaSrMn_{0.97}Cr_{1.06}O_x + ZrO_2$ (w 10 % Sc_2O_3)
48	69.81	2.76		3.45	19.29	3.48	1.21	$LaSrMn_{1.25}Cr_{.44}O_x + ZrO_2$ (w 9 % Sc_2O_3)
49	71.34	10.66	2.69	15.31				La.8Sr.2Mn1.15Ox
50	63.35			0.82	29.84	6		ZrO2 (w 9 % Sc_2O_3) +Mn.03
51	70.96	2.7		4.14	7.43	1.75	**13.04**	CrOx enriched
52	76.77	2.73		2.94	12.46		**5.11**	CrOx enriched
53	73.19	9.96	2.44	12.78			1.63	$La_{.8}Sr_{.2}Mn_{1.03}Cr_{.13}O_x$
54	66.96			0.96	27.55	4.54		

Doped ZrO_2 and LSM interface also show nano-pores.

Cr Contamination: Nanostructure Degradation of LSM/SSZ Baseline Cell

Original TPB Degradation & Formation of $(CrMn)O_x$ on SSZ grain surfaces

- Additional $(CrMn)O_x$ enriched crystals appear to nucleated at the original TPBs.
- Additional $(CrMn)O_x$ enriched crystals appear to grown on SSZ grain surfaces.

Applying an ALD coating layer on the internal surface of cathode: Ideal Cr-inert should possess the multi-functionality of:

- Fully conformal to prevent Sr outward diffusion and prevent Cr inward diffusion.
- Highly active towards electrochemical reactions.
- Super stable upon the electrochemical operation at elevated temperatures.

Choice of Cr tolerance ALD Layer: $Mn_{0.8}Co_{0.2}O_x$ is ordinary interconnect coating materials, excellent layer to **prevent Cr penetration**.

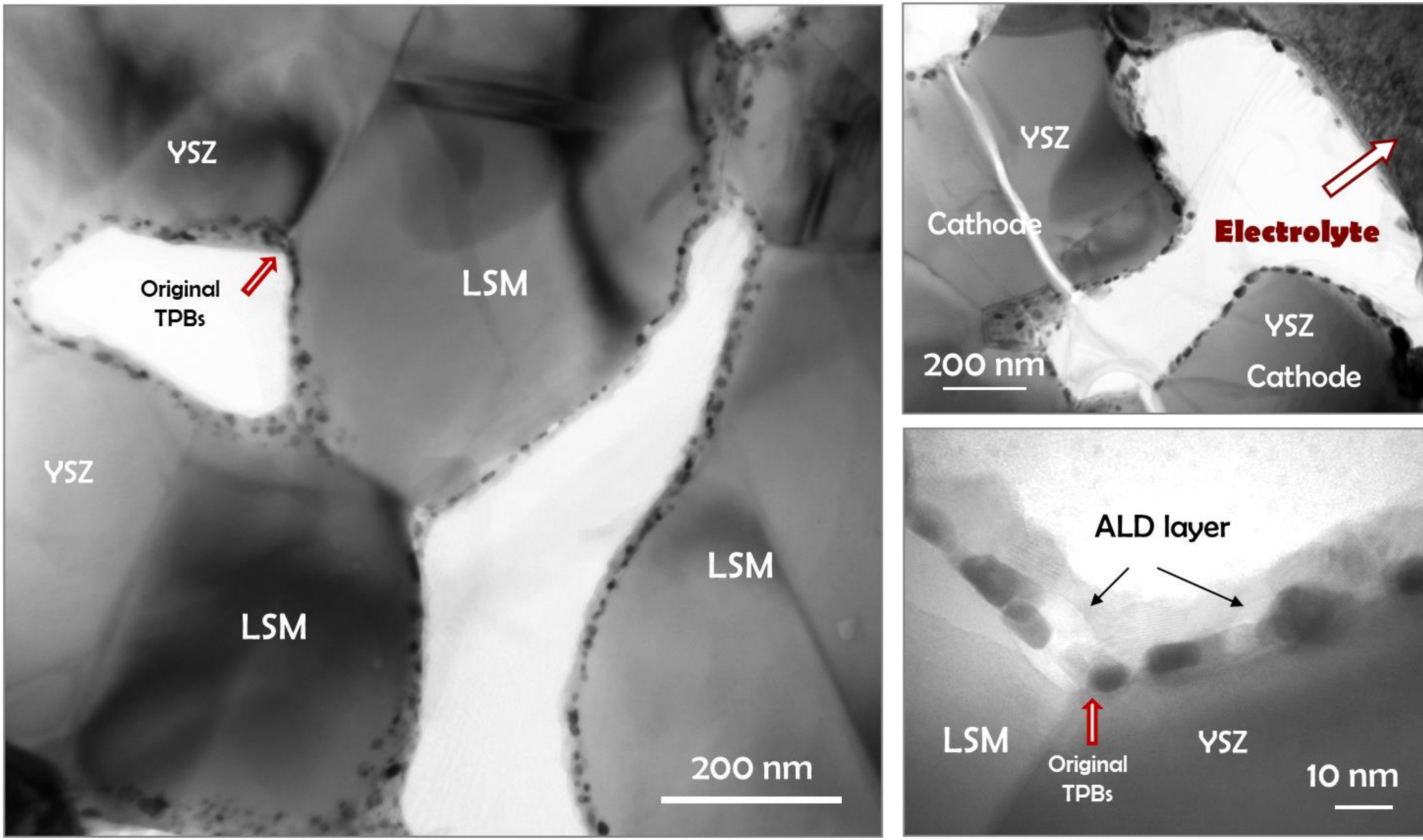
Overview

- Project Background & Technical Challenges
  - Alternate to interconnect coating: Cr-resistant cathode through infiltration
  - ALD & technical challenges for the development of ALD coated Cr-resistant cathode
- **ALD- Enabled Chromium Tolerant Air Electrode**

  LSM/YSZ Cathode
  - LSM/YSZ: Baseline Performance & nanostructure degradation induced by Cr poisoning
  - **Cell power density & longevity increase introduced by an ALD coating**
  - **ALD-enabled Significantly increased power density & durability against contamination**

  LSCF/SDC Cathode
  - Baseline nanostructure degradation induced by Cr poisoning
- Summary

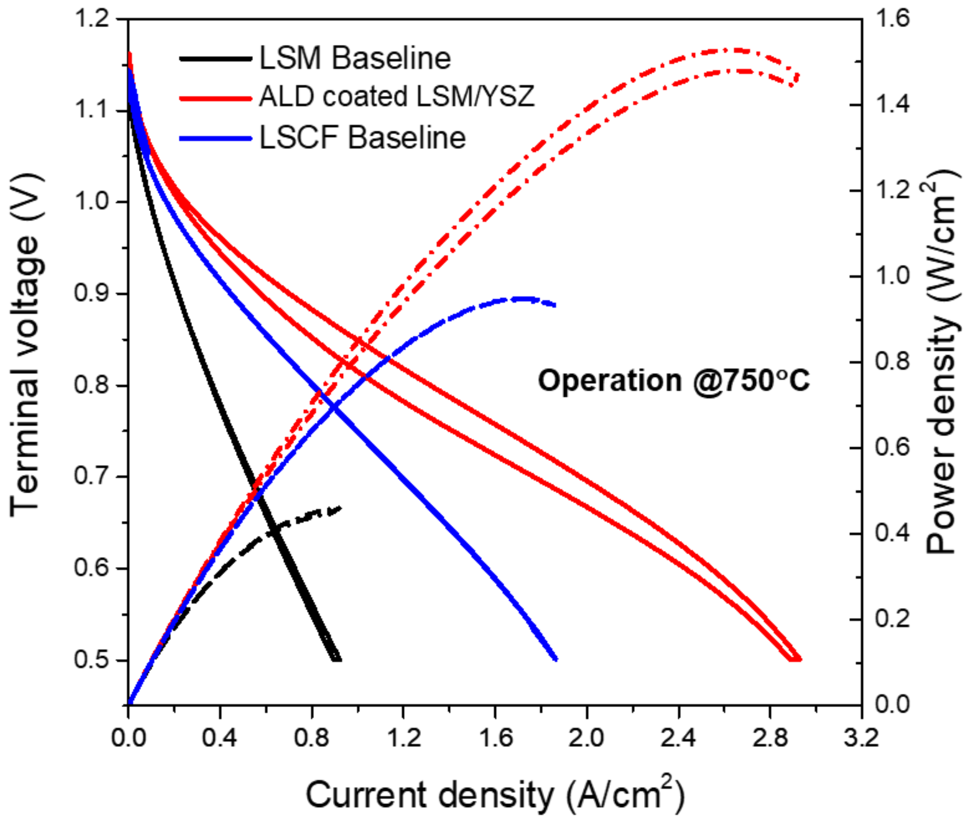
Structure Requirement for ALD Layer: Fully Conformal and Uniform

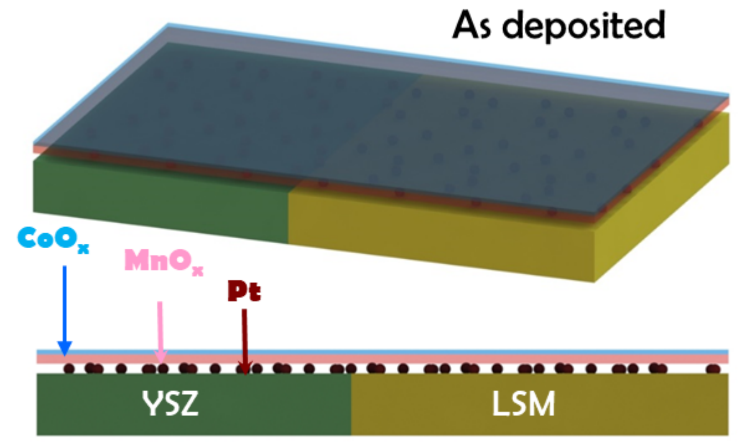


After operation at 750C for 120 hours:

- Stable nanostructure at ALD layer are at active layer and at the cathode-electrolyte interface.
- Conformal & uniform; ALD layer is with nano-pores for gas penetration; Covering the original TPBs.

Structural Requirement for ALD Layer: Enhancement Cell Performance
Large 380% power density enhancement of commercial SOFCs





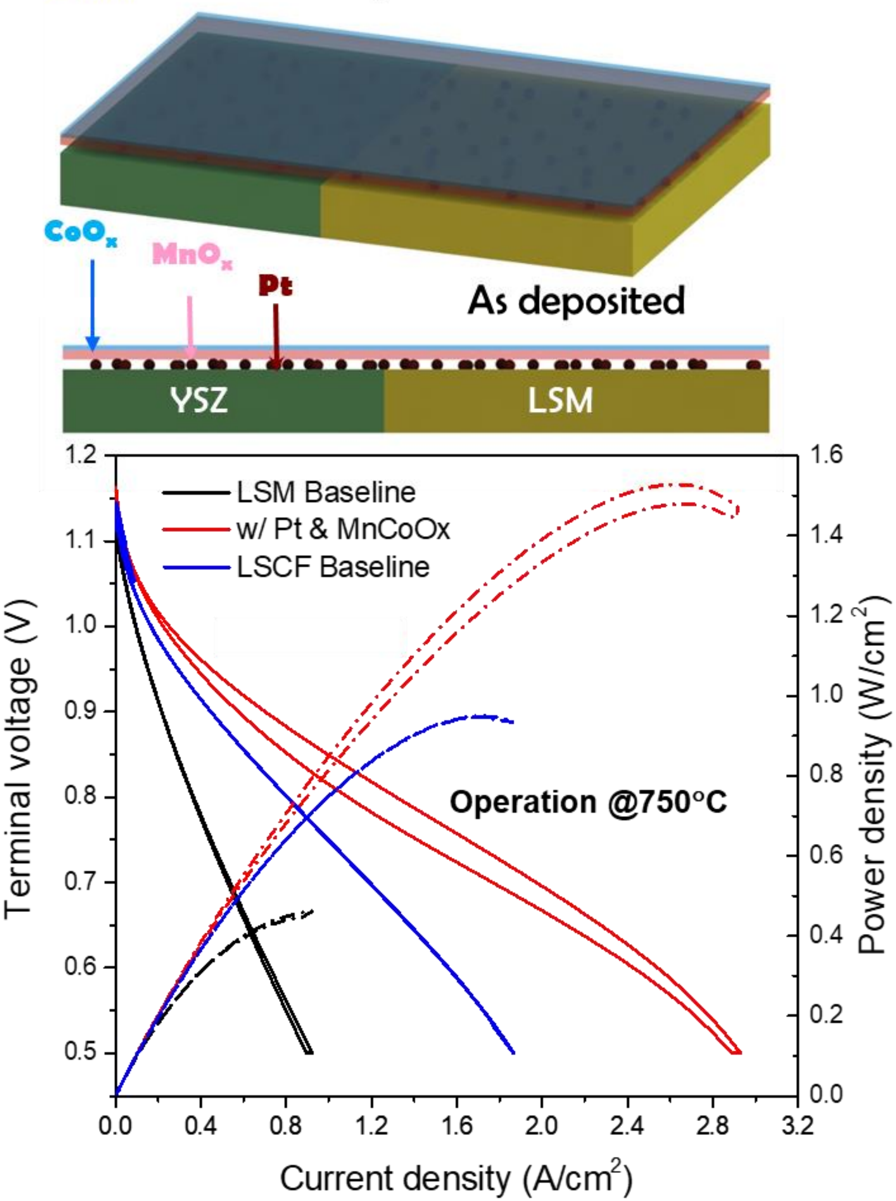
ALD coated LSM/YSZ cell:

- power density is **380%** of that from the LSM/YSZ baseline at 750°C.
- power density is **170%** of that from the LSCF/SDC baseline at 750°C.

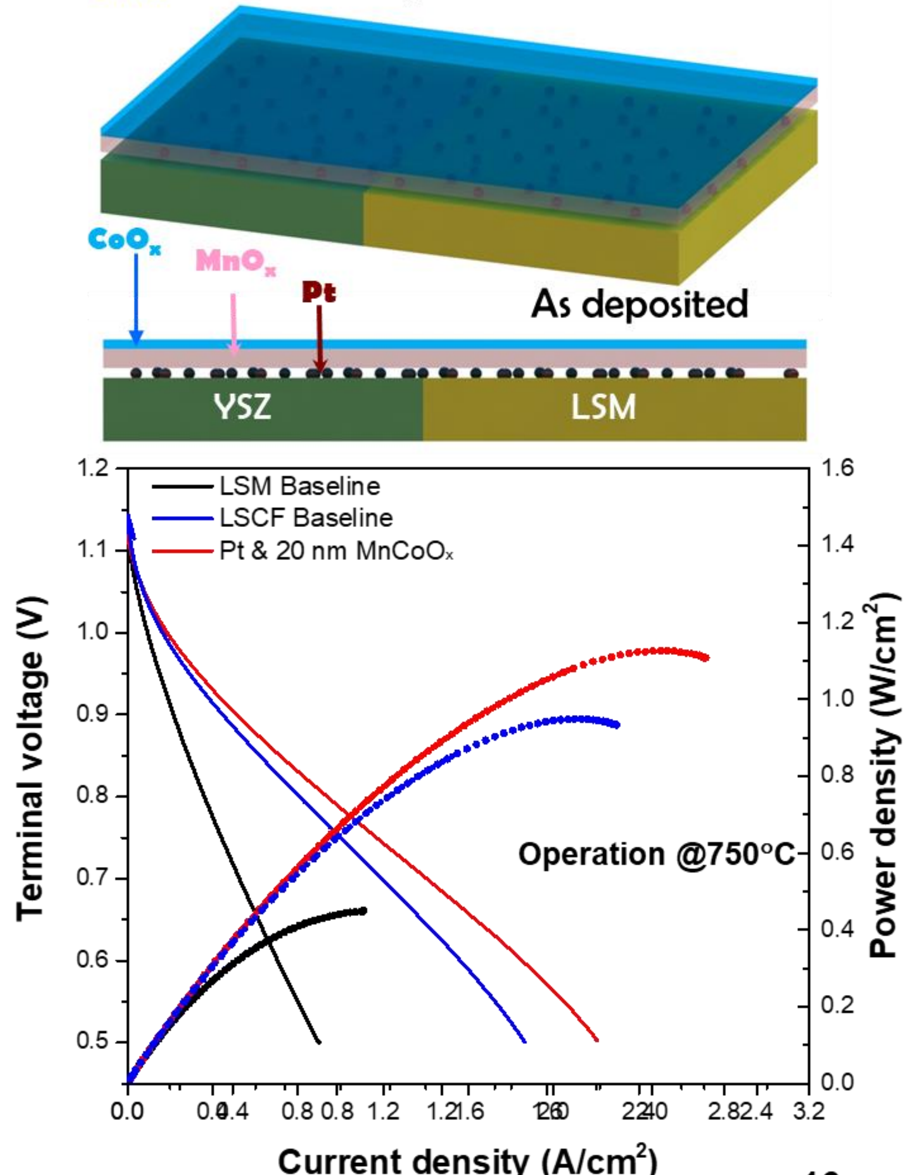
Surface architecture	R_{total} (Ω/cm²)	R_s (Ω/cm²)	R_p (Ω/cm²)	*i* at 0.8 V (A/cm²)	P at 0.8 V (W/cm²)	Factor enhancement to LSM/YSZ	Factor enhancement to LSCF/SDC
LSM/YSZ Baseline	0.619	0.045	0.574	0.350	0.28	1	/
ALD LSM/YSZ	0.324	0.051	0.273	1.320	1.06	380%	170%
LSCF/SDC Baseline	0.350	0.110	0.239	0.790	0.63	/	1

Tuning the Cell Performance by Adjusting ALD Layer Thickness (no Cr)

10 nm thick $MnCoO_x$ capping ~ 3 nm Pt particles

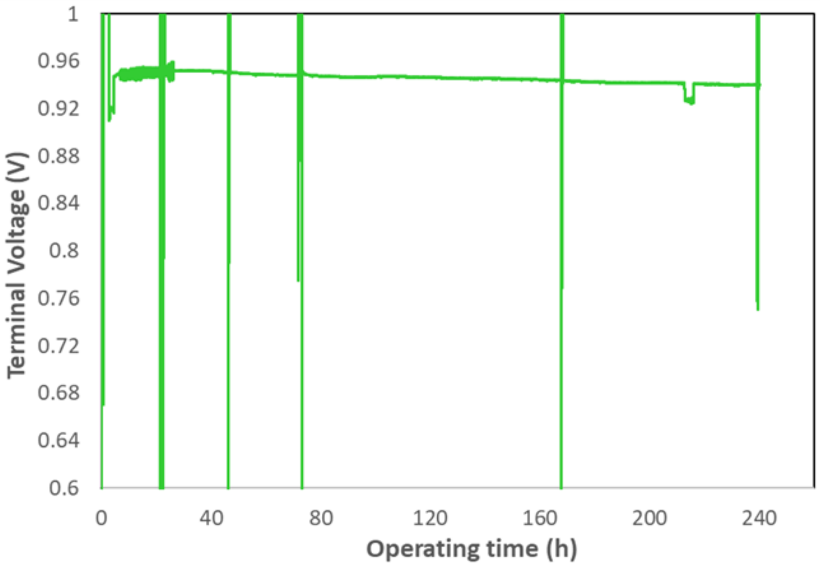


20 nm thick $MnCoO_x$ capping ~ 3 nm Pt particles



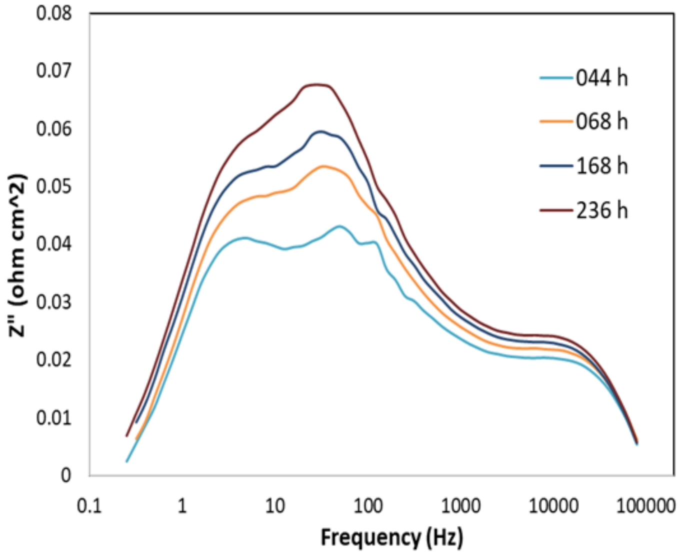
10 nm ALD layer, peak power density is 380% of baseline. 20 nm ALD layer, peal power density is 280 % of baseline.

Stable Performance of ALD Coated Cell Upon Operation With Cr



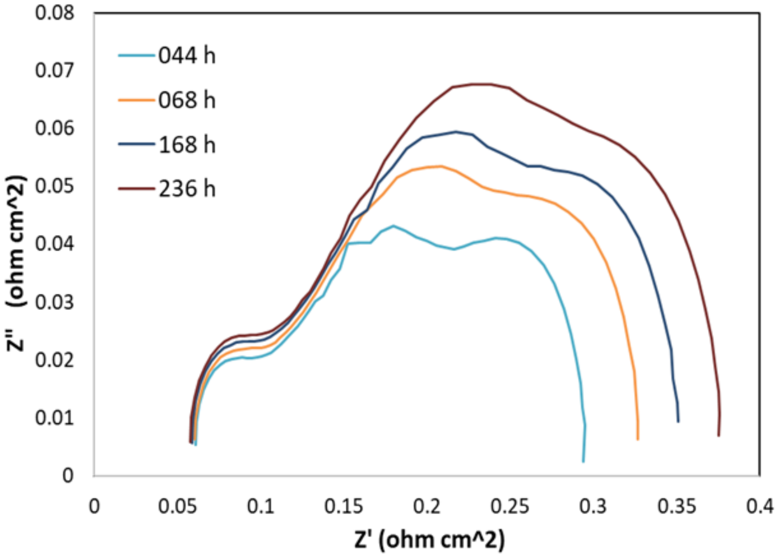
ALD coated LSM based cell at 0.3 A/cm²

Degradation rate is 0.054 V per 1000 h



Rs and Rp (taken at 0.3 A/cm²) changes

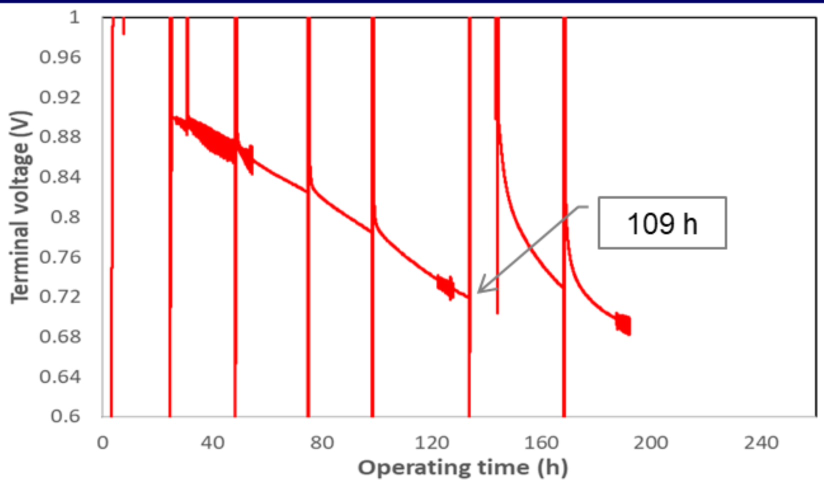
Operating time (h)	Rs (Ω cm²)	Rp (Ω cm²)
44	0.06	0.304
68	0.058	0.328
168	0.058	0.354
236	0.055	0.381

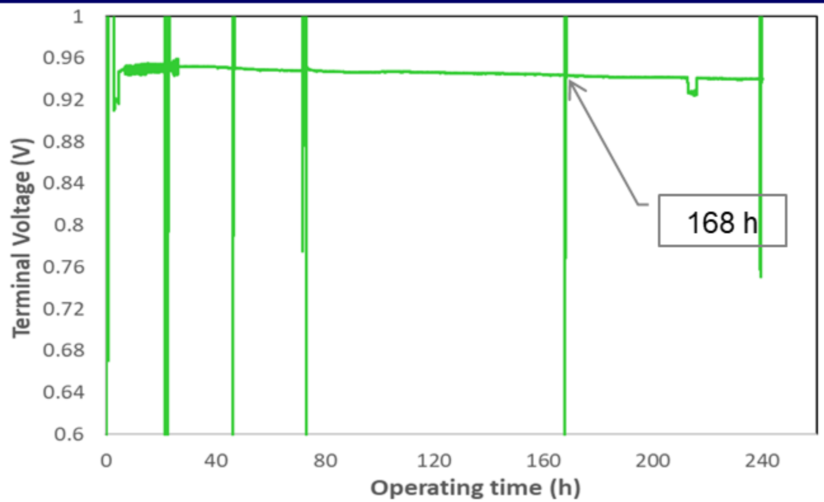


LSM/YSZ with ALD coating of 20 nm $Mn_{0.8}Co_{0.2}O_x$ layer, operation with Cr contamination.

- Zero hour: peak power density is 280 % of baseline @ zero hour;
- 168 hours: peak power density is 200 % of baseline @ zero hour.

Comparison of Baseline & ALD Coated Cells Upon Cr Contamination





LSM based Baseline Cell:

baseline at 0.3 A/cm²

Degradation rate is 1.68 V per 1000 h

Operating time (h)	Peak power density (W/cm²)	Percentage degradation (%)
0	0.862	-
24	0.605	29.8 %
50	0.45	47.8 %
74	0.375	56.5 %
109	0.307	64.4 %

ALD Coated Cell LSM Based Cells

ALD coated **cell** at 0.3 A/cm²

Degradation rate is 0.054 V per 1000 h

Operating time (h)	Peak power density (W/cm²)	Percentage degradation (%)
23	1.254	-
44	1.127	0.101276
68	1.073	0.144338
168	1.015	0.19059

Baseline Cell: Peak power density remained to be 36% of baseline @ zero hour after 109 hours operation.

ALD coated one: Peak power density remained to be 200% of uncoated baseline @ zero hour after 168 hours operation. ALD coated cell power density is ~ 600% of that baseline cell upon operation with Cr contamination.

Cr tolerance: Large performance enhancement (> 200% power density) by ALD coating of Cr-tolerant $Mn_{0.8}Co_{0.2}O_x$ and remained to be stable even operation with Cr contamination.

Overview

- Project Background & Technical Challenges
  - Alternate to interconnect coating: Cr-resistant cathode through infiltration
  - ALD & technical challenges for the development of ALD coated Cr-resistant cathode
- **ALD Enabled- Chromium Tolerant Air Electrode**

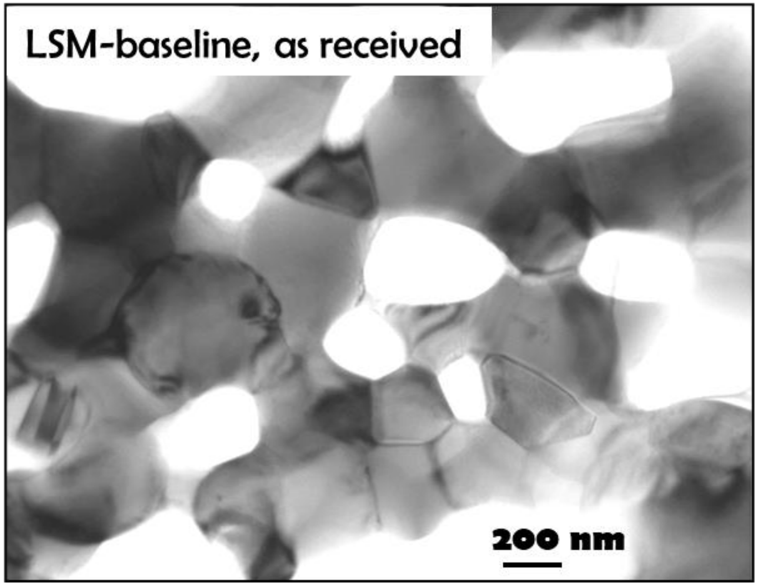
  LSM/YSZ Cathode

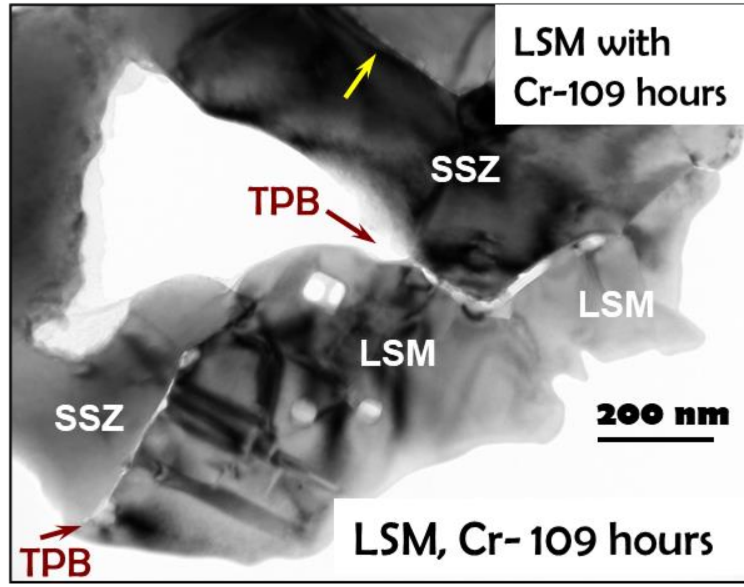
  - LSM/YSZ: Baseline Performance & nanostructure degradation induced by Cr poisoning
  - Cell power density & longevity increase introduced by ALD coating
  - ALD-enabled Significant increased power density & durability against contamination

  LSCF/SDC Cathode

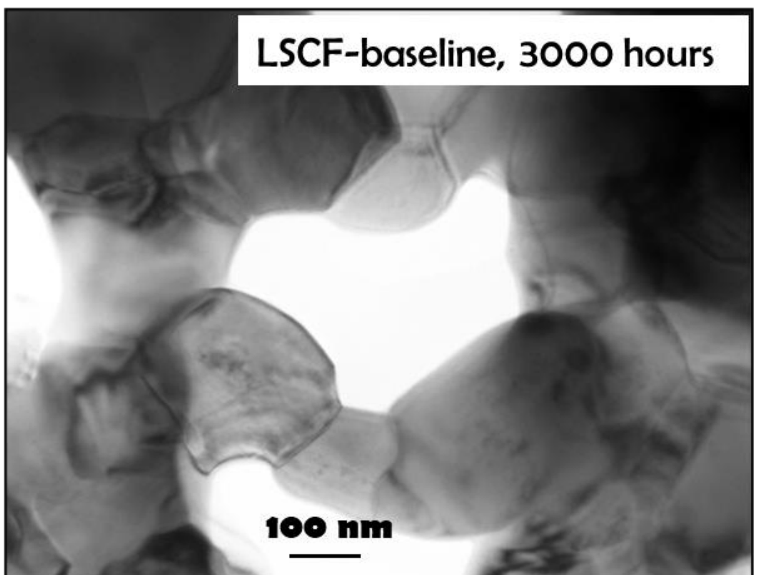
  - **Baseline nanostructure degradation induced by Cr poisoning**
- Summary

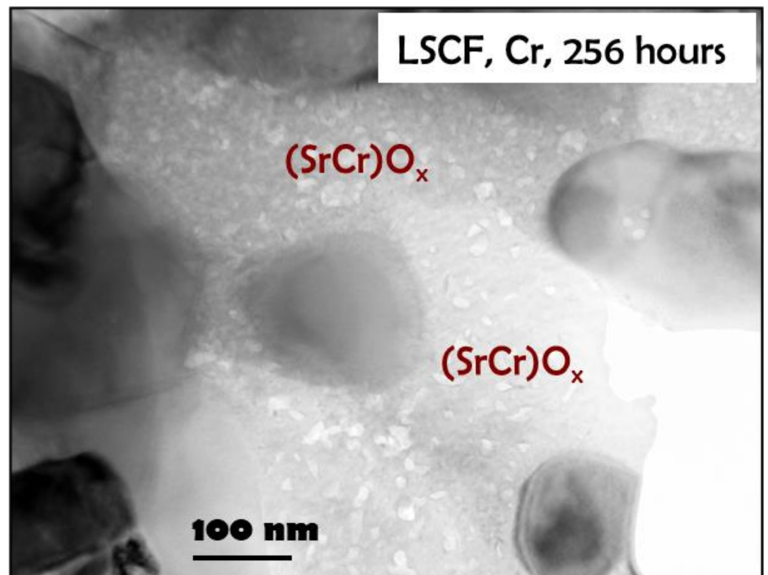
Cr contamination: Different Degradation between LSM and LSCF based Cells





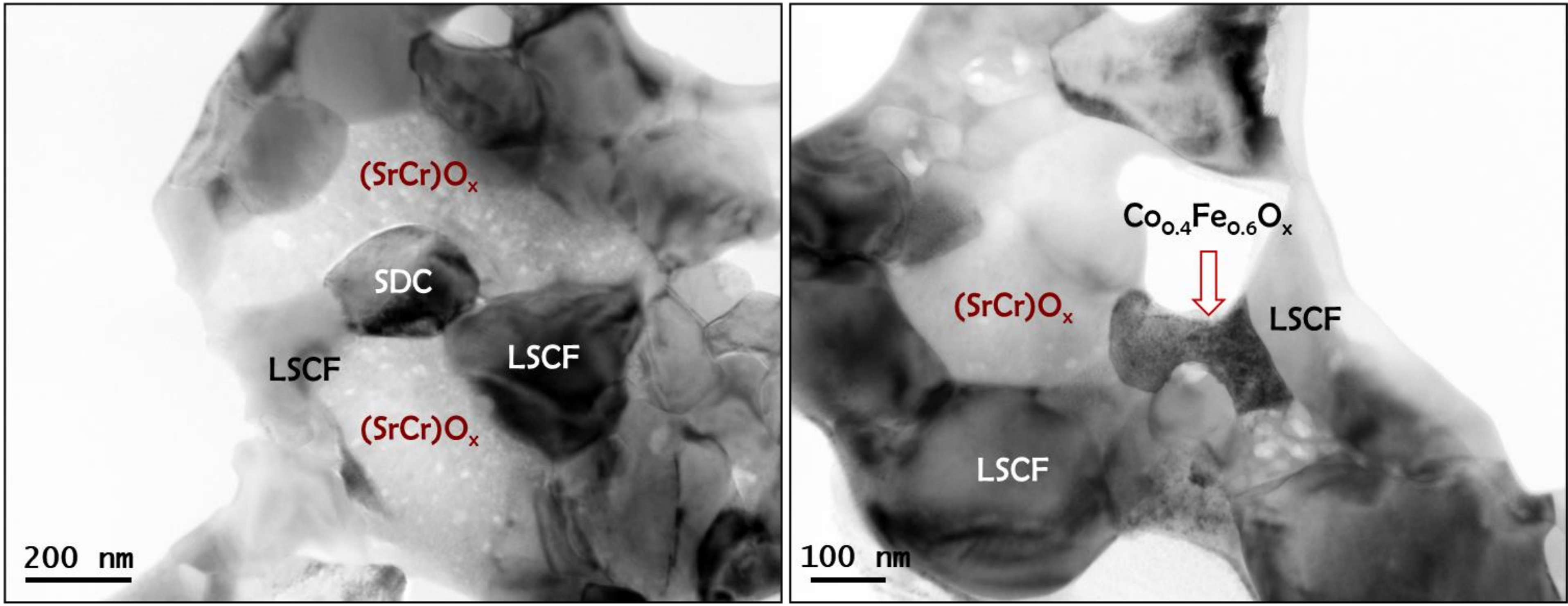
LSM: Cr is attacking the TPB. No accumulation at the original pore region.





Accelerated Sr segregation induced by Cr contamination

Cr contamination: Different Degradation Mechanisms from LSM & LSCF Cells



Accelerated Sr segregation induced by Cr contamination

LSCF-SDC cathode nanostructure degradation caused by Cr-contamination.

- $(SrCr)O_x$ are filling the original pores of the LSCF/SDC after 256 hours operation at 750°C.
- Formation of (FeCo)Ox nano-grains at LSCF/LSCF surface grain boundaries.

ALD layer on LSCF/SDC backbone ideally needs to be conformal to prevent the Sr evaporation/Segregation and their further interaction with Cr vapors.

Summary

LSM/YSZ or LSM/SSZ based cells:

- **LSM/SSZ baseline performance & nanostructure degradation by Cr**
  - Peak power density loss of 64% after 109 hours operation. Dramatic increase in R_p.
  - Cracking at LSM/SSZ interface, LSM grains. SSZ remains intact, but with $(CrMn)O_x$.
- **ALD coating $(MnCo)O_x$/Pt dramatically improves the Cr resistance**
  - Power density is 280-380% of the baseline cell depending on the ALD layer thickness.
  - For cell with a 20 nm thick ALD layer, there is a large performance enhancement (> 200% power density) induced by ALD coating of Cr-tolerant $Mn_{0.8}Co_{0.2}O_x$.
  - For cell with 20 nm thick ALD layer, after 168 hours at 750°C power density of ALD-coated cell is ~ 600% of that baseline cell upon operation with Cr contamination for 109 hours.

LSCF/SDC cells:

- **LSCF/SDC baseline performance & nanostructure degradation by Cr**
  - With the Cr source, there is no apparent Sr surface segregation phase even for the baseline cell operated for 3000 hours at 750°C.
  - With the Cr source, there is significant amorphous $(SrCr)O_x$ phase accumulated in the original pore region.

- There is completely different nanostructure degradation mechanisms between LSM and LSCF cells induced by Cr contamination.
- LSCF based cells ideally need the conformal ALD layer to prevent Sr migration and Cr contamination.

ACKNOWLEDGEMENTS

DOE-SOFC Program

National Energy Technology Laboratory

Program Manager: Dr. Joseph Stoffa

Program Manager: Dr. Debalina Dasgupta

Program Manager: Sarah Michalik

Technology Manager: Dr. Shailesh Vora