Materials and Approaches for the Mitigation of SOFC Cathode Degradation in SOFC Power Systems

Prabhakar Singh, Chiying Liang, Boxun Hu, Manoj Mahapatra, Sridevi Krishnan, Byung Jun and Rampi Ramprasad

Department of Materials Science and Engineering
Center for Clean Energy Engineering, University of Connecticut, CT

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Technical Contributors

UConn:

UConn:	Prabhakar Singh	Professor
	Manoj K Mahapatra	Assistant Professor in Residence
	Rampi Ramprasad	Professor
	Boxun Hu	Post-doctoral fellow
	Sridevi Krishnan	Post-doctoral fellow
	Chiying Liang	Graduate Student
	Byung Jun	Graduate Student

Program Manager: Dr. Patcharin N. Burke, National Energy Technology Laboratory

Outline

- **Accomplishments**
- **Background**
- **Experimental**
  - **Fabrication and testing of Cr Getter**
  - **Electrochemical Testing without and with a Cr Getter**
  - **Characterization-SEM-EDX, XRD, FIB-TEM**
- **Results and Discussion**
- **Future Work**
- **Acknowledgements**

Accomplishments

- An efficient chromium getter for capturing Cr vapor species, present in the cathode atmosphere of SOFC power generation system, has been developed and tested.
- Developed chromium getter shows excellent affinity for gaseous Cr species. Cr species are captured close to the air inlet.
- Distribution of the chromium deposition has been studied using FIB-TEM,SEM-EDX and XRD for the tested getter for 500 hrs.
- Half-cell electrochemical testing of LSM/YSZ/LSM symmetric cell in dry air, chromium vapor/dry air with / without getter has been conducted for 100 h and post-test analytical study (XRD, SEM-EDS, and FIB-TEM) are in progress.

- Getter design can be tailored to meet various SOFC systems configurations.
- Getter materials can be used for capturing Cr originating from BOP and IC.
- Approaches for scale up (higher TRL) have been developed.

Meeting the DOE SOFC program mission

Program Outcome

- Graduate / Undergraduate students trained - 5
- Post-doctoral fellow: 2
- Patent disclosure: 1
- Technical Publications
  - Technology Focused > 5
  - Enabled adjacency areas >5
- Technical presentations >5
- Outreach: Middle and High School, Davinci Program, STEM

Select peer reviewed publications

- V Sharma, MK Mahapatra, P Singh, R Ramprasad, "Cationic surface segregation in doped $LaMnO_3$" J Mater Sci 50 (8), 3051- 3056, 2015
- B Hu, MK Mahapatra, P Singh, "Performance regeneration in lanthanum strontium manganite cathode during exposure to H_2O and CO_2 containing ambient air atmospheres" Journal of the Ceramic Society of Japan 123 (4), 199-204, 2015
- B Hu, M Keane, MK Mahapatra, P Singh," Stability of strontium-doped lanthanum manganite cathode in humidified air" Journal of Power Sources 248, 196-204, 6, 2014
- B Hu, MK Mahapatra, M Keane, H Zhang, P Singh, "Effect of CO_2 on the stability of strontium doped lanthanum manganite cathode" Journal of Power Sources, 1-10, 2, 2014
- MK Mahapatra, P Singh, "Fuel Cells: Energy Conversion Technology" Future Energy (Second Edition), 511-547 (Book Chapter)

Enabled adjacency areas (selected):

- S Gupta, S Prabhakar "Manganese Doped Lanthanum-Strontium Chromite Fuel Electrode for Solid Oxide Fuel Cell and Oxygen Transport Membrane Systems" ECS Transactions 66 (3), 117-123, 2015
- N Li, A Verma, P Singh, JH Kim, "Characterization of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$–$Ce_{0.8}Gd_{0.2}O_2$ composite cathode for intermediate temperature solid oxide fuel cells" Ceramics International 39 (1), 529-538,7, L Ge, A Verma, R Goettler, D Lovett, RKS Raman, P Singh, " Oxide scale morphology and chromium evaporation characteristics of alloys for balance of plant applications in solid oxide fuel cells" Metallurgical and Materials Transactions A 44 (1), 193-206
- S Gupta, MK Mahapatra, P Singh, "Lanthanum chromite based perovskites for oxygen transport membrane" Materials Science and Engineering R 90, 1-36, 1 2015
- KT Jacob, P Panwar, P Gupta, P Singh, " Use of Composition-Graded Bi-Electrolyte Cells for Thermodynamic Studies on Lanthanum Aluminates" Journal of The Electrochemical Society 161 (6), H343-H349, 2014

Technical reports, Presentations and outreach (selected):

- J Hardy, J Stevenson, P Singh, M Mahapatra, E Wachsman, M Liu , Effects of Humidity on Solid Oxide Fuel Cell Cathodes" Pacific Northwest National Laboratory, 2015
- S KRISHNAN, V SHARMA, MK MAHAPATRA, P SINGH, " Probing for cationic dopants in lanthanum manganite for solid oxide fuel cell applications" The American Physical Society 2015
- P Singh, T Suzuki, J Akedo, MF Han, S Kuehn, R Lee, JW Son, Y Fujishiro, "Regional Editor's Special Issue" Trend of Current Research on Solid Oxide Electrochemical Cells" Preface JOURNAL OF THE CERAMIC SOCIETY OF JAPAN 123 (1436) 2015
- V Sharma, S Krishnan, B Hu, MK Mahapatra, P Singh, R Ramprasad," Cationic surface segregation in doped $LaMnO_3$: A first principles thermodynamics study" NETL SECA Meeting Poster, 2015

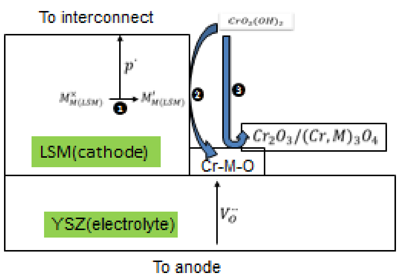
Background

- **SOFC cathode are prone to poisoning and degradation arising from (a) impurities present in the incoming air (intrinsic and extrinsic impurities) and (b) interactions with the electrolyte.**
  - **Intrinsic gas phase impurities – H2O, CO2,….**
  - **Extrinsic gas phase impurities – CrOx, CrO(OH)x…**
    - **Degradation due to solid–gas and solid–solid interactions**
    - **Exolution and compound formation**
    - **Surface coverage and resistance to oxygen reduction**
- **BOP components and cell interconnections contribute to Cr evaporation and poisoning of the cathode.**
  - **Poisoning is due to coverage of active surface and TPB, compound formation and deposition of chromia.**
- **Approaches for mitigation of chromium poisoning include minimization of chromium evaporation from exposed metallic surfaces – alloy chemistry modification and surface coating**
- **There is limited/ no literature on capturing chromium vapor before reaching active cathode.**

From the inlet: $2Cr_2O_3 + 4H_2O + 3O_2 = 4CrO_2(OH)_2$

1. $2M^{\times}_{M(LSM)} + O^{\times}_{O(LSM)} + V^{\cdot\cdot}_{O(YSZ)} = 2M'_{M(LSM)} + O^{\times}_{O(YSZ)} + V^{\cdot\cdot}_{O(LSM)} + 2p^{\cdot}_{(LSM)}$
2. $CrO_2(OH)_{2(gas)} + M^{\times}_{M(LSM)} = Cr - M - O_{(nuclear)} + H_2O_{(gas)}$
3. $CrO_2(OH)_{2(gas)} + Cr - M - O_{(nuclear)} = Cr_2O_3/(Cr,M)_3O_4 + H_2O_{(gas)}$

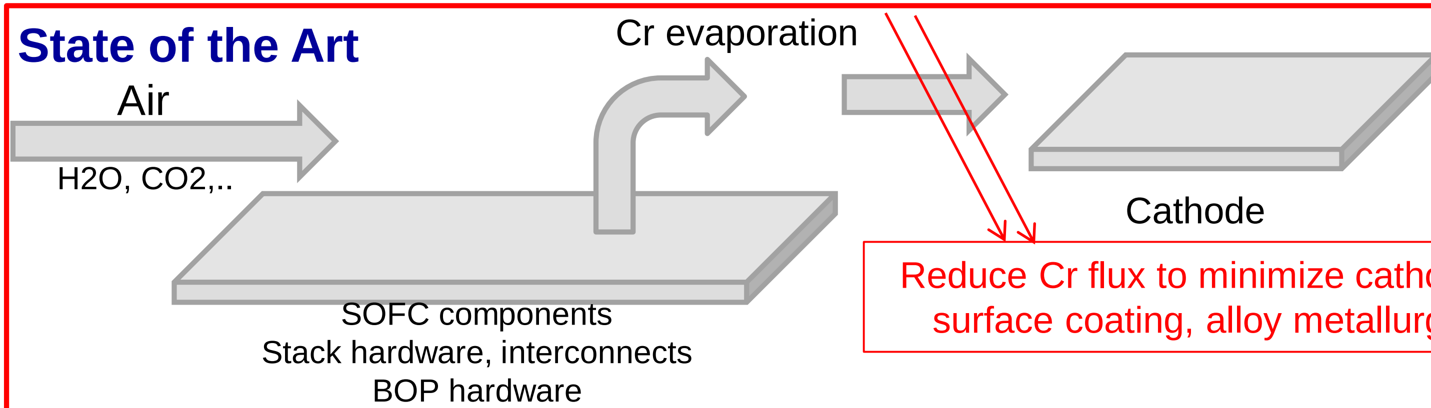
WhereIn M represents for Mn or Sr



Jeffrey W. Fergus/ International Journal of Hydrogen Energy 32 (2007) 3664– 3671
J. Mater. Chem. A, 2014, 2, 11114–11123

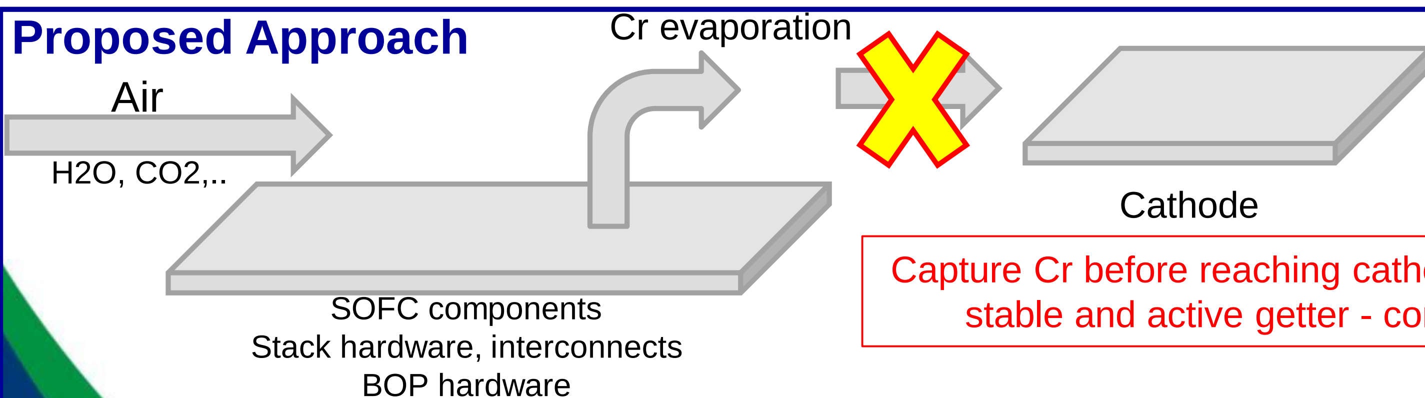
Background

State of the Art



Reduce Cr flux to minimize cathode poisoning by surface coating, alloy metallurgy modification

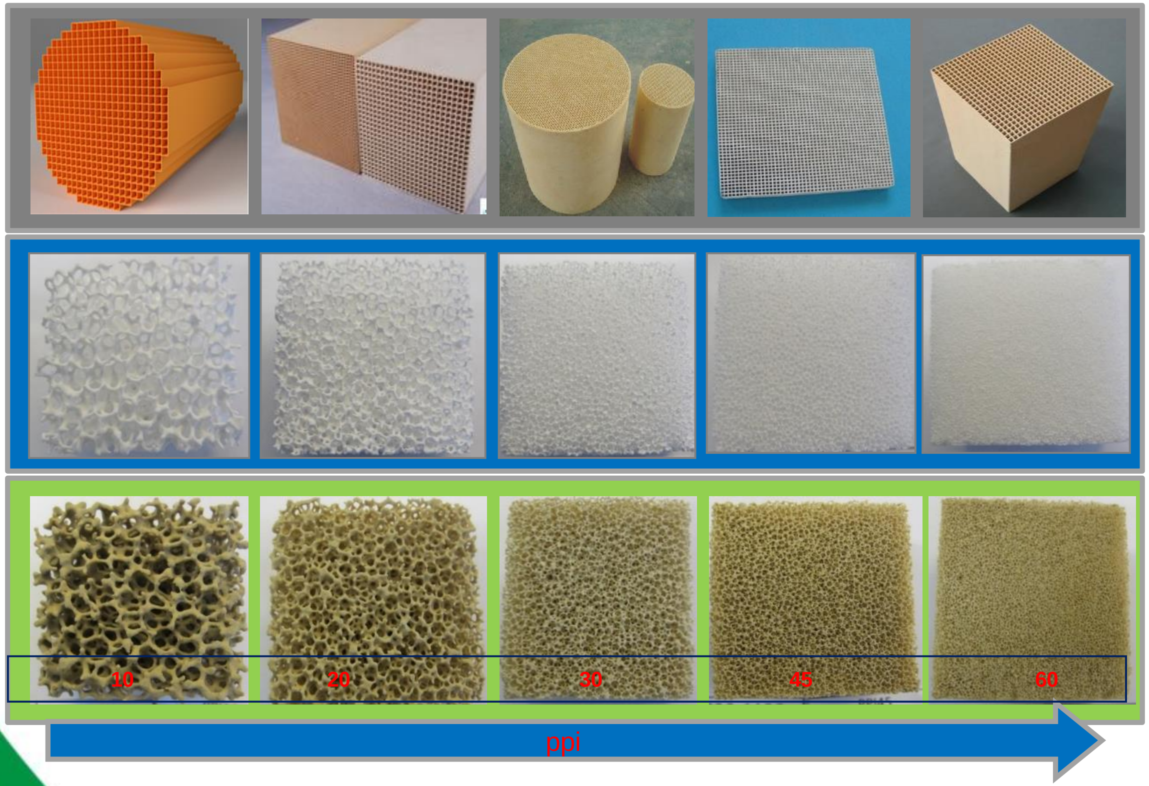
Proposed Approach



Capture Cr before reaching cathode by employing stable and active getter - complex oxides

Getters containing complex oxides where all cations are capable of reacting and forming stable Cr compounds

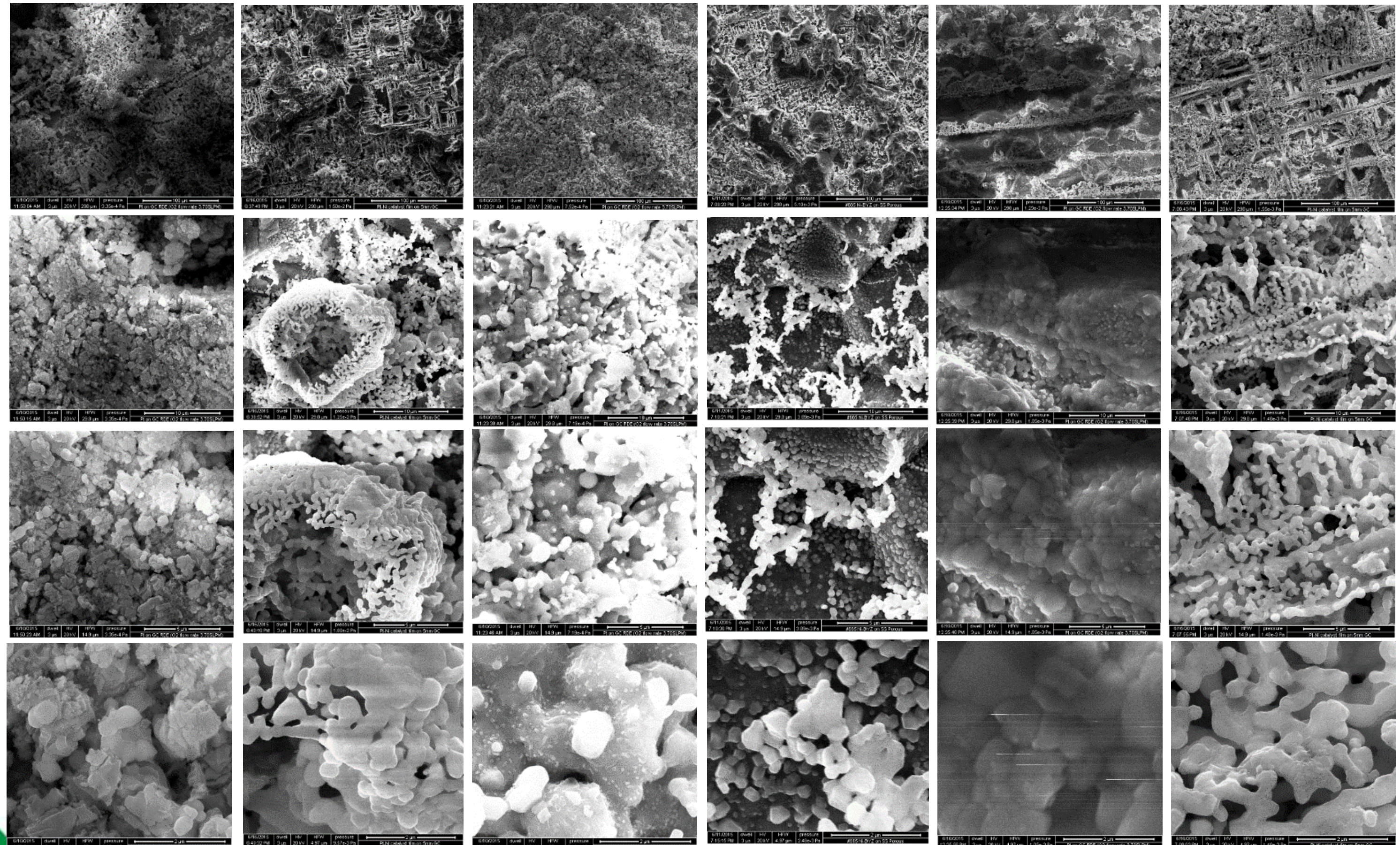
HSA Low dP Support



A wide variety of support materials and configurations are available for application in SOFC system. Selection will be based on:

- Materials stability in SOFC atmosphere
- Materials interaction with applied coatings
- Design flexibility

Morphology and Substrate interactions

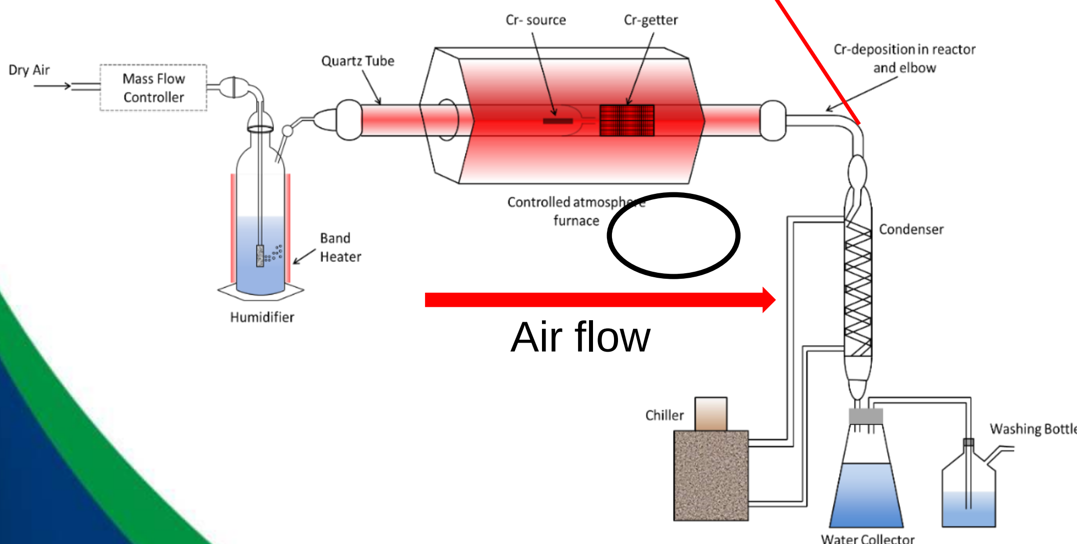


1000C 2h	1000C 2h 850C 10h	1100C 2h	1100C 2h 850C 10h	1200C 2h	1200C 2h 850C 10h

Coating uniformity, surface morphology and substrate interactions have been examined as function of heat treatment conditions

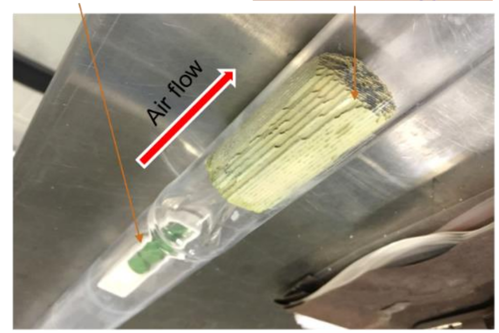
Experimental Setup

No discoloration of the quartz elbow



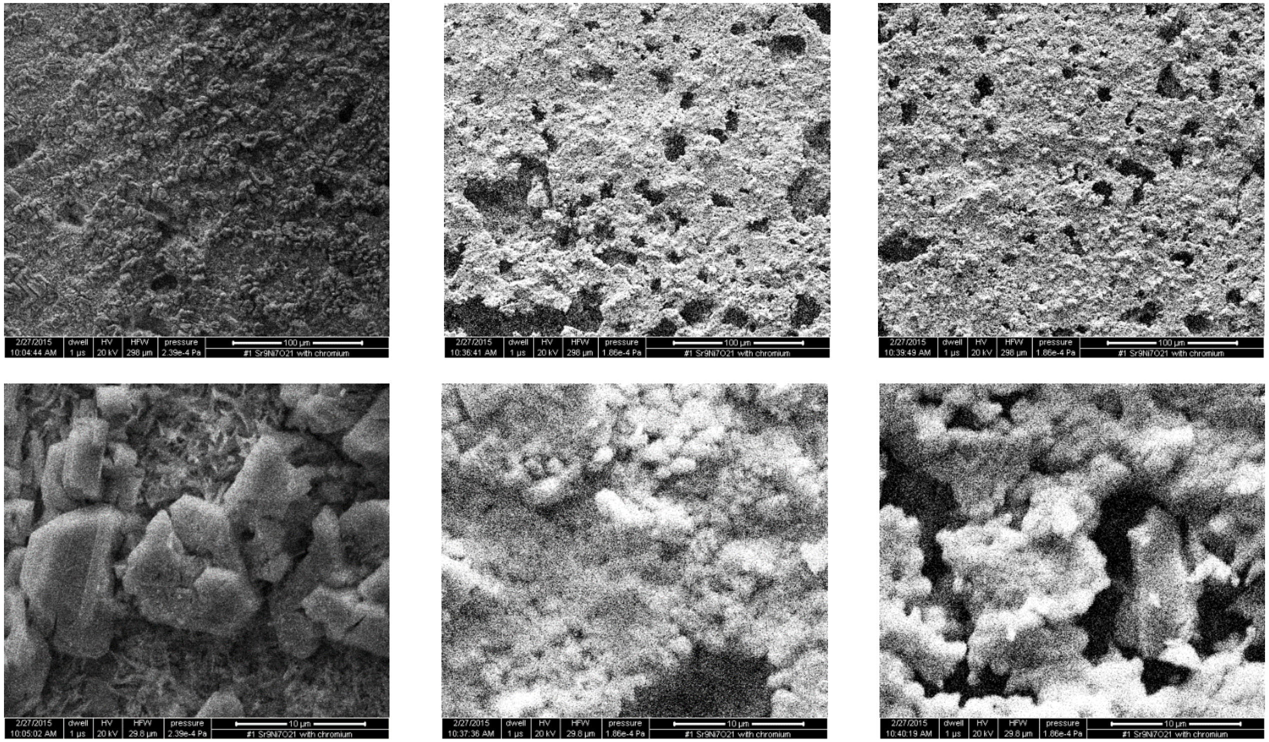
Chromium source

Getter and support



Cr source	– Cr2O3
Cr. Getter	– ABOx over cordierite
Temperature	– 850C
Time	– 500 hrs.
Exposure atmosphere	– Air -3% H2O

Surface Morphology: Inlet to outlet



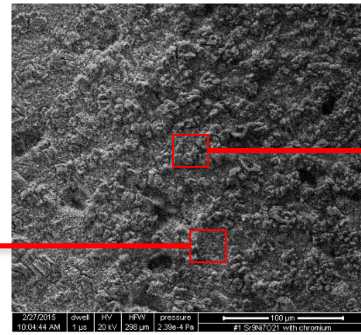
Lower magnification

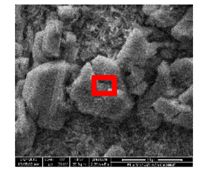
Higher magnification

400 microns **15 mm** **30 mm**

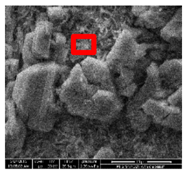
Distance from Air Inlet

Inlet morphology and chemistry: At 418 microns





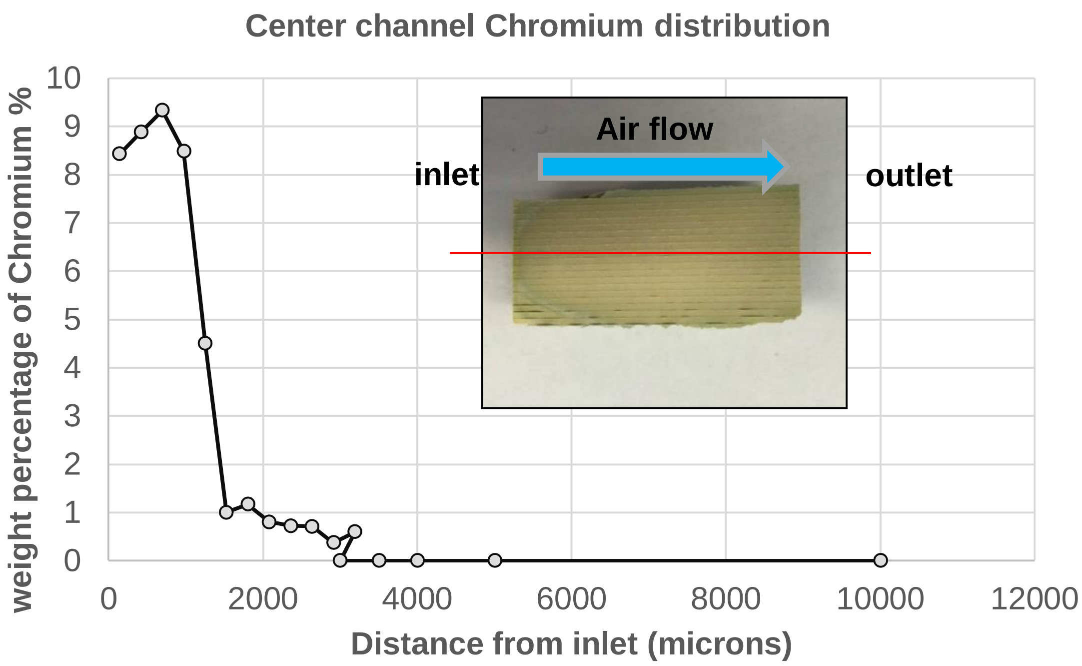
Element	Wt %	At %	K-Ratio
AlK	5.64	15.17	0.0378
SrL	81.07	67.18	0.6838
CrK	7.51	10.49	0.0727



Element	Wt %	At %	K-Ratio
O K	30.95	67.65	0.0648
AlK	3.39	4.39	0.0207
SrL	57.58	22.98	0.4635
CrK	2.27	1.52	0.0209

Cr interaction and localized association is observed near the air inlet. XRD analysis will be performed to study compound formation.

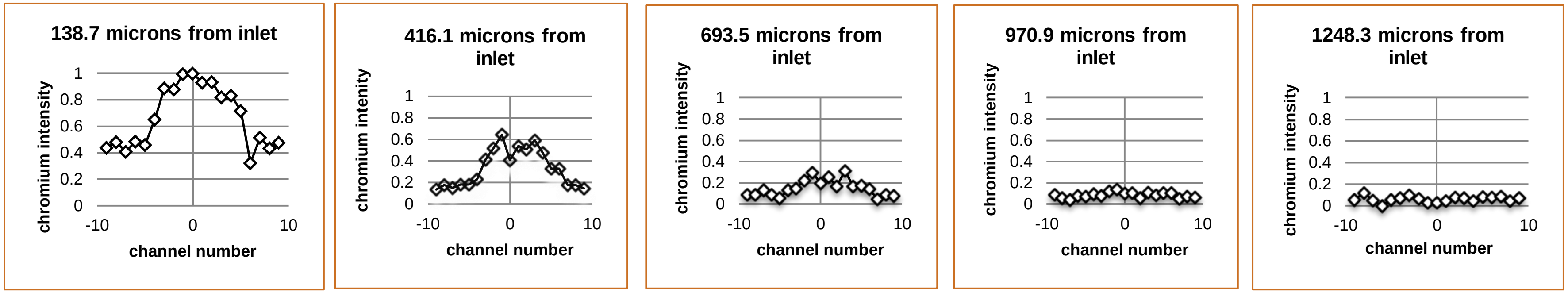
Cr Intensity Profile near air inlet



Chromium weight percentage along chromium getter goes to approximately zero before 3 mm from inlet.

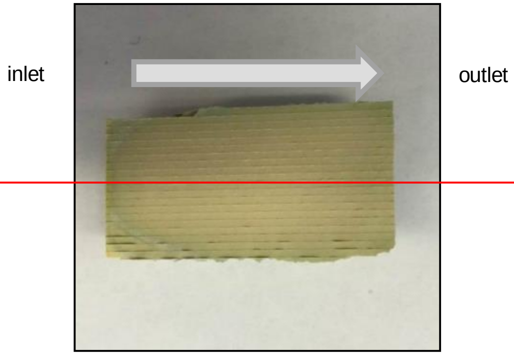
Cr Intensity Profile near air inlet

Initial ~1200 microns near inlet



Air Flow Direction

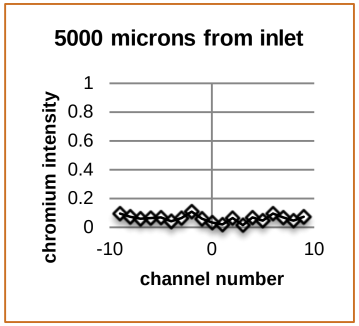
Distance from Inlet

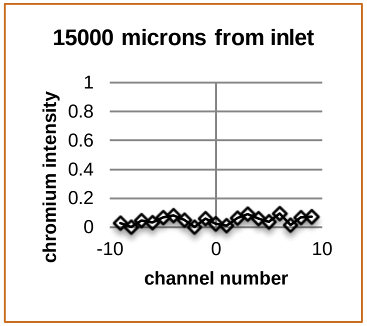


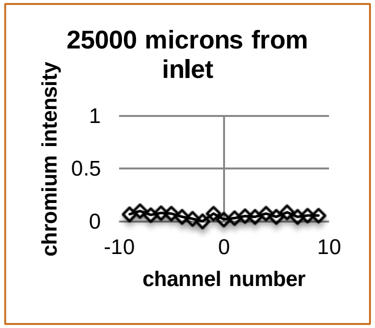
Higher Cr concentration is observed near the inlet. Center channels show higher concentration because of air flow configuration

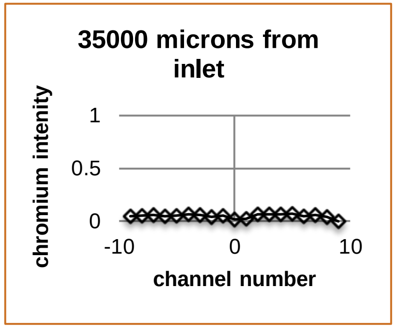
Cr Intensity Profile – Entire length

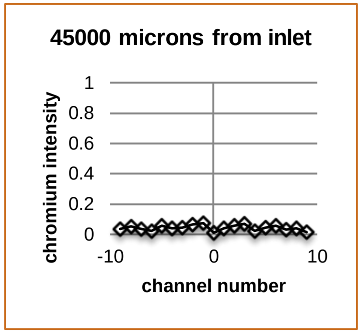
Profile over the entire length







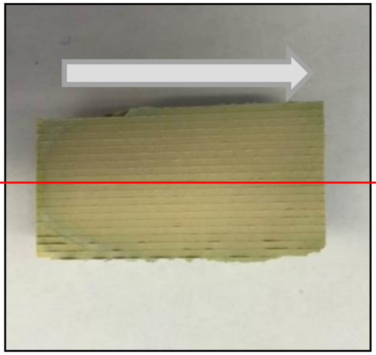




Air Flow Direction

Distance from Inlet

inlet



outlet

Cr intensity remains flat after 5mm distance from the inlet.

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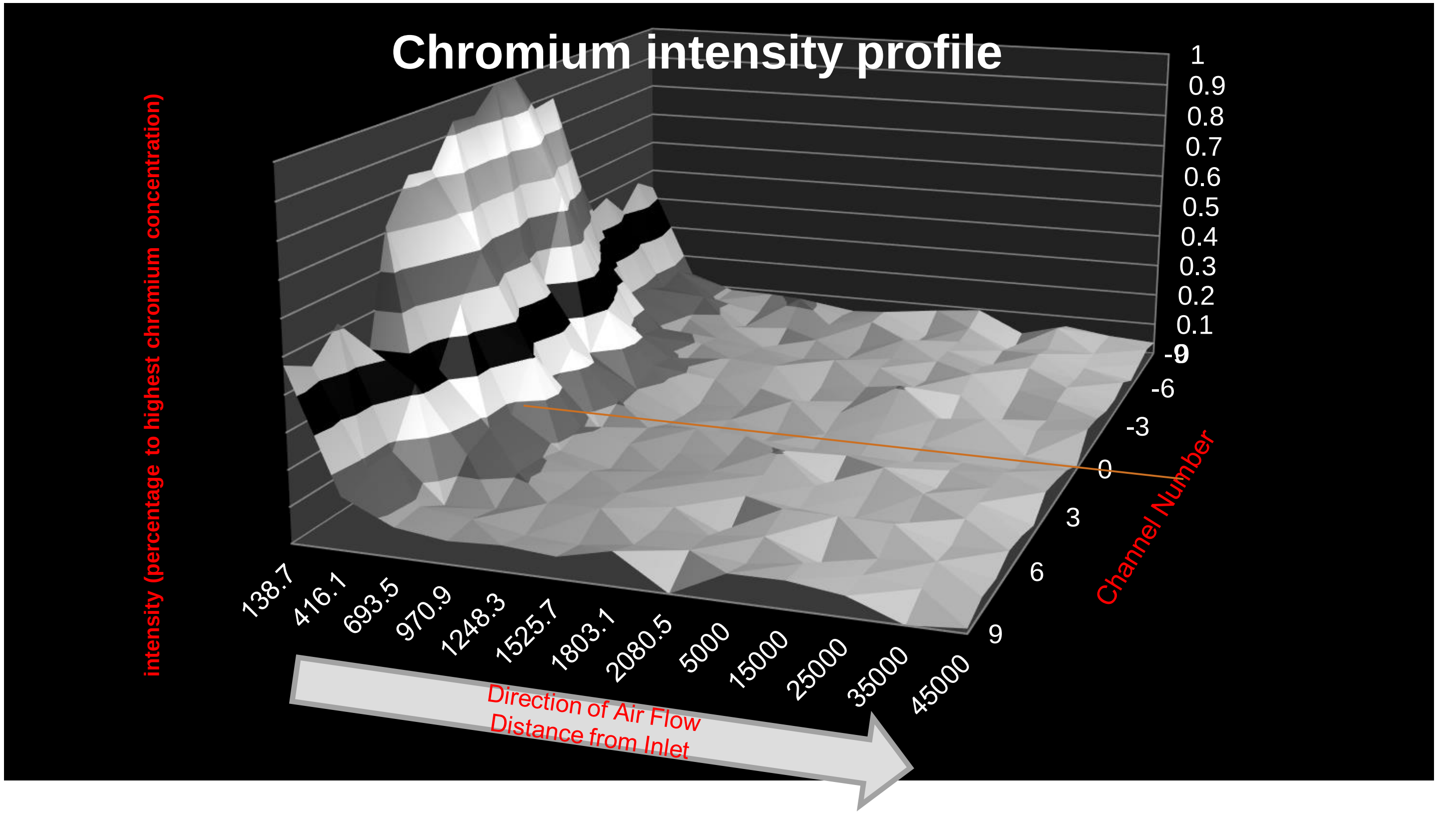
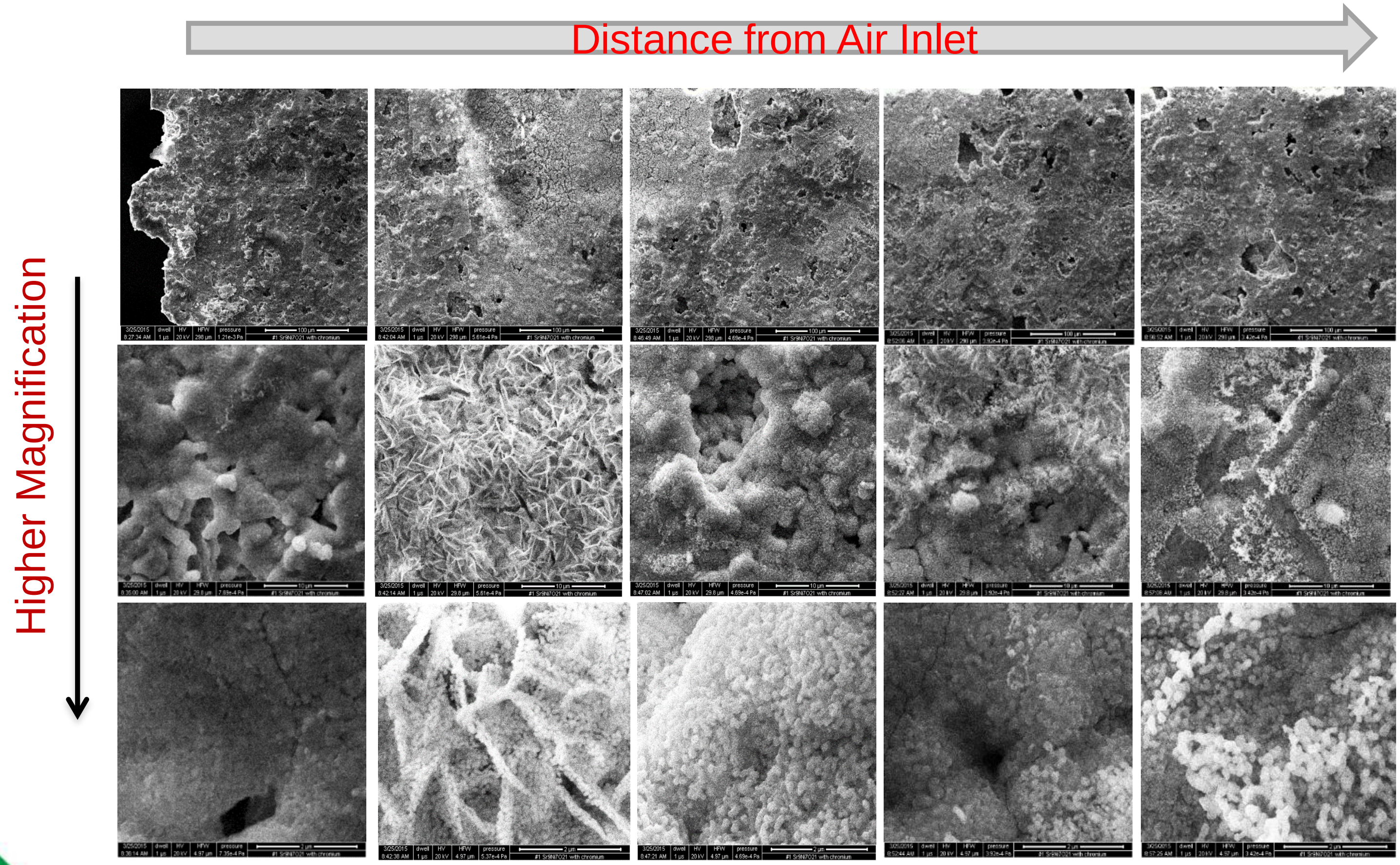
Cr Intensity Profile of last chromium getter for comparison

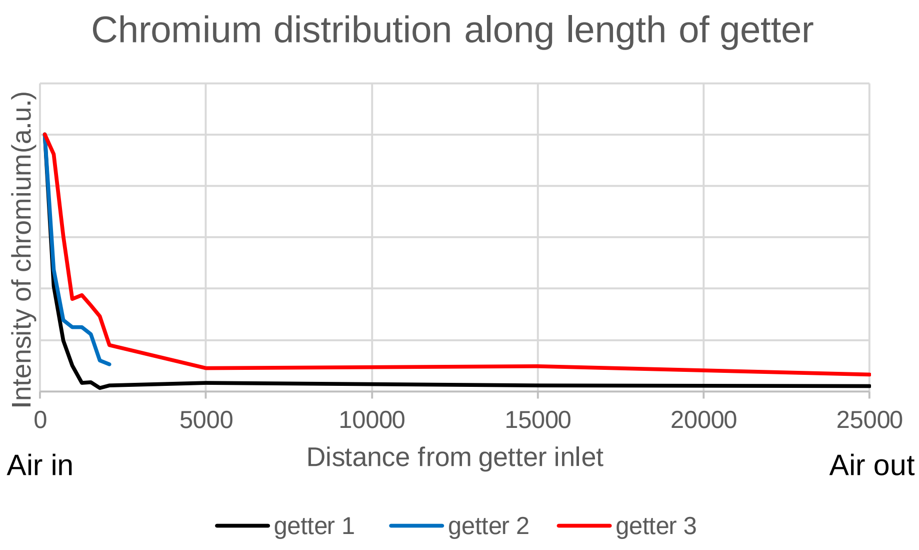


Higher Cr intensity (analysis performed using EDS technique) is observed near the air inlet (~ 1200micron). Flat Cr profile is observed over the entire length after ~1500 micron.

Post tested coating

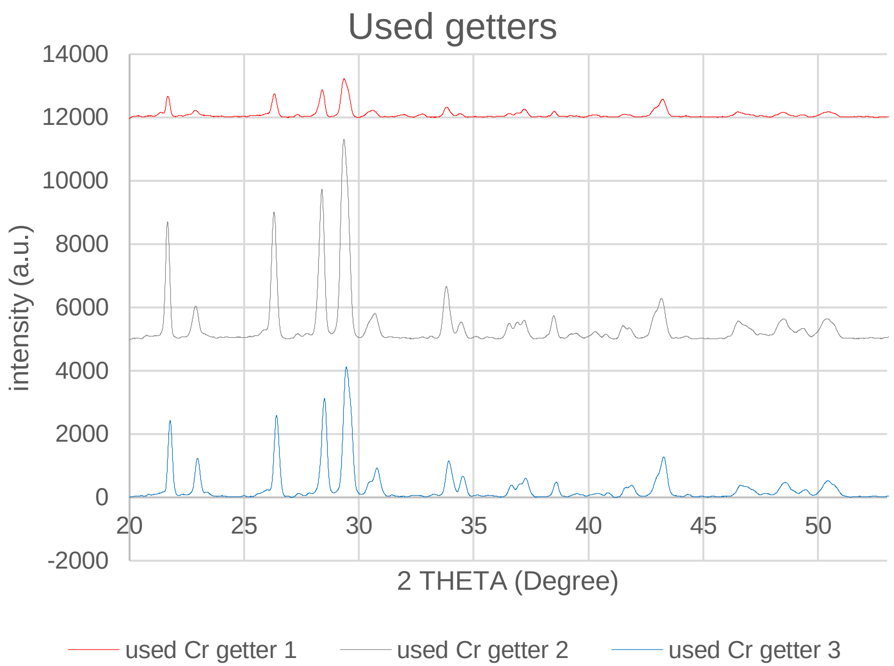


Cr Intensity Profile of getter 1, 2 and 3



Sample	Heat treatment step 1	Heat treatment step 2	Chromium evaporation test		Substrate
			Temperature	Time	
Used getter 1	950 C for 2hrs	850 C for 10 hrs	850 C	500 hrs	Cordierite
Used getter 2	950 C for 2hrs	850 C for 10 hrs			
Used getter 3	1000 C for 2hrs	850 C for 10 hrs			

XRD pattern of 3 used chromium getters



Gas phase chromium interaction with the coating and substrate leads to stable compound formation.

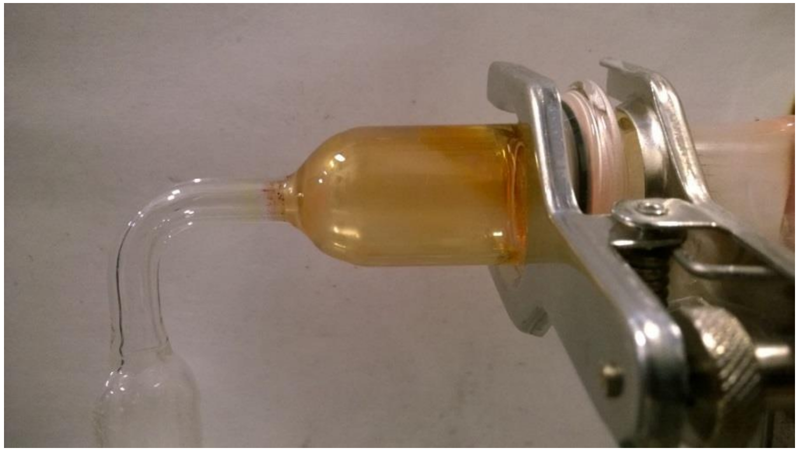
Sample	Heat treatment step 1	Heat treatment step 2	Chromium evaporation test		Substrate
			Temperature	Time	
Used getter 1	950 C for 2hrs	850 C for 10 hrs	850 C	500 hrs	Ceramic channels
Used getter 2	950 C for 2hrs	850 C for 10 hrs			
Used getter 3	1000 C for 2hrs	850 C for 10 hrs			

Getter 1 and 3 were coated 2X

Elbow pictures at outlet

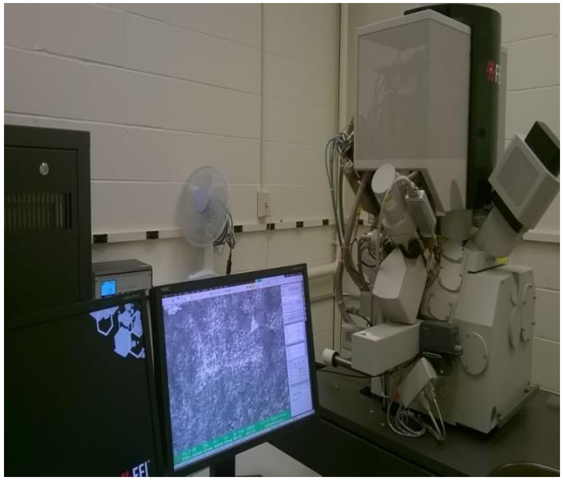
Reactor elbow discoloration due to Cr-vapors

Without getter

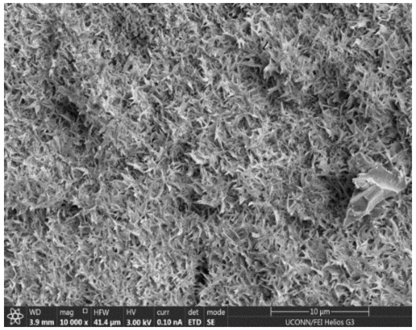


With getter

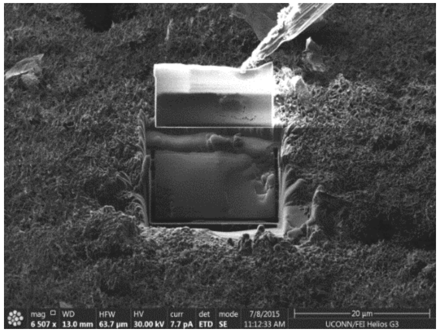
FIB/STEM for Structural and Compositional Analysis



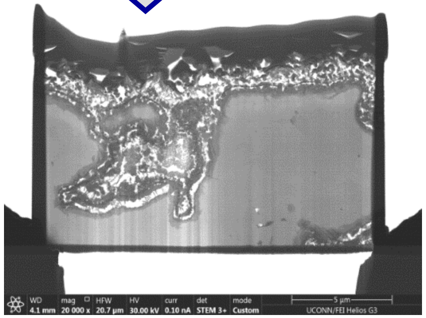
UCONN/FEI
Helios G3 nanofabrication
produces ultra-thin
samples for S/TEM



Original Cr/Getter surface



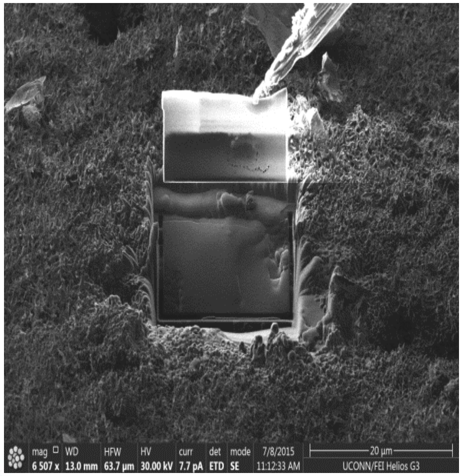
Cr/Getter surface (FIB cutting)

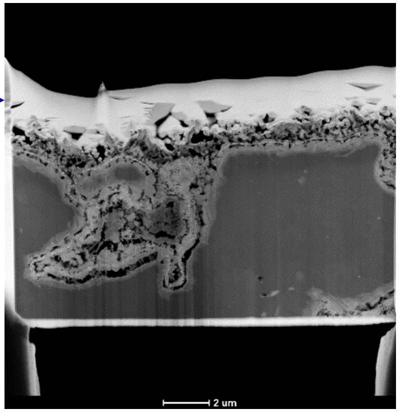


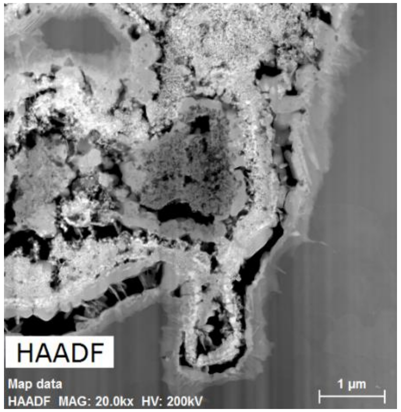
<1 µm thickness sample (After FIB cutting)

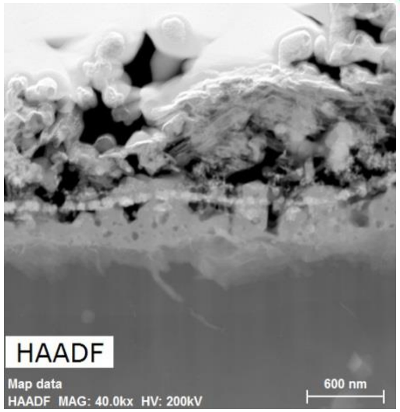
FIB X-Sectional Evaluation

Lower magnification

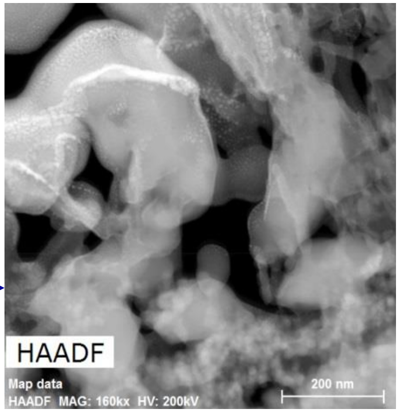


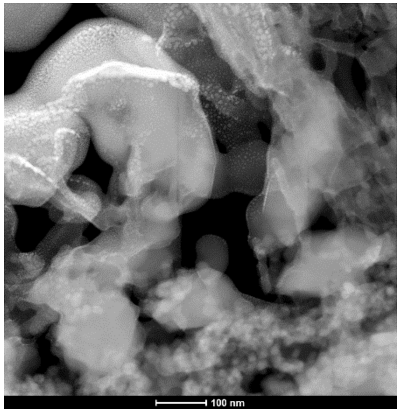


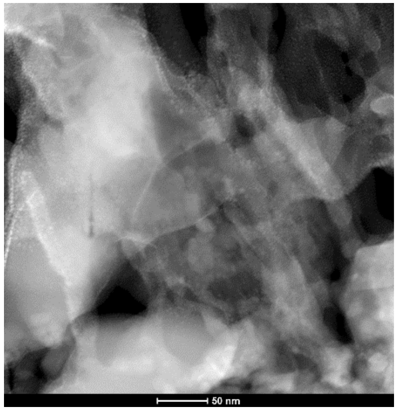




Higher magnification

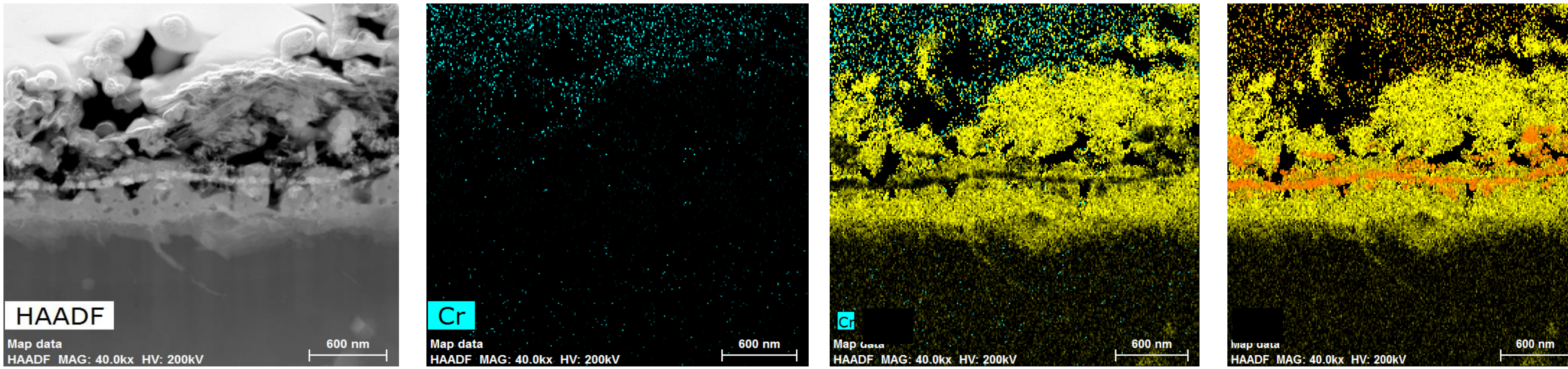


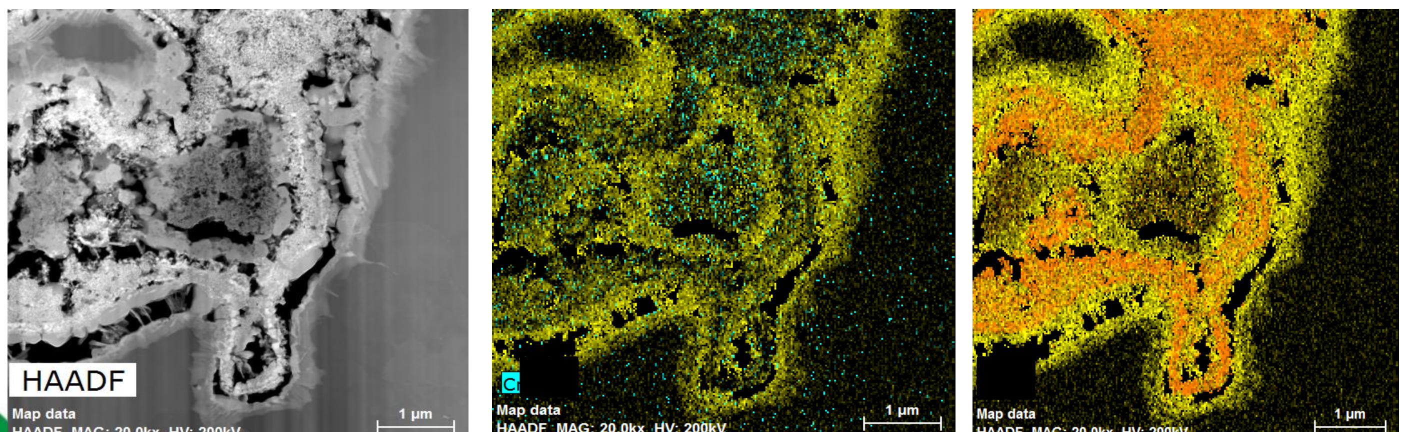




FIB-STEM Characterization

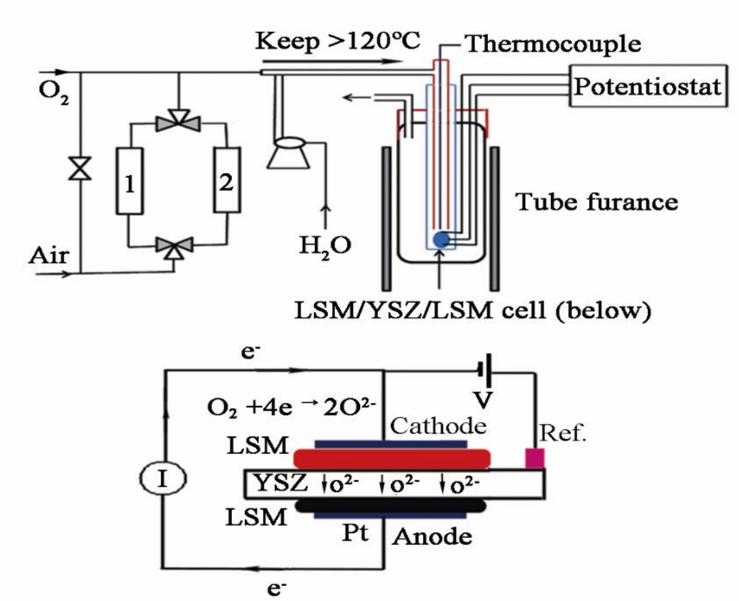
The FIB sample was taken from a posttest getter (an inlet surface has the most Cr deposits) after 500 hour test at 850°C in 3% H_2O/air.



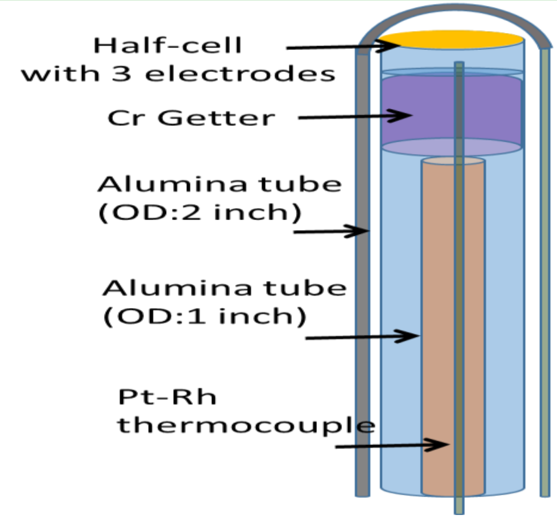


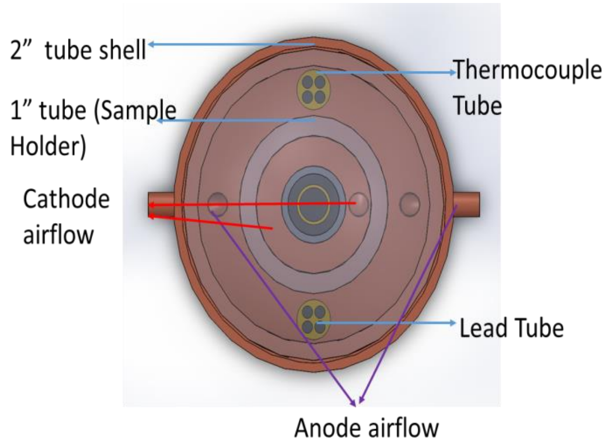
UCONN/FEI Talos F200X S/TEM high angle annular dark field (HAADF)

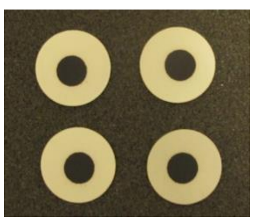
Electrochemical Tests using Getters



Scheme for the stability tests







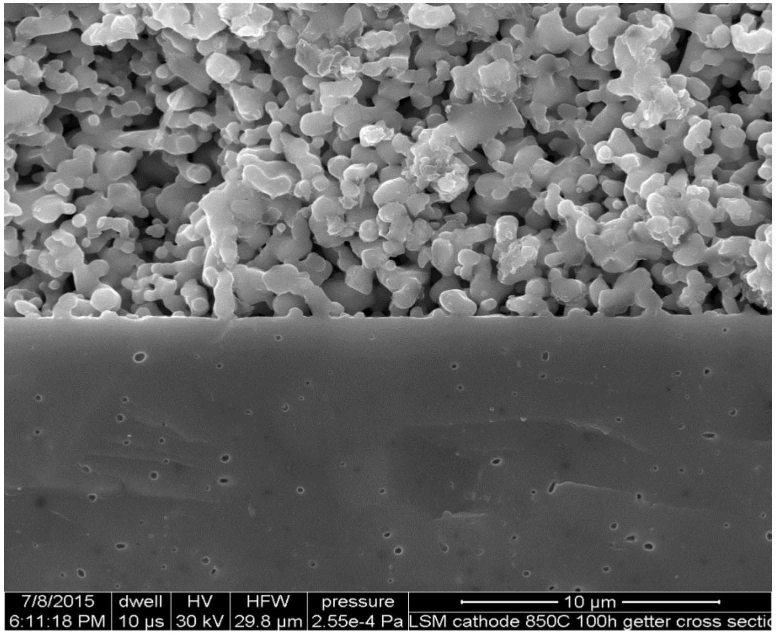
2.5 cm

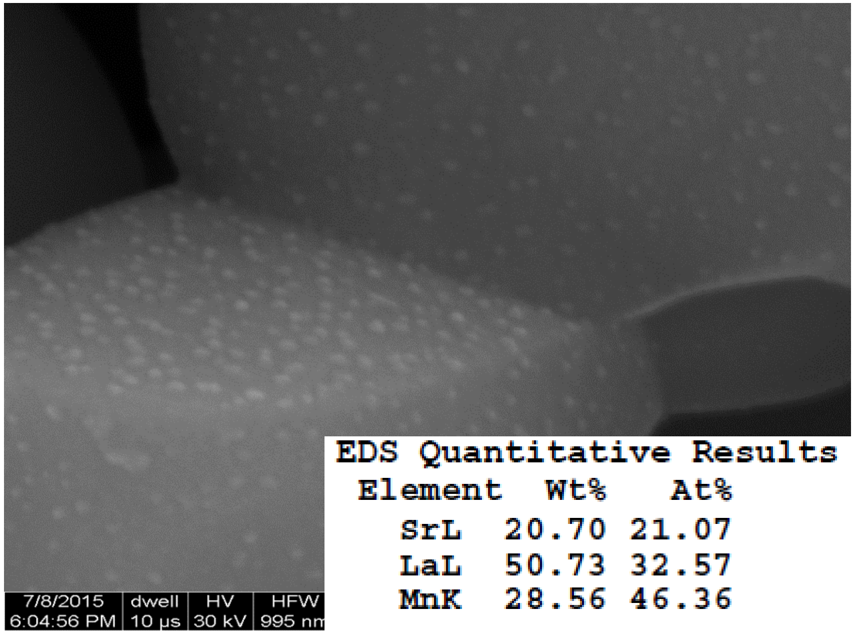
LSM/YSZ/LSM cells

Screen printer for LSM electrodes

Results & Discussion

LSM cathode in 3% H2O/air at 850°C with 0.5 V bias for 100 h (no Cr source)





EDS Quantitative Results

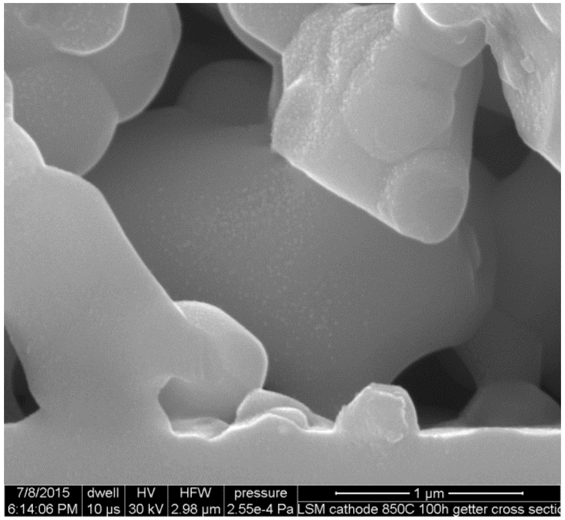
Element	Wt%	At%
SrL	20.70	21.07
LaL	50.73	32.57
MnK	28.56	46.36

Formation of SrO may react with $CrO_2(OH)_2$ species in wet air: $SrO + CrO_2(OH)_2 = SrCrO_4 + H_2O$

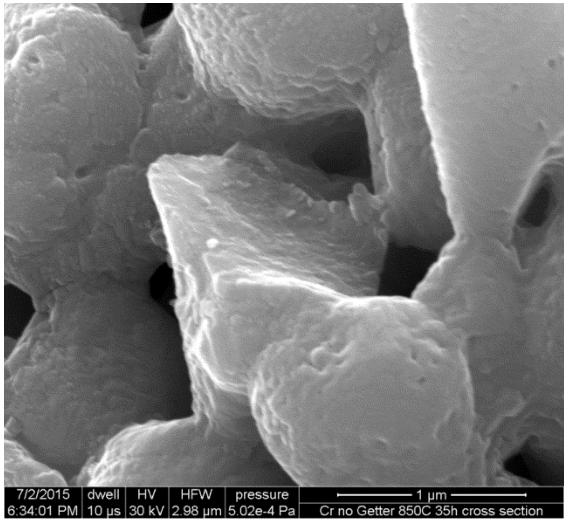
1. B. Hu, M. Keane, M. K. Mahapatra, P. Singh, *J. Power Sources*, 2014, 248, 196-204.
2. Z. Yang, G. Xia, P. Singh, J.W. Stevenson, *J. Power Sources, 2006,* 155, 246-252.

Post-test Surface Morphologies of the Half-cell Cathodes

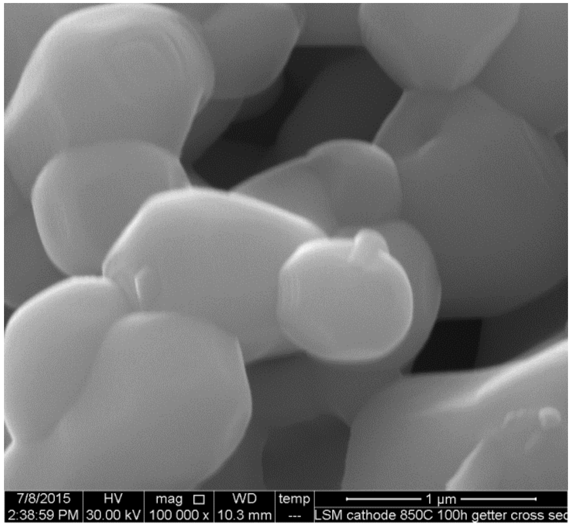
All tests have been performed at 850°C using 3% H_2O/air. Tests will be repeated to understand morphological and chemical reproducibility.



no Cr, no getter



with Cr, no getter



with Cr, with getter

Summary

- An efficient chromium getter for capturing Cr vapor species, present in the cathode atmosphere of SOFC power generation system, has been developed and tested.
- Developed chromium getter shows excellent affinity for gaseous Cr species. Cr species are captured close to the air inlet.
- Distribution of the chromium deposition has been studied using FIB-TEM,SEM-EDX and XRD for the tested getter for 500 hrs.
- Half-cell electrochemical testing of LSM/YSZ/LSM symmetric cell in dry air, chromium vapor/dry air without and with a getter has been conducted for 100 h and post-test analytical study (XRD, SEM-EDS, and FIB-TEM) are in progress.
- Getter materials and design can be tailored to meet various SOFC systems configurations.
- Getter materials can be used for capturing Cr originating from BOP and IC.
- Approaches for scale up (higher TRL) have been developed.

Future Work

- **Use thermochemistry to develop and optimize getters**
- **Use P:B methodology to optimize getter utilization**
- **Use conventional coatings to develop porous layer**
- **Optimize SA using various coating techniques**
- **Select substrates – channels, foams, fibrous**
- **Test and validate long term performance (2-5KHrs.)**
- **Transfer technology**

Increase TRL level and work with SOFC manufacturers for implementation and testing in SOFC

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Thank you