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

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UCONN

CENTER FOR CleanEnergy ENGINEERING
UNIVERSITY OF CONNECTICUT

Technical Contributors

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Presentation Outline

- Project Objectives
- Benefits of technology to the Program
- Accomplishments
- Background
- Experimental
    - Fabrication and testing of Cr Getter
    - Electrochemical Testing
    - Characterization-SEM-EDX, XRD, XPS, FIB-TEM
- Results and Discussion
- Future Work
- Acknowledgements

Project Objectives

The overall objective of the proposed research program is to develop cost effective materials, modifications of the material chemistry and the exposure environments that inhibit long term solid-gas and solid-solid interactions to minimize/mitigate the degradation of SOFC cathode. The objectives include:

a. **Develop and demonstrate the viability of the application of cost effective 'chromium getter' to capture the chromium species originating from the metallic stack and BOP components,**
b. **Develop modified cathode compositions to control and prevent oxide segregation and compound formation at the surface and interfaces during exposure to "Real world" air exposure,**
c. **Develop cathode contact layer and modification to avoid chromium poisoning originating from metallic current collector/interconnect.**

Simple and complex oxides ranging from pure and doped oxide (AO_x), spinel (AB_2O_4), perovskites (ABO_3), and double-perovskites (A_2BO_4) will be examined as efficient and stable chromium getter capable of forming thermodynamically stable chromites and chromates to further reduce the emanating gaseous Cr species by 3 to 4 orders of magnitude. Architectures utilizing high surface area nano and micro-sized getter particles in the contact layer as well as supported on highly porous ceramic backbone will be developed and experimentally tested and validated in the laboratory. Computational and experimental tools will be employed to rationally design materials to mitigate the adverse effects of the contaminants on the surface segregation, and compound formation. In-depth understanding of the cathode degradation in 'real world' atmosphere (work performed in our laboratory under the ongoing research projects) and existing laboratory capabilities will be leveraged for materials development. The proposed technology development program will transfer the technology and processing knowhow to materials suppliers and the SOFC industry to accelerate the demonstration and deployment.

Benefits of Technology to the Program

Potential benefits of this project will lead to:

- Mitigation the LSM and LSCF degradation arising from the presence of moisture and chromium species in the real-world cathode environment.
- Significantly increase the performance stability and long-term reliability of SOFCs, thus accelerating the demonstration and deployment of the technology.
- Design flexibility for the integration in wide range of SOFC systems configuration
- Flexibility of operation from 600-1000C
- Use of non-strategic and non-noble low cost metal oxides for getter synthesis
- Ease of getter synthesis and fabrication
- High Cr capture capacity through tailored high surface area powder and coatings
- Replaceable unit with getter health monitoring and sensing
- Scalable design for application in distributed and centralized power generation

The innovation will also find application in related high temperature electrochemical systems such as OTM and SOEC for the prevention of Cr assisted performance degradation. The proposed approach for Cr capture can also be applied to oxycombustion and other advanced combustion techniques for the reduction of Cr vapor in the exhaust gas stream.

Accomplishments

- Mechanisms for cathode degradation in "Real world Air Atmosphere" due to dopant exolution, structural changes and interfacial compound formation has been developed and documented.
- Concept of capturing gas phase chromium vapor species, originating from SOFC sub-systems (e.g. HX) and cell components (e.g. IC), have been developed utilizing fundamental thermochemical principles and solid-gas interaction mechanisms.
- Getter materials selection basis has been developed based on reaction product morphology, substrate structure and reaction processes.
- In-situ electrochemical and ex-situ transpiration tests have been conducted for periods up to 500 hrs to assess the Cr capture tendency of fabricated getters.
- Getter and test cells have been characterized using EIS,SEM, EDS, FIB, TEM, and ICP techniques to examine the Cr capture trend.

➢ Chromium getter shows excellent affinity for capturing gaseous Cr species. Cr species are captured close to the air inlet.
➢ Electrochemical and transpiration tests show excellent blockage of Cr vapor for entering into cathode electrode.
➢ Scale up of getter materials, support structure and HSA getter deposition processes are being developed and optimized.

❖ 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.

Accomplishments - Program Outcome

- Graduate / Undergraduate students being trained - 3
- Post-doctoral fellow: 2
- Patent disclosure: 1
- Technical Publications in progress - 3
- Outreach: Middle and High School, Davinci Program, STEM

Peer reviewed publications

- V Sharma, MK Mahapatra, S Krishnan, Z Thatcher, BD Huey, P Singh, R. Ramprasad "Effects of Moisture on (La, A)MnO3 (A = Ca, Sr, Ba) Solid Oxide Fuel Cell Cathodes: A First-principles and Experimental Study" Journal of Materials Chemistry A DOI: 10.1039/C6TA00603E 2016
- B Hu, MK Mahapatra, P Singh " Performance regeneration in lanthanum strontium manganite cathode during exposure to H2O and CO2 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, 196-20 2014
- B Hu, MK Mahapatra, M Keane, H Zhang, P Singh " Effect of CO2 on the stability of strontium doped lanthanum manganite cathode" Journal of Power Sources, 1-10 2015
- B Hu, MK Mahapatra, V Sharma, R Ramprasad, N Minh, S Misture, "Durability of lanthanum strontium cobalt ferrite ((La0.60Sr0.40)0.95(Co0.20Fe0.80)O3-x) cathodes in CO2 and H2O containing air" Proceedings of the 39th International Conference on Advanced Ceramics 2015
- V Sharma, MK Mahapatra, P Singh, R Ramprasad "Cationic surface segregation in doped LaMnO3" J Mater Sci 50 (8), 3051- 3056, 2015

Technical Report, Book Chapters and News release

- P Singh "Developing chromium capture technology prevents poisoning of solid oxide fuel cell" American Ceramic Society Bulletin 95 (2), 16-17VJ 2016
- MK Mahapatra, P Singh "Fuel Cells: Energy Conversion Technology" Future Energy (Second Edition),, 511-54
- 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

Technical Presentations

- Sharma, S Krishnan, B Hu, MK Mahapatra, P Singh, R Ramprasad "Cationic surface segregation in doped LaMnO3: A first principles thermodynamics study" NETL SOFC Meeting, Pittsburgh 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
- Prabhakar Singh, Chiying Liang, Boxun Hu, Manoj Mahapatra and Byung Jun "Chromium Poisoning in High Temperature (600-1000C) Electrochemical Systems" 145th TMS Annual Meeting, Nashville 2016
- Chiying Liang ,Boxun Hu, Sridevi Krishnan, Manoj Mahapatra, Rampi Ram Prasad and Prabhakar Singh "Mitigation of Chromium Poisoning in SOFC" International Conference and Exposition on Advanced Ceramics and Composites, American Ceramic Society 2016

US Patent Application

- U.S. Patent Application No.: 14/821,677 "High temperature electrochemical systems and related methods"

Accomplishments - Program Outcome

Industrial/ National Laboratory Network

- **LG Fuel Cells** — **Fuel Cell Energy**
- **Praxair** — **Saint Gobain**
- **ITN** — **General Electric**
- **InnoSense** — **Accumentrics**
- **Cummins Power** — **Pacific Northwest National Laboratory**
- **Naval Undersea Warfare Center**

Cr Getter findings, cathode degradation in air containing H_2O and CO_2, experimental techniques and materials

Technical publications in preparation

- In-operando validation of the mitigation of Cr assisted cathode poisoning
- Evaluation of Cr getter by transpiration technique
- Book chapter – Cathode poisoning
- Cr assisted poisoning and morphological changes in LSM and LSCF

Enabled adjacency areas (selected):

- S. Gupta and P. Singh "Nickel and Titanium Doubly Doped Lanthanum Strontium Chromite for High Temperature Electrochemical Devices" Journal of Power Sources 2015 Accepted
- Sapna Gupta, Joseph Adams, Jamie Wilson, Eric Eddings, Manoj Mahapatra, Prabhakar Singh "Performance and post-test characterization of an OTM system in an experimental coal gasifier" Applied Energy Accepted
- S Gupta, Y Zhong, M Mahapatra, P Singh Processing and electrochemical performances of manganese-doped lanthanum- strontium chromite in oxidizing and reducing atmospheres". International Journal of Hydrogen Energy, 2015
- S Gupta, P. Singh "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− δ–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

Background

Durability of Cathode Materials under "Real World" Air Exposure Atmospheres

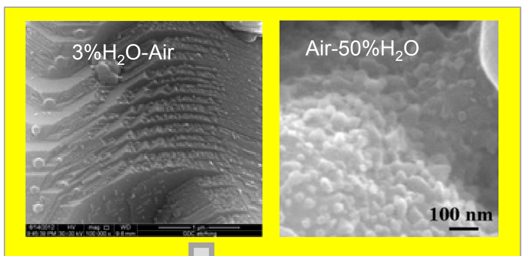
- **Issue:** Presence of impurities (H_2O/CO_2/Cr-vapor) in air degrades cathode and long-term SOFC performance.
- **Approach:** Experimentally measure performance degradation and characterize chemical and morphological changes; Develop degradation mechanisms and optimize materials chemistry utilizing computational modeling

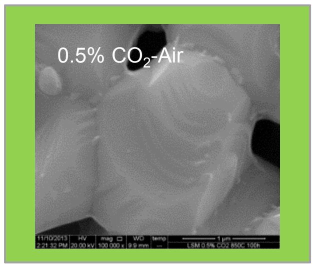
Presence of moisture in air:

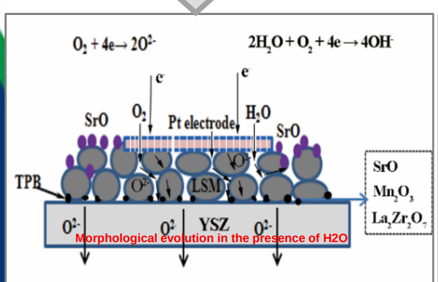
- **Presence of moisture in air degrades electrochemical performance and the degradation increases with moisture content, exposure temperature, and cathodic bias. Both ohmic and non-ohmic resistances increase with increase in moisture content**
- **Electrode surface shows SrO/Sr(OH)$_2$ segregation (nM particles) and formation of $La_2Zr_2O_7$ and MnO_x at electrode–electrolyte interface**

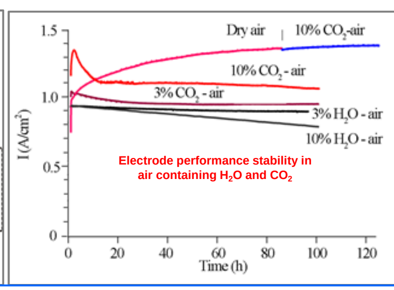
Presence of CO_2 in air:

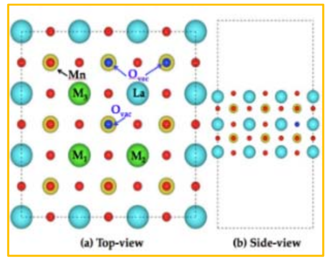
- **Presence of CO2 (up to 3%) in air shows little to no influence on cathode performance degradation (100 hrs. tests).**
- **$La_2O_2CO_3$ and $SrCO_3$ form below 800°C but only $SrCO_3$ at 850°C and above.**
- **Pre-activated electrode shows insignificant degradation even at higher CO_2 (~10%CO_2) content.**



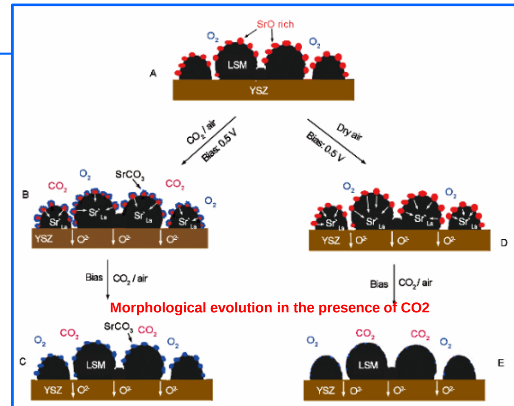








Top-view and side-view of the (La,M)O terminated (M = Ca, Sr and Ba) model with the all-possible dopant substitution

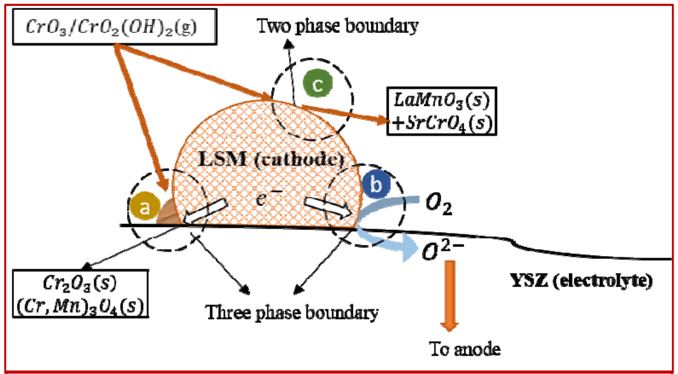


Significant reduction in Cr evaporation has been achieved by alloy, atmosphere and materials chemistry modifications.

- Boxun Hu, Michael Keane, Manoj K. Mahapatra, Prabhakar Singh "Stability of strontium-doped lanthanum manganite cathode in humidified air" Journal of Power Sources 248, 196-204, 2014
- Boxun Hu, Manoj Mahapatra, Michael Keane, Heng Zhang and Prabhakar Singh "Effect of CO2 on the stability of Doped Lanthanum Manganite Cathode" Journal of Power Sources, 268, 404-413, 2014

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.**



Schematic of chromium poisoning at three phase boundary (a and b: Three phase boundary reactions; c: Two phase boundary reaction) (TMS Meeting, Feb. 2016)

At three phase boundary,

$$2\{CrO_3,\ CrO_2(OH)_2\}(g) + 6e^- = Cr_2O_3 + \{3O^{2-},\ 3O^{2-} + H_2O\}$$

$$2M^{\times}_{M(LSM)} + O^{\times}_{O(LSM)} + V^{\cdot\cdot}_{O(YSZ)} = 2M'_{M(LSM)} + O^{\times}_{O(YSZ)} + V^{\cdot\cdot}_{O(LSM)} + 2p^{\cdot}_{(LSM)}$$

$$CrO_{3(gas)}(CrO_2(OH)_{2(gas)}) + M^{\times}_{M(LSM)} = Cr - M - O_{(nuclear)}(+H_2O_{(gas)}))$$

$$CrO_{3(gas)}(CrO_2(OH)_{2(gas)}) + Cr - M - O_{(nuclear)} = Cr_2O_3/(Cr,M)_3O_4(+H_2O_{(gas)})$$

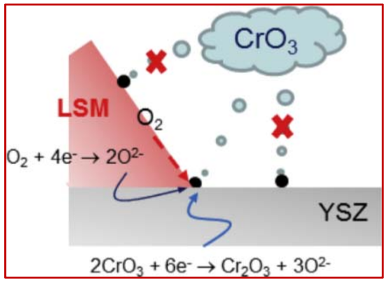
Wherein M represents Mn or Sr.

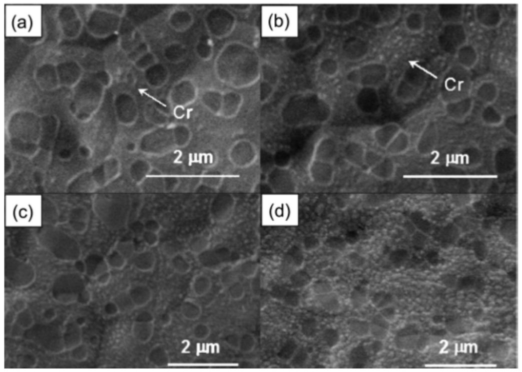
At three phase boundary,

$$O_2(g) + 4e^- = 2O^{2-}$$

At two phase boundary,

$$La_{1-x}Sr_xMnO_3 + x\{CrO_3, CrO_2(OH)_2\}(g) = (1-x)LaMnO_3 + \{xSrCrO_4, xSrCrO_4 + H_2O(g)\}$$

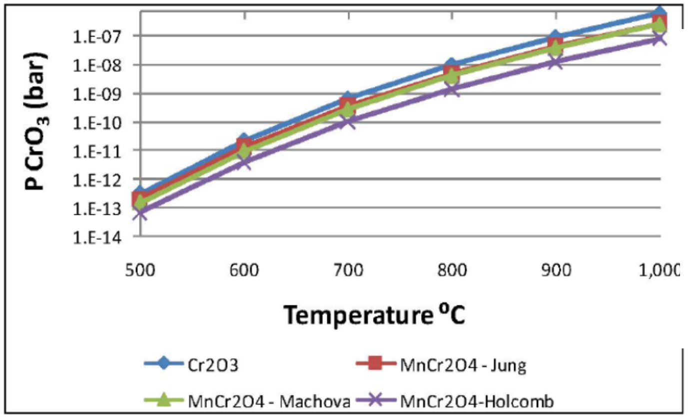




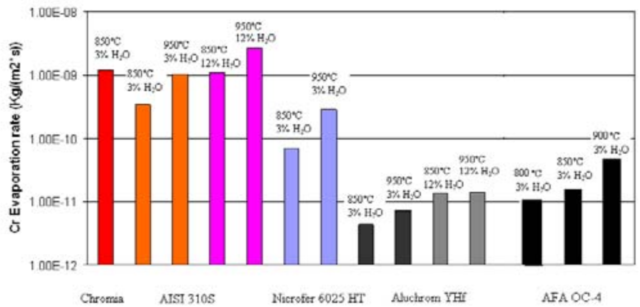
SEM micrographs of the YSZ electrolyte surface in contact with a LSM electrode coating in the presence of a FeCr alloy at 900 C after cathodic polarization for (a) 5 min, (b) 15 min, (c) 30 min, (d) 4 h,

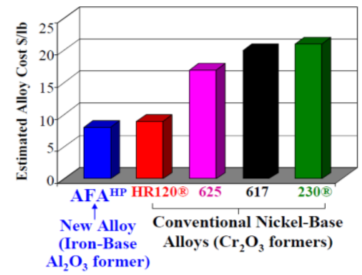
Background – Mitigation Schemes

- **There is limited/ little literature on capturing chromium vapor before reaching active cathode.**
- **Approaches for mitigation of chromium poisoning include minimization of chromium evaporation from exposed metallic surfaces – alloy chemistry modification and surface coating**



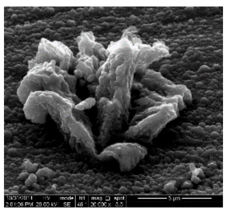
Calculated partial pressure of CrO_3 over Cr_2O_3 and $MnCr_2O_4$.

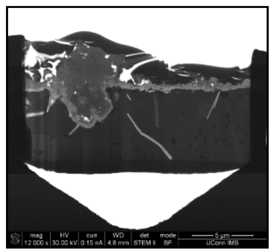


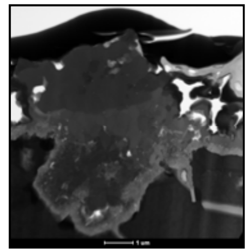


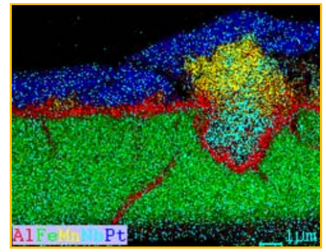
AFA Oxidation and Passivation – 850C, 500 hrs.

Scale morphology and elemental distribution



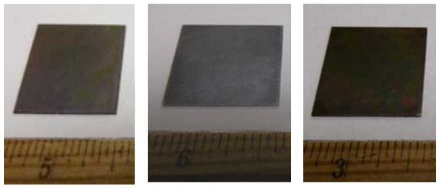






Protective Ceramic Coatings

Solid Oxide Fuel Cell (SOFC) Balance-of-Plant Components (InnoSense LLC (SBIR Phase 1)



YSZ – 2 Layer Film on 6 Sides Fired 800 °C

Lighter discoloration with coating

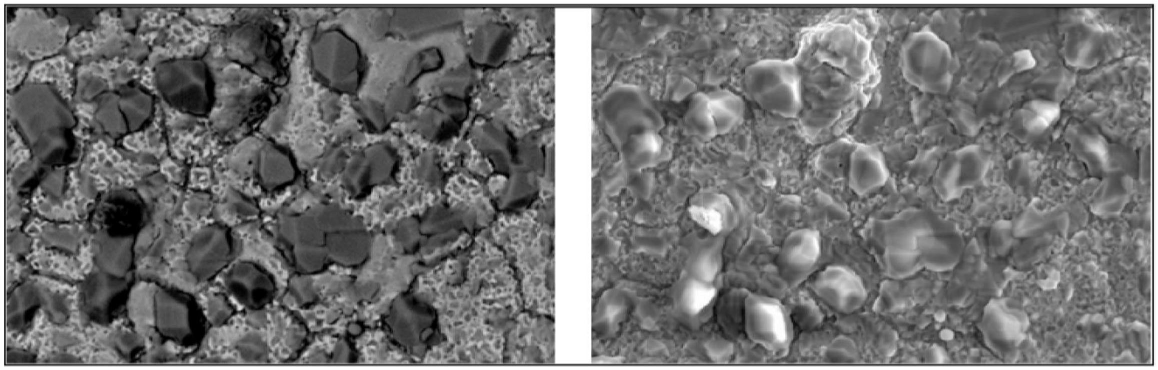
Without coating

With coating

Background

Literature – Air Products ITM Report

- Coated alloy samples reduced Cr contamination
- Performance of coated alloy sample was only slightly better
- Cr deposits formed on the active ITM surface led to reduction in oxygen flux



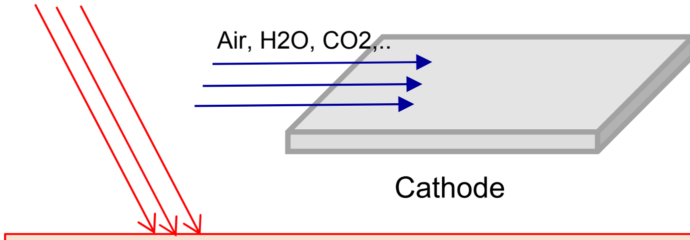
DEVELOPMENT OF ITM OXYGEN TECHNOLOGY FOR INTEGRATION IN IGCC AND OTHER ADVANCED POWER GENERATION Final Scientific /Technical Report
Phillip A. Armstrong, Ph.D. July 2015
DE-FC26-98FT40343
Air Products and Chemicals, Inc.

AIR PRODUCTS

- Use of MgO based getter is speculated based on report.
- References: Chapter 6, Chapter 14, Chapter 16
- Limited data on the use of cathode (LSCF) powder for capturing Cr from IC exists. Long term performance remains unknown

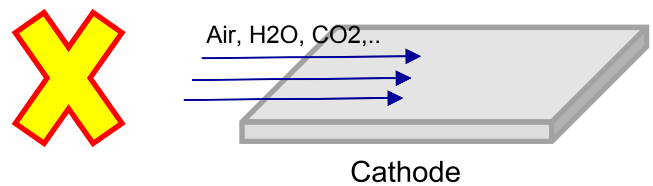
Approach

State of the Art



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

Proposed Approach



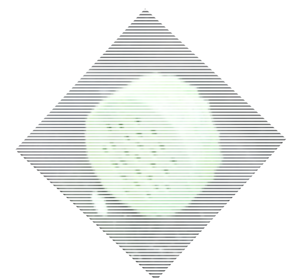
Capture Cr before reaching cathode by employing stable and active getter - complex oxides

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

Cr Getter : Materials, Structure and Reaction Mechanisms

Selection Matrix → Test Validation → Manufacturing

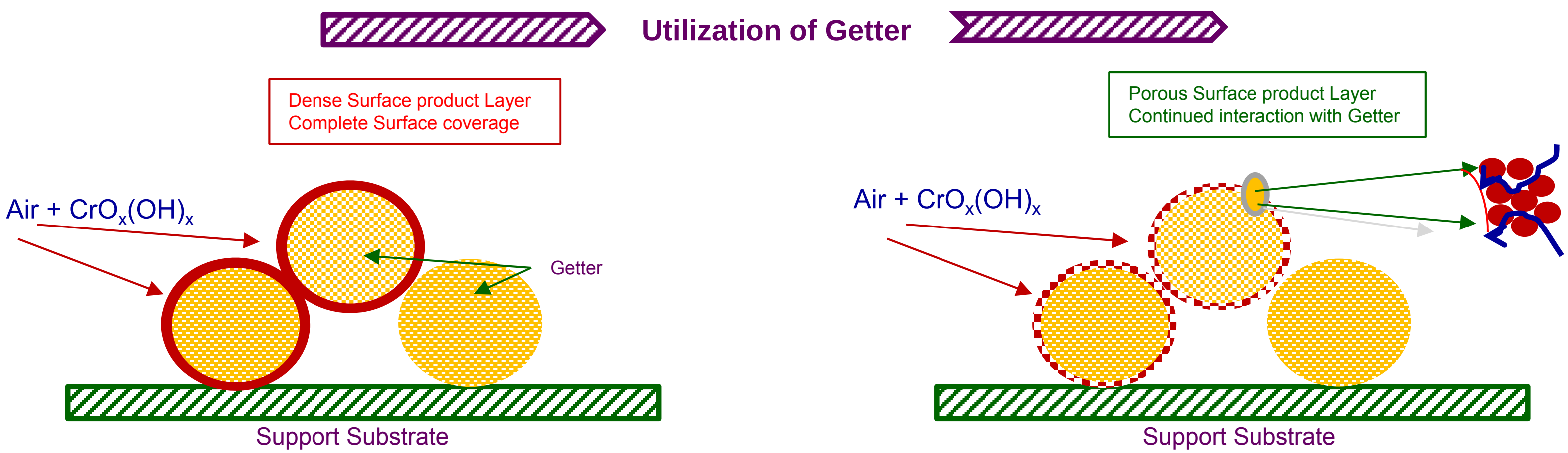
Cr Gettering from BOP and IC
Materials selection, synthesis and test validation
Scale up and validation in large SOFC systems



Getters have been extensively used in chemical, electronics, metal manufacturing and nuclear industries for the removal of trace gas phase impurities.

Getter Materials, support and Fabrication

- **Thermodynamic requirement**:
  - $\Delta G\ (CrO_x/\ MO.Cr_2O_3) < \Delta G\ (CrO_x/Cr_2O_3)$
  - $\sum P_{CrOx,\ CrO(OH)x\ (Air/Cr2O3)} \ll \sum P_{CrOx,\ CrO(OH)x\ (MO/Cr2O3)}$
- **Physical requirement**:
  - Structural / chemical stability of MO in ambient air
  - Gas Phase and substrate interactions
- **Morphological requirement:**
  - $(Porosity, Vol)_{Reaction\ Product} < (Porosity, Vol)_{Reactant}$

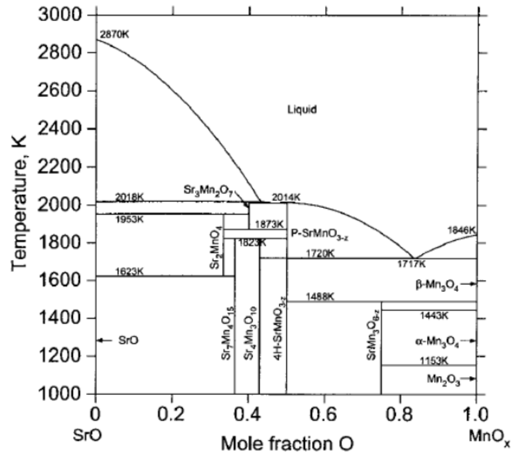


Getter Materials, support and Fabrication

- **Materials selection**
  - ✓ Thermochemistry - Chemical stability and free energy minimization
  - ✓ Physical properties - Resistance to hydrolysis, support reaction
  - ✓ Product morphology - Porous product layer with access to substrate
- **Support selection**
  - ✓ High surface area - Support HSA porous getter materials coating
  - ✓ Chemical stability - Resistant to interaction with coating
  - ✓ Structure - Porous, low dP, allows diffusion through coating
  - ✓ Form - Cartridge, conformable overlay, bond coat
- **Fabrication Processes**
  - ✓ Porous coating - Precursor solution, sol-gel, slurry
  - ✓ Heat treatment - Adherence and HSA
  - ✓ Tailored porosity - Scaffolding

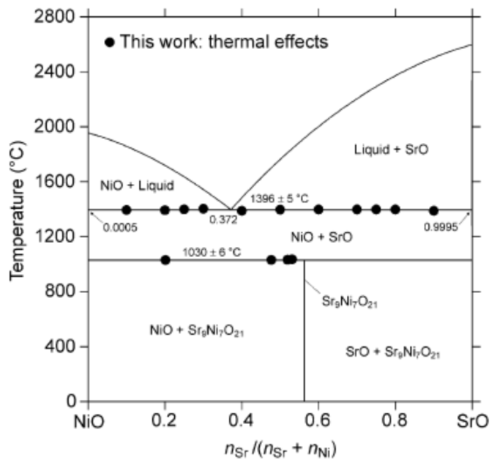
Two different approaches for mitigating Cr poisoning arising from BOP and IC have been considered.

Materials Selection- Phase diagram



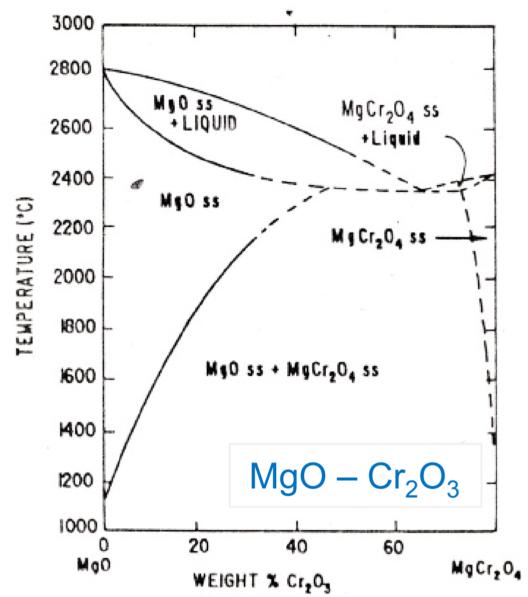
SrO - MnOx

JPEDAV (2004) 25:311-319



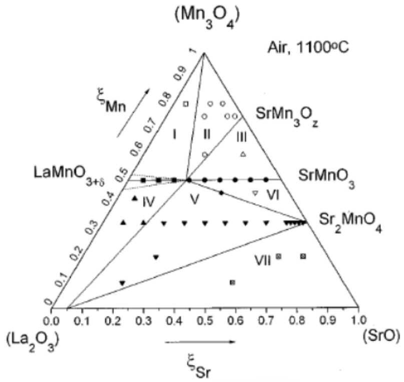
SrO - NiO

M. Zinkevich / Journal of Solid State Chemistry 178 (2005) 2818–2824



MgO – Cr_2O_3

Oxide solid solutions and mixtures from Alkaline earth and Transition metal group are preferred and considered over single phases due to chemical stability and resistance to interactions with gas phase impurities.



Chromium vapors: Gr-II MO Interactions

$Cr_2O_3 + 1.5O_2(g) = 2CrO_3(g)$
$2Cr_2O_3 + O_2(g) + 4H_2O(g) = 4CrO(OH)_2(g)$
$Cr_2O_3 + 1.5O_2(g) + 2H_2O(g) = 2CrO_2(OH)_2(g)$

$CrO_3(g) + SrO = SrCrO_4$
$CrO_2(OH)_2(g) + SrO = SrCrO_4 + H_2O(g)$
$2CrO(OH)_2(g) + 2SrO + O_2(g) = 2SrCrO_4 + 2H_2O(g)$

$2CrO_3(g) + 4SrO = 2Sr_2CrO_4 + O_2(g)$
$2CrO_2(OH)_2(g) + 4SrO = 2Sr_2CrO_4 + O_2(g) + 2H_2O(g)$
$CrO(OH)_2(g) + 2SrO = Sr_2CrO_4 + H_2O(g)$

$2CrO_3(g) + 3SrO = Sr_3Cr_2O_4 + 2.5O_2(g)$
$2CrO_2(OH)_2(g) + 3SrO = Sr_3Cr_2O_4 + 2.5O_2(g) + 2H_2O(g)$
$2CrO(OH)_2(g) + 3SrO = Sr_3Cr_2O_4 + 2H_2O(g) + 1.5O_2(g)$

$4CrO_3(g) + 6SrO = 2Sr_3Cr_2O_8 + O_2(g)$
$4CrO_2(OH)_2(g) + 6SrO = 2Sr_3Cr_2O_8 + O_2(g) + 4H_2O(g)$
$4CrO(OH)_2(g) + 6SrO + O_2(g) = 2Sr_3Cr_2O_8 + 4H_2O(g)$

$CrO_3(g) + CaO = CaCrO_4$
$CrO_2(OH)_2(g) + CaO = CaCrO_4 + H_2O(g)$
$2CrO(OH)_2(g) + 2CaO + O_2(g) = 2CaCrO_4 + 2H_2O(g)$

$CrO_3(g) + BaO = BaCrO_4$
$CrO_2(OH)_2(g) + BaO = BaCrO_4 + H_2O(g)$
$2CrO(OH)_2(g) + 2BaO + O_2(g) = 2BaCrO_4 + 2H_2O(g)$

$CrO_3(g) + MgO = MgCrO_4$
$CrO_2(OH)_2(g) + MgO = MgCrO_4 + H_2O(g)$
$2CrO(OH)_2(g) + 2MgO + O_2(g) = 2MgCrO_4 + 2H_2O(g)$

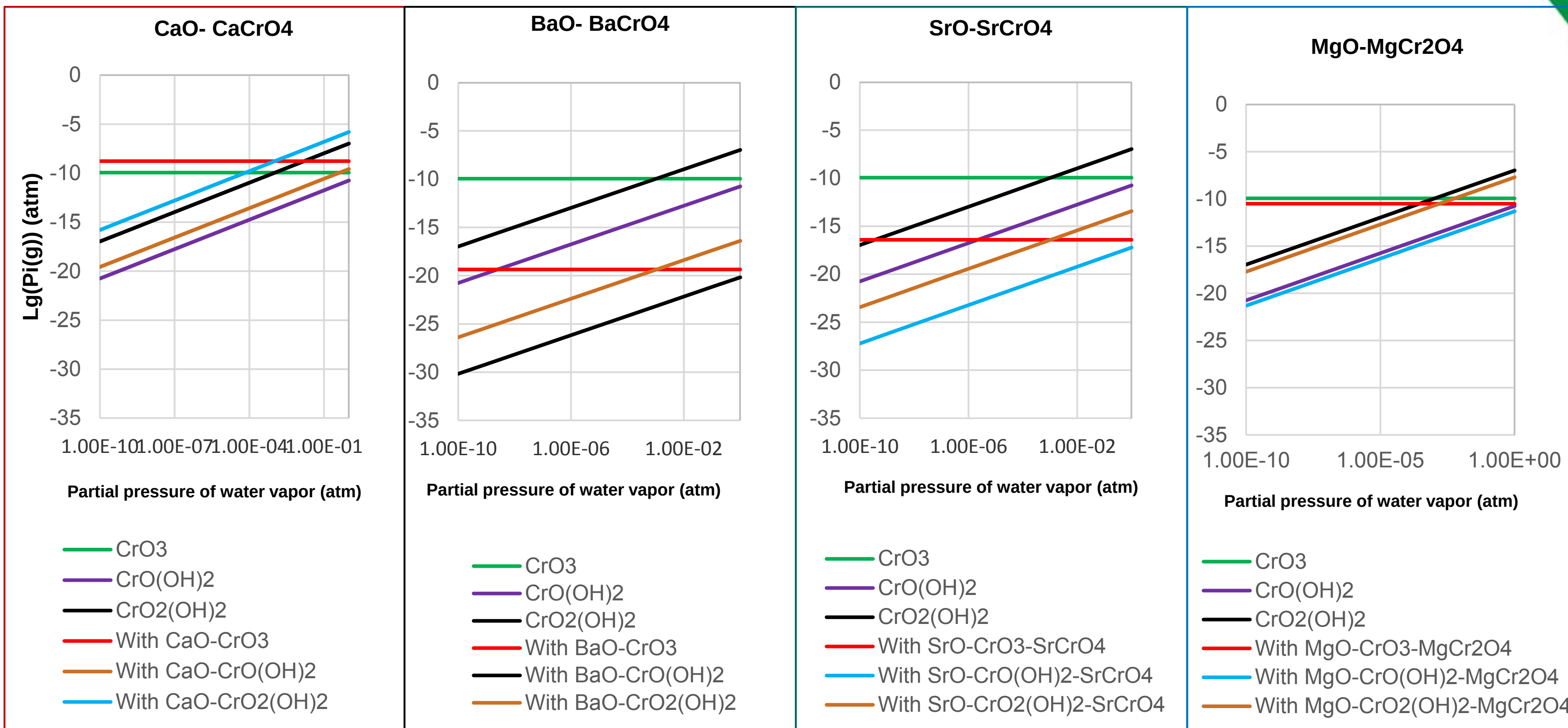
$2CrO_3(g) + MgO = MgCr_2O_4 + 1.5O_2(g)$
$4CrO(OH)_2(g) + 2MgO = 2MgCr_2O_4 + 4H_2O(g) + O_2(g)$
$2CrO_2(OH)_2(g) + MgO = MgCr_2O_4 + 1.5O_2(g) + 2H_2O(g)$

$2CrO_3(g) + MgO = MgCr_2O_3 + 2O_2(g)$
$2CrO(OH)_2(g) + MgO = MgCr_2O_3 + 2H_2O(g) + O_2(g)$
$2CrO_2(OH)_2(g) + MgO = MgCr_2O_3 + 2O_2(g) + 2H_2O(g)$

HSC Database is used to calculate the phase co-stability and eqlbm. CrOx {CrO3, CrO(OH)2 and CrO2(OH)2}pressure using pure solid phases formation.

Interactions with CaO, BaO, SrO & MgO

Thermochemistry: Co-stability of reaction products



$$P_{BaO/CrOx,(OH)x} < P_{SrO/CrOx,(OH)x} < P_{MgO/CrOx,(OH)x} < P_{CaO/CrOx,(OH)x}$$

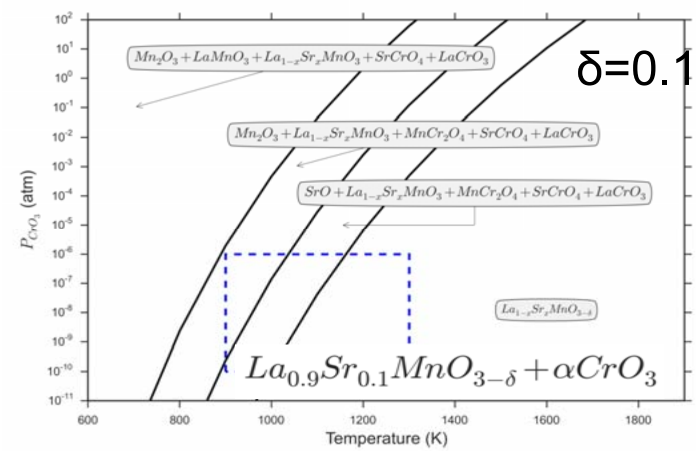
Thermochemistry – Eqlbm. Cr Pressure

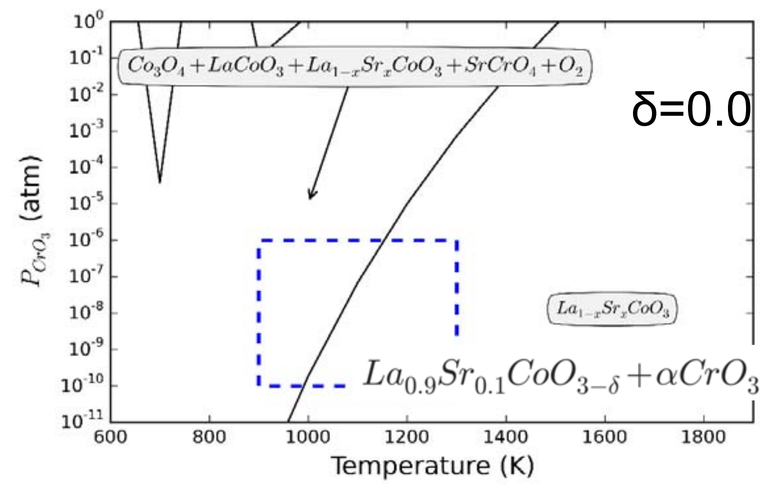
Gr II		Chromium vapor pressure			water vapor pressure
Oxides reactants	Products	Log P(CrO3)	Log P(CrO(OH)2))	Log P(CrO2(OH)2)	P(H2O)
MgO	MgCrO4	-7.35E+00	-9.670788145	-5.89049607	0.03
	MgCr2O4	-10.52454137	-12.84742013	-9.237091479	
	MgCr2O3	-13.58297699	-15.90585574	-12.12556367	
BaO	BaCrO4	-19.3711882	-21.69406695	-17.91377487	
CaO	CaCrO4	-8.776154142	-11.09903289	-7.31874082	
SrO	SrCrO4	-1.64E+01	-17.21788015	-13.43758807	
	Sr2CrO4	-15.29011061	-17.61298936	-13.83269728	
	Sr3Cr2O4	-23.10338349	-25.42626224	-21.64597017	
	Sr3Cr2O8	-16.39579929	-18.71867804	-14.93838597	
None	None	-9.954834771	-10.75483478	-6.974542703	

Conditions: 850C, Air-3% H2O, All solid phases are pure

Reaction Energetics of LSM & LSC with CrO_3

- **Thermodynamically favorable reaction pathways explored using first principles thermodynamics.**
- **Energetics of the reaction between (La, Sr)MnO_3 and (La, Sr)CoO_3 with the CrO_3 is studied.**
- **List of possible products included in the product pool:**
  - **Elemental metals, binary oxides & ternary oxides**
  - **Other products like $Mn_xCr_{3-x}O_4$, $SrCrO_4$, $LaCrO_3$, $CoCr_2O_4$**

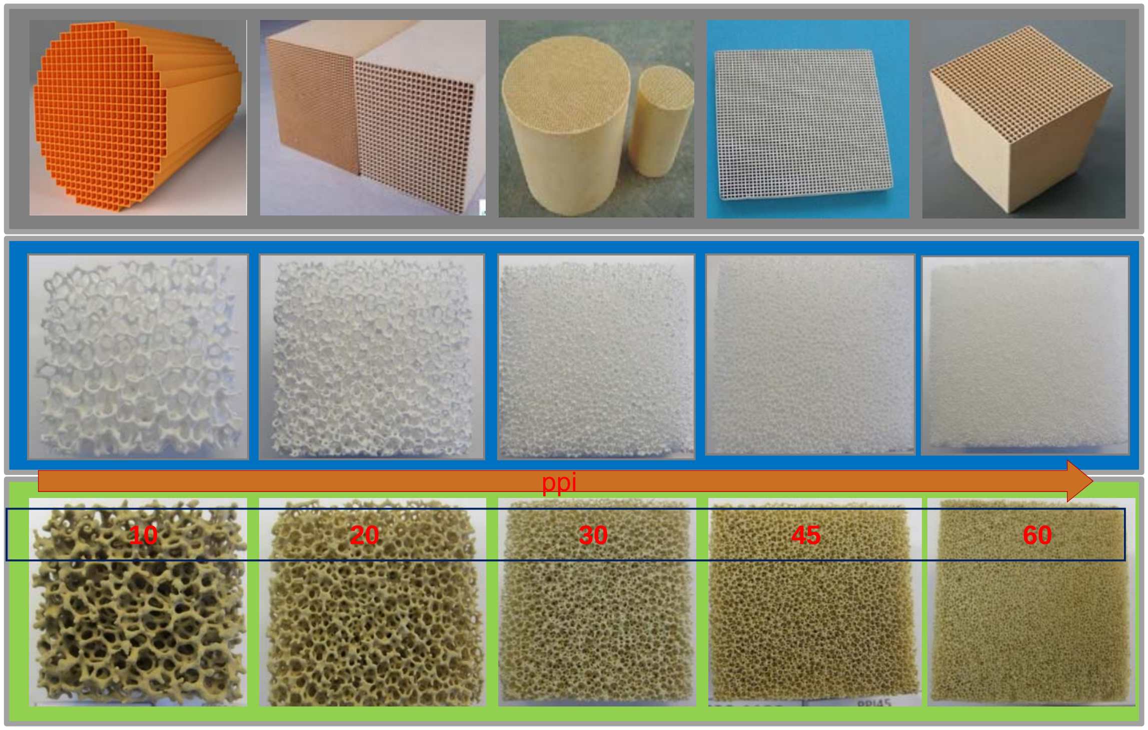




- No reaction in the experimental (P_{CrO3},T) range was observed for LSM without oxygen vacancy.
- For LSM with oxygen vacancy, the spinel compounds $MnCr_2O_4$ and $SrCrO_4$ coexist as favorable reaction products.
  - The mole fraction of $SrCrO_4$ is ~2 orders of magnitude less than that of $MnCr_2O_4$
- For LSCO without oxygen vacancy, $SrCrO_4$ is found as favorable reaction product, whereas the $CoCr_2O_4$ is not favored as products in line with experimental observations.

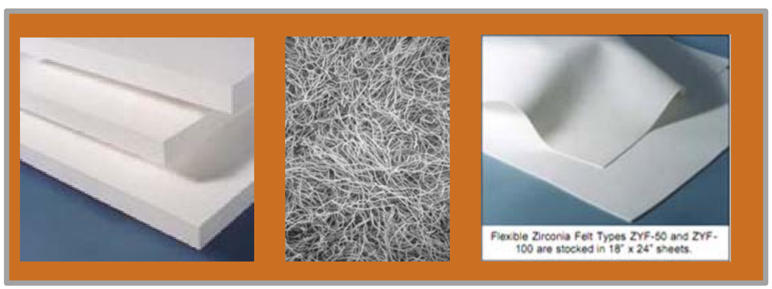
Results and Discussion

HSA Low dP Support



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

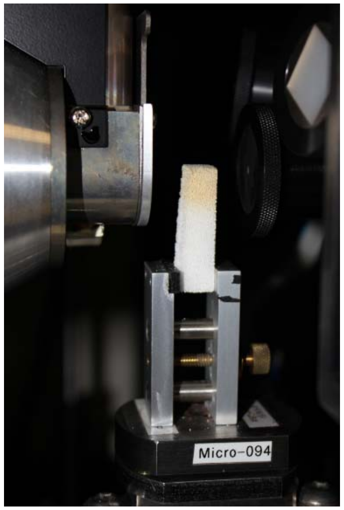
- Materials stability in SOFC atmosphere
- Materials interaction with applied coatings
- Design flexibility

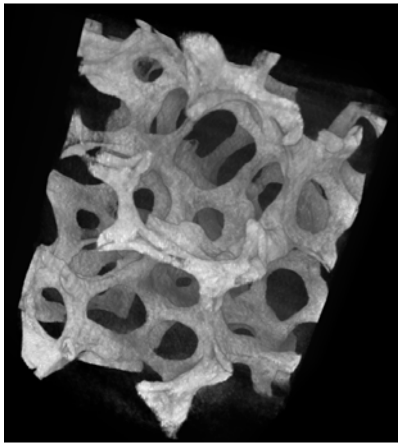


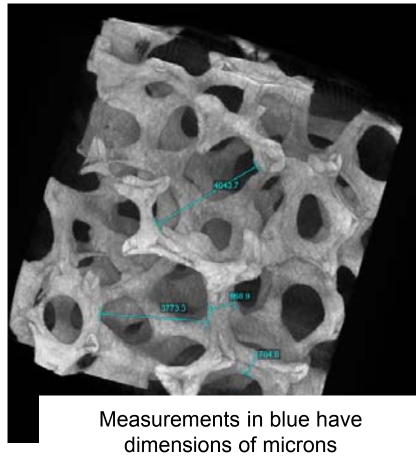
Flexible Fibrous Support in Al2O3, ZrO2, Mullite and other oxides

- HSA support
- High permeability
- Favorable contact and mixing

3D Representation







Measurements in blue have dimensions of microns

Tomography's performed on porous alumina samples

- 4ppi and 60ppi samples

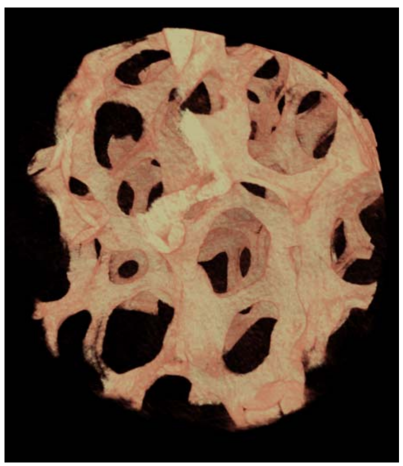
3D Visualizations able to resolve the alumina structure

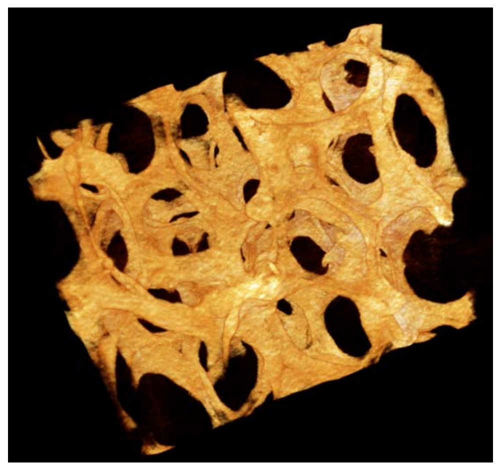
- Coarse alumina sample appears to have a rough surface texture
- Fine alumina sample may have same surface roughness, but further imaging at 10X did not provide contrast between air and alumina

After 3 imaging sessions where sample was exposed to 60kV X-ray beam, fine alumina sample began to discolor (appear to have a yellowish tint) where exposed to X-rays

3D imaging shows alumina structure thickness to be on the order of $700 - 850\mu m$ with pore sizes around 4.0mm

Surface of alumina matrix appears to have roughness





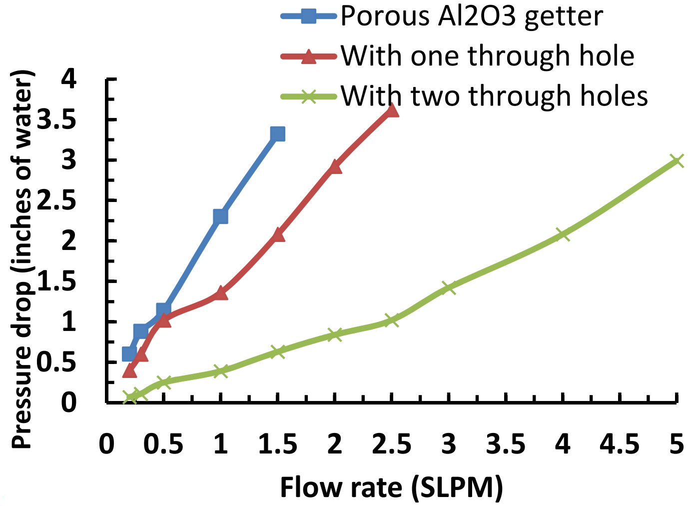
Additional coloring is available in Xradia's 3D Viewer software

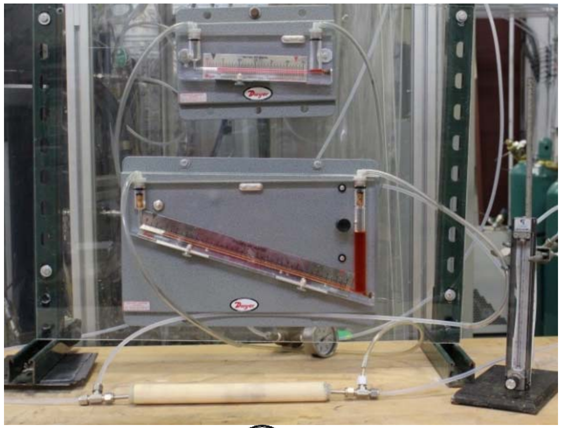
Color provides no additional information & is purely aesthetic

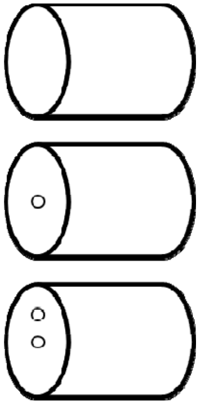
Porous Al_2O_3 Getter

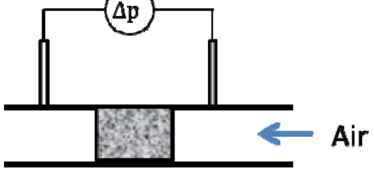
- Getter properties:
- Material: Al_2O_3
- Porosity: 85%
- Dimension: diameter-21 mm, length-37 mm
- Through hole diameter: 1 mm

Getter



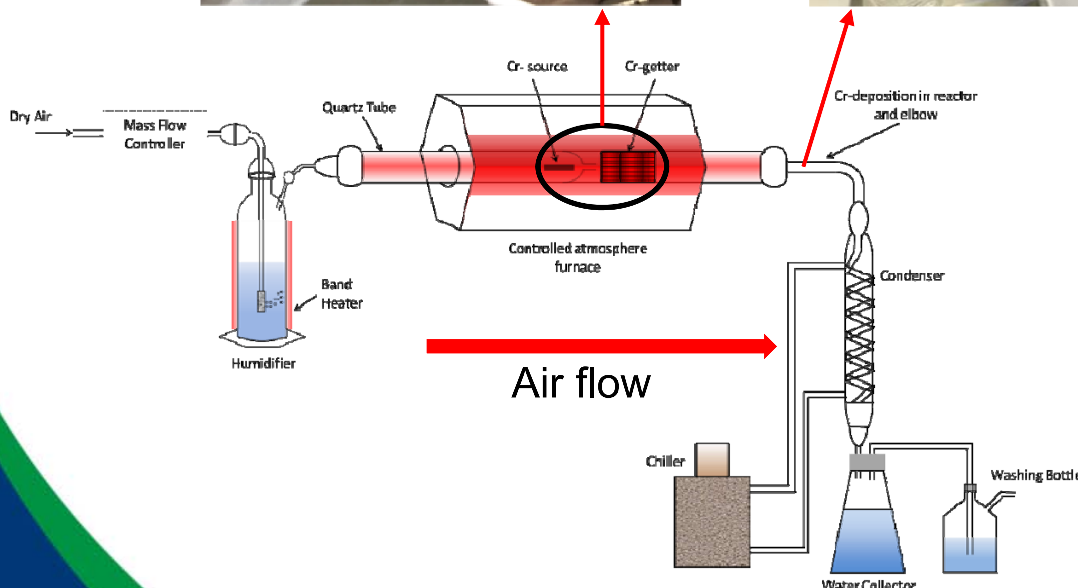






Pressure drop measurement setup

Experimental Setup



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

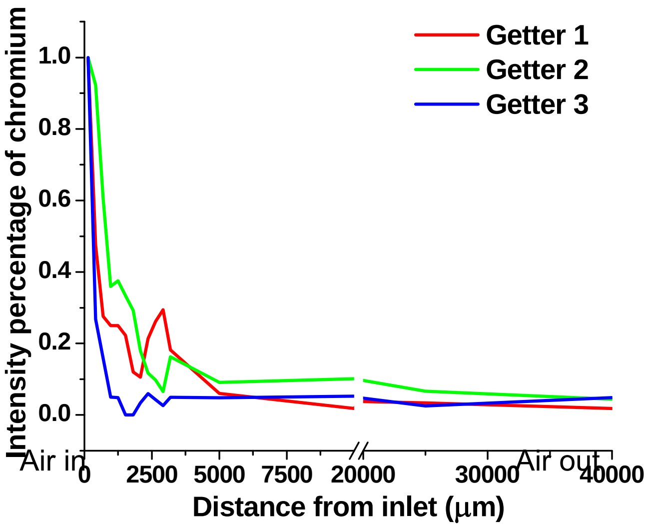
Elbow pictures at outlet

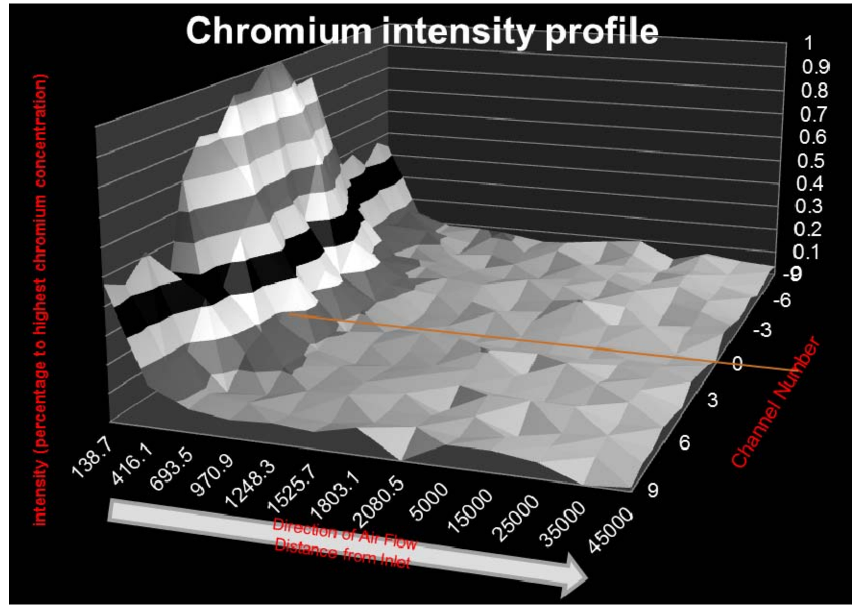
Reactor elbow discoloration due to Cr-vapors

Without getter

With getter

Cr Intensity Profile of getter 1, 2 and 3



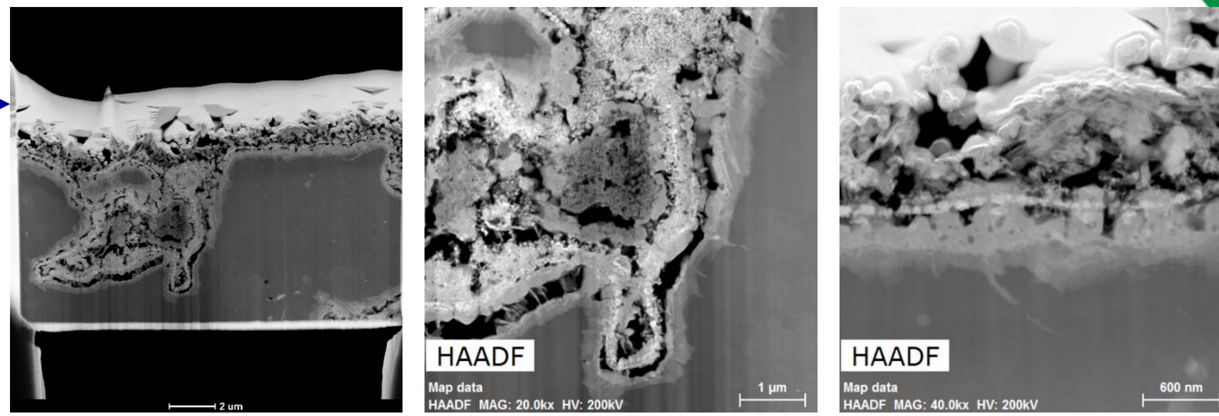


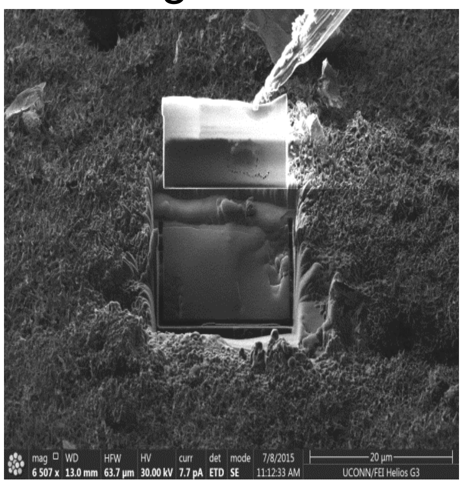
Higher Cr intensity (analysis performed using EDS technique) is observed near the air inlet (~ 1200 micron). Flat Cr profile is observed over the entire length after ~1500 micron indicating little/no Cr.

Getter	Treatment of cordierite substrate	Chemistry	Coatings		Chromium evaporation test		Substrate
			1st layer	2nd layer	Temperature	Time	
1	None	Solution: aqueous solution of 0.6 M of $Sr(NO_3)_2$ and 0.4 M of $Ni(NO_3)_2 \cdot 6H_2O$	Heat treatment at 950C for 2 h	None	850 C	500 hrs	Cordierite
2	None		Heat treatment at 1000C for 2 h	Heat treatment at 850C for 10 h			
3	Boil in 20wt% of nitric acid for 3 hours; sonic cleaning in 0.1 M of hydrochloric acid and DI water		Heat treatment at 950C for 2 h	Heat treatment at 850C for 10 h			

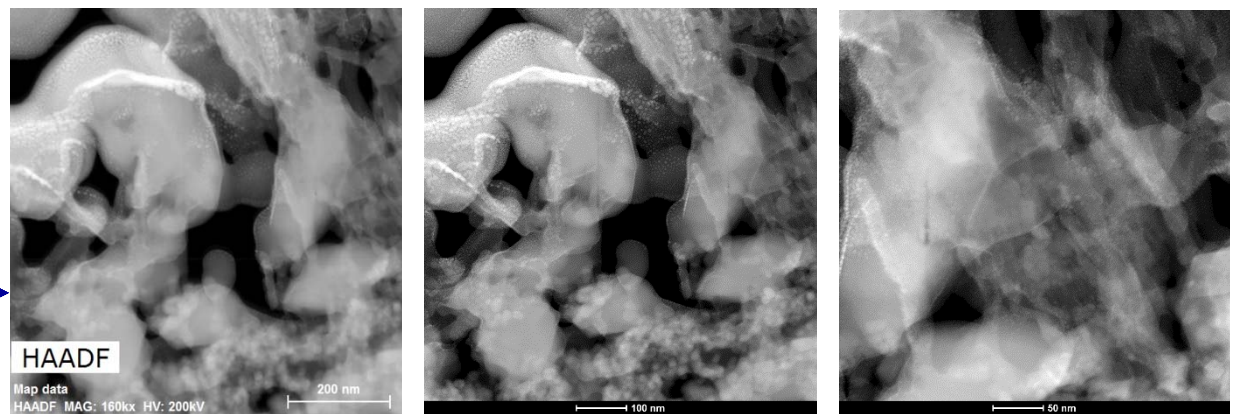
FIB X-Sectional Evaluation

Lower magnification



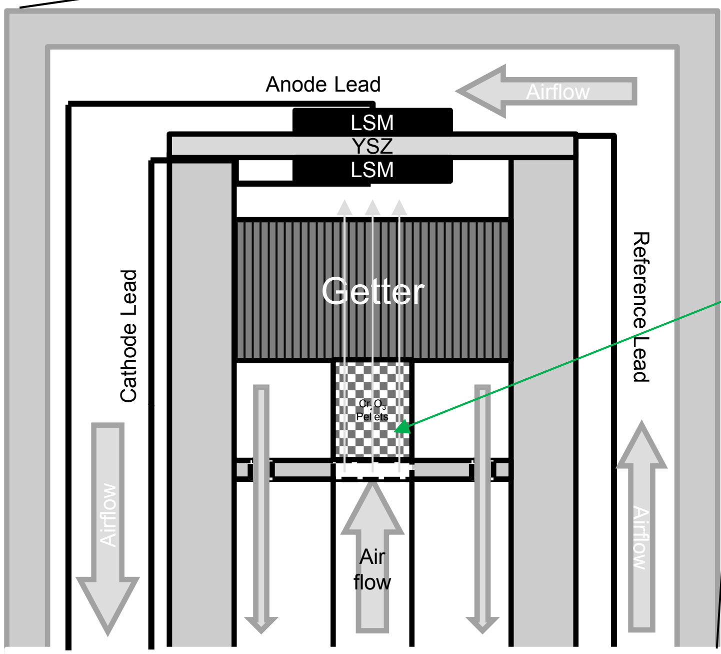


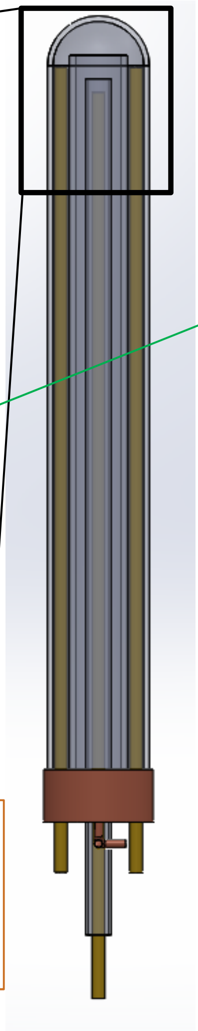
Higher magnification

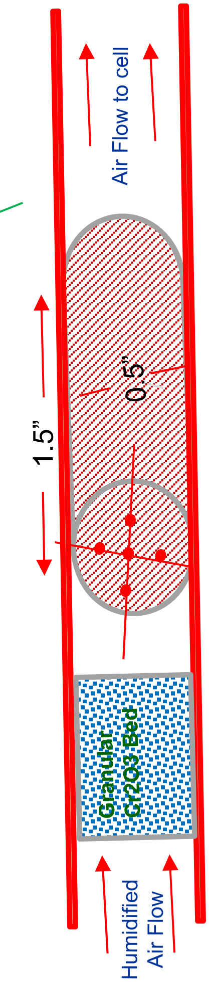


In-Operando Electrochemical Characterization

Test assembly : Half cell configuration







Temperature: 850° C
Cathode atmosphere: 3% H_2O/air (balance), flow rate: 50 - 500 sccm
Anode atmosphere: dry air, flow rate: 150 sccm
Cathodic Bias vs reference: 0.5 V
Getter: cordierite /alumina fiber supported SrNiOx

Overall Cell Performance Comparisons

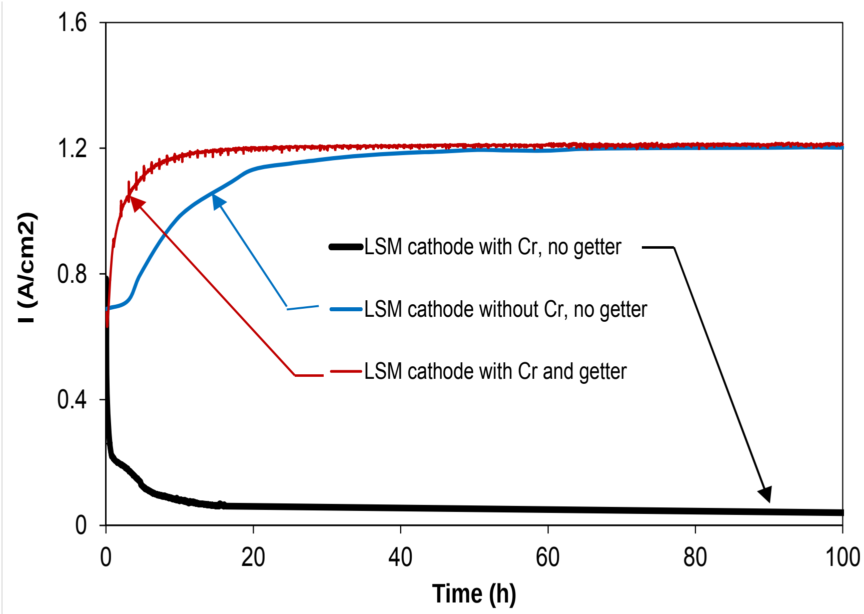
LSM Cathodes with a Getter and without a Getter under Exposure of Cr Vapor

Operating Conditions

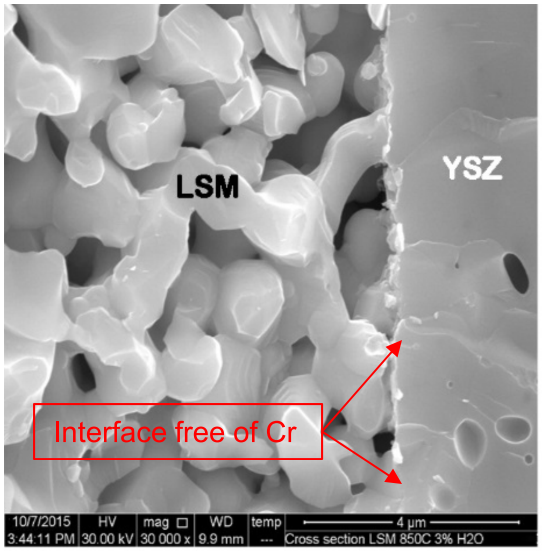
	Blank test (no Cr, no getter	Control test (with Cr, no getter)	Getter test (with Cr and getter)
Temperature	850C	850C	850C
Cathode Atmosphere	3% H2O/air	3% H2O/air, Cr vapor	3% H2O/air, Cr vapor
Anode Atmosphere	Dry air	Dry air	Dry air
Cathodic Bias	0.5 V	0.5 V	0.5 V
Getter	No	no	yes
Test time with EIS*	1-100 h	1-100 h	1-100 h

Air Flow Rate (SCCM) : 50, 100, 200, 500 and 1000

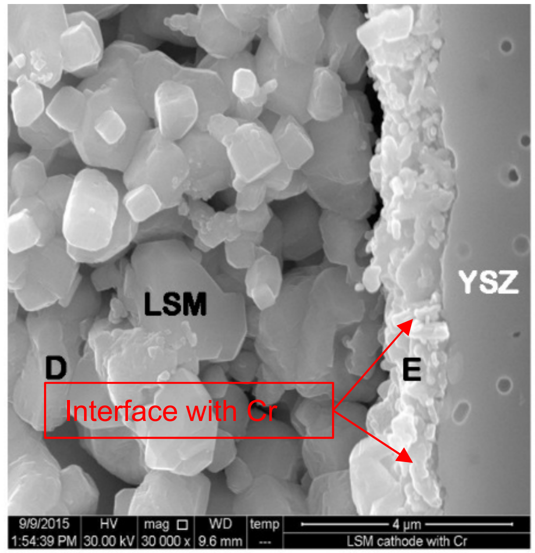
Tests completed/ In progress



Half cell tests – Base line; With Cr source; With Cr source & getter



Base line (A)

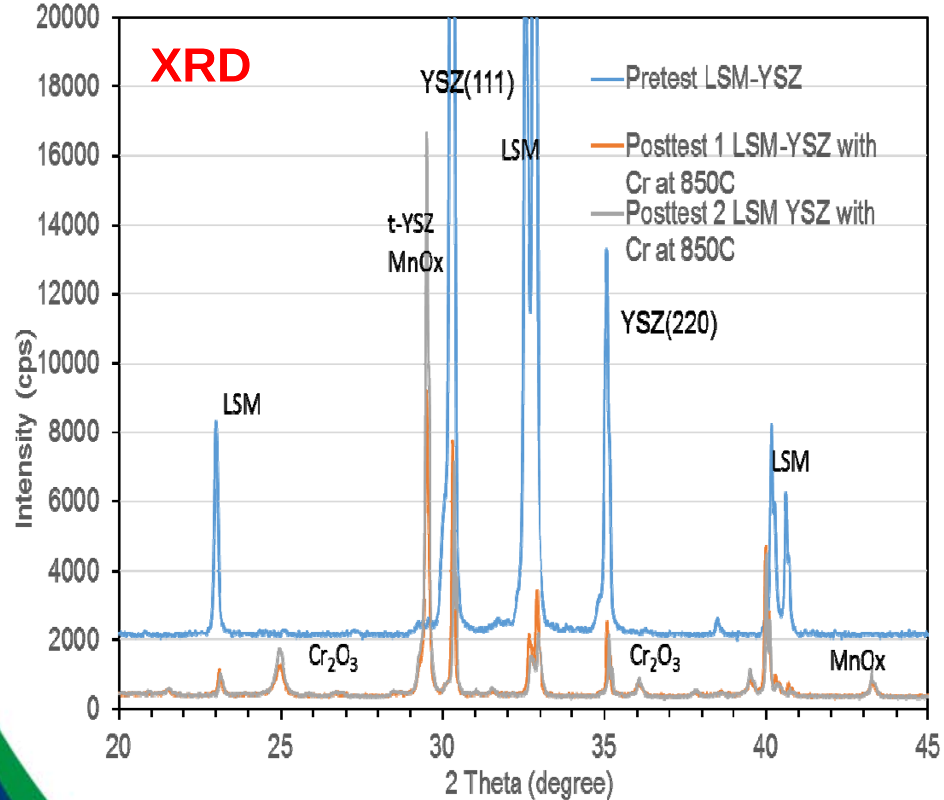


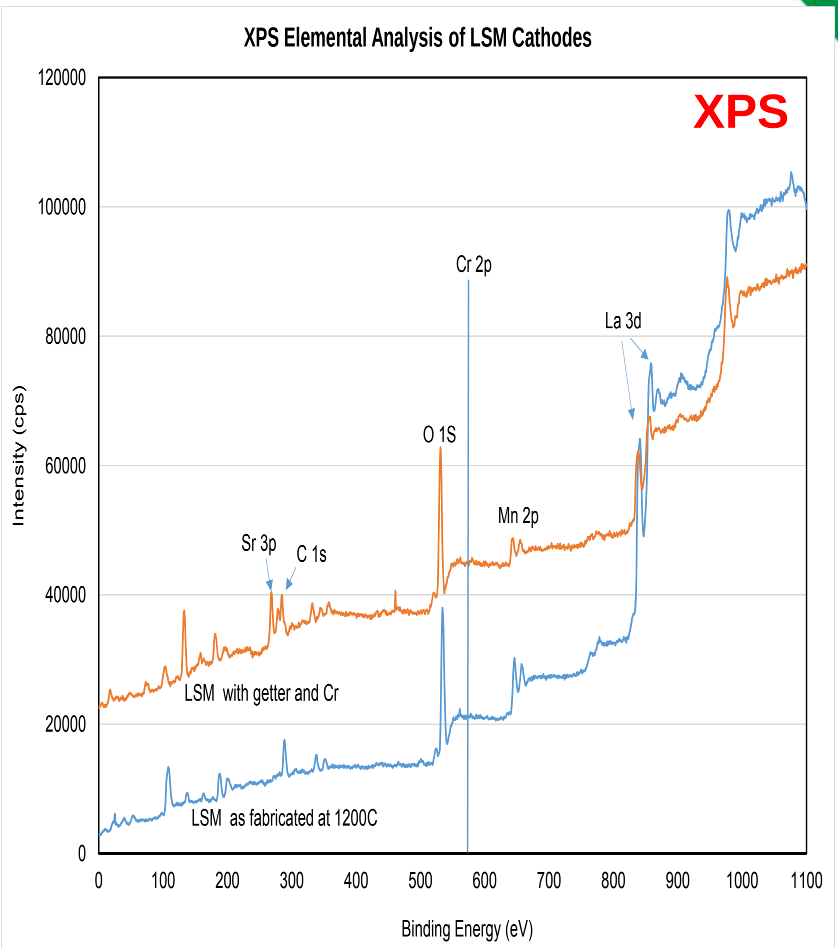
With Cr Source (B)

With Cr Source & getter (C)

Morphologies comparisons of the LSM cathode with no Cr, no getter (A), with Cr, no getter (B), and with Cr, with getter (C).

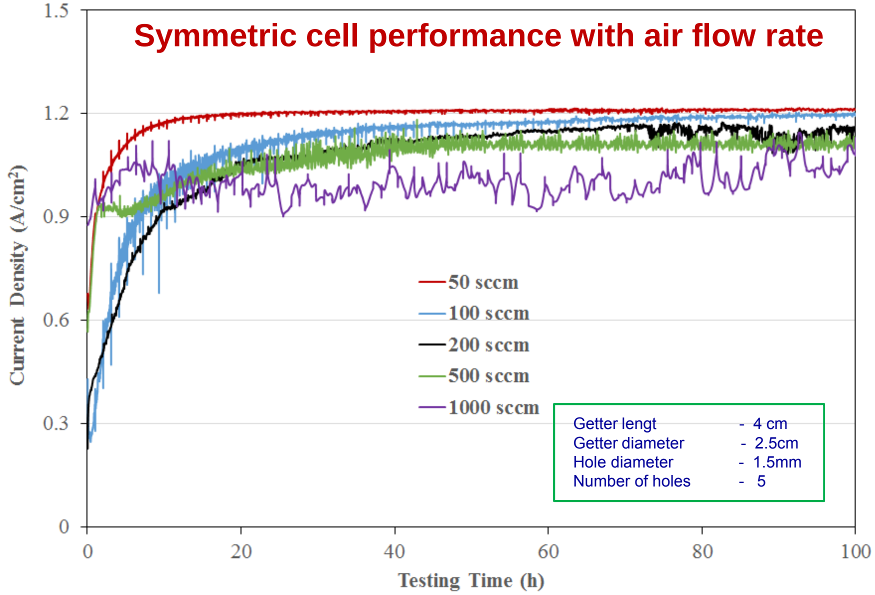
XRD and XPS Analysis: Presence of Cr_2O_3 in tested cell

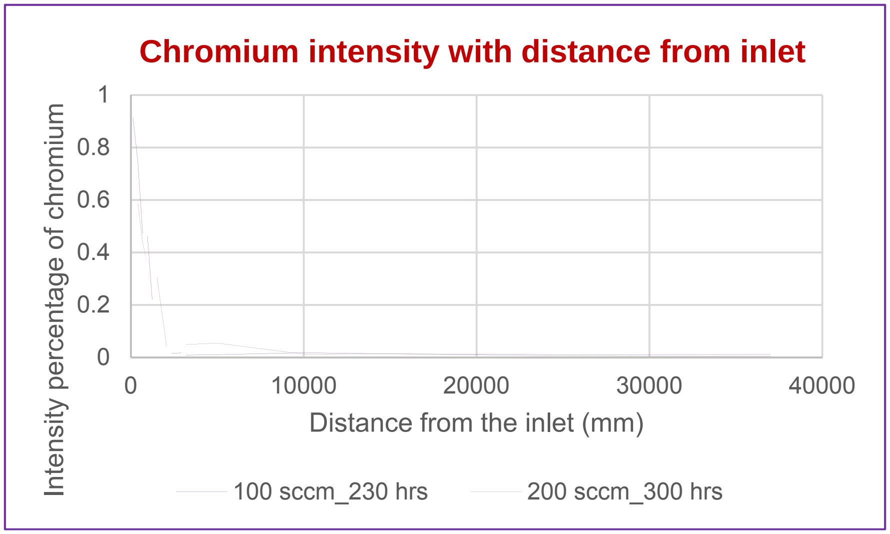




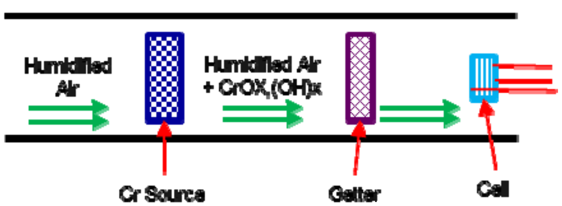
Overall Cell Performance Comparison

Humidified air flow rates varying from 50-500sccm showed little / no effect on the symmetric cell performance degradation indicating the effectiveness of getter at higher flow rates.





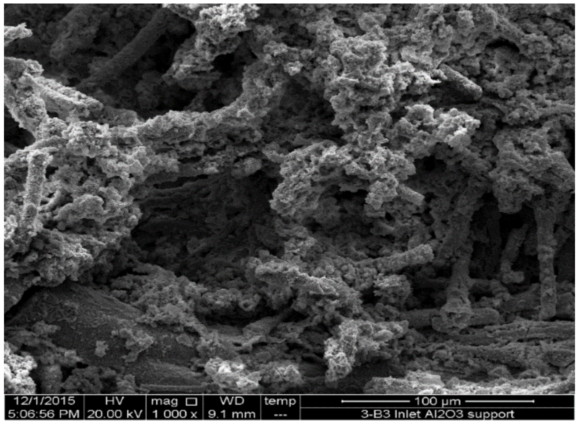
EDAX measurement by using probe area of 277μm*277μm



Half Cell with Cr and Getter

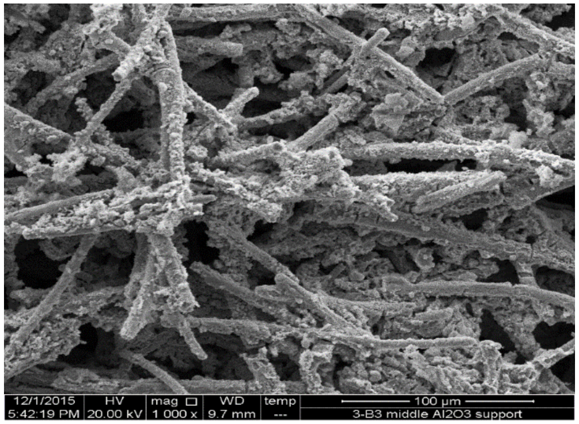
Posttest Getter Morphology

Getter inlet



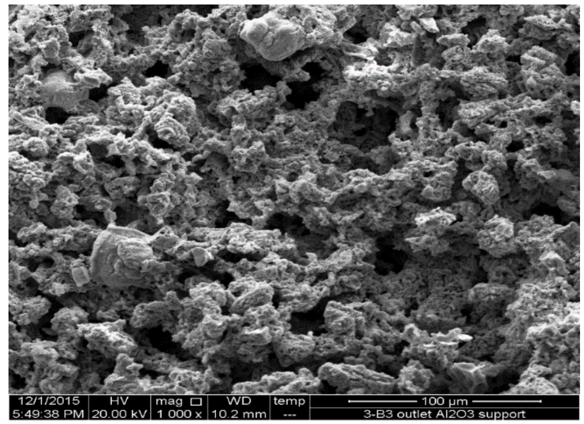
Cr atom%: 1.07%

Getter middle



Cr atom%: 0.1%

Getter outlet



Cr atom%: 0%

Decrease of Cr concentration →

Cr species were captured mostly at the inlet of the SrNiOx coated getter

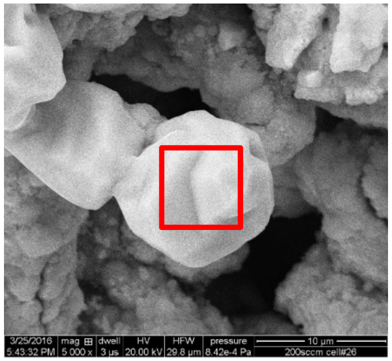
Getter Morphology

200 sccm

inlet

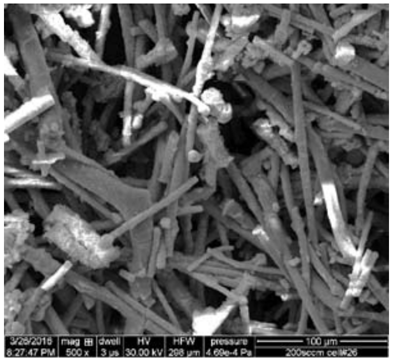
Element	Wt %	At %	K-Ratio
AlK	11.68	26.28	0.0403
SrL	56.14	38.90	0.3096
CrK	11.51	13.44	0.1016
NiK	20.67	21.38	0.2008
Total	100.00	100.00	

Cr dominating particles at inlet



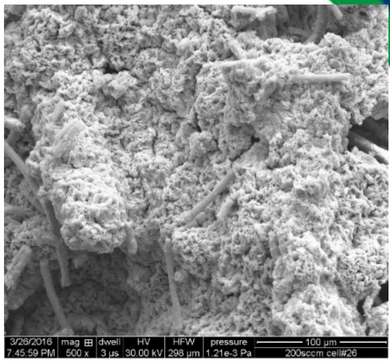
Element	Wt %	At %	K-Ratio
AlK	1.35	3.54	0.0078
SrL	67.43	54.53	0.5481
CrK	27.27	37.16	0.2652
NiK	3.96	4.77	0.0405
Total	100.00	100.00	

3mm



Element	Wt %	At %	K-Ratio
AlK	16.18	33.62	0.0463
SrL	43.68	27.94	0.1952
CrK	0.89	0.96	0.0081
NiK	39.25	37.47	0.3889
Total	100.00	100.00	

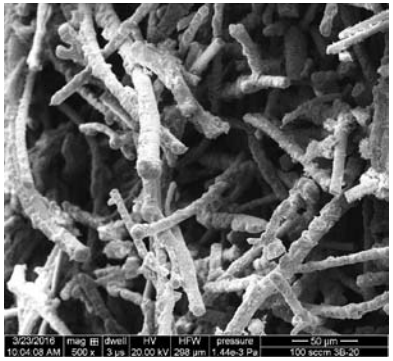
Outlet ~ 35mm



Element	Wt %	At %	K-Ratio
AlK	6.51	13.74	0.0121
SrL	13.77	8.95	0.0481
CrK	0.07	0.08	0.0007
NiK	79.65	77.24	0.7942
Total	100.00	100.00	

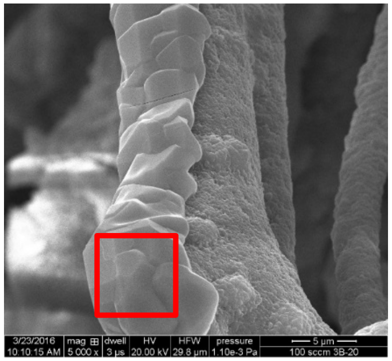
100 sccm

inlet



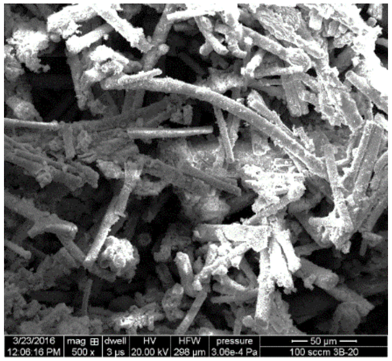
Element	Wt %	At %	K-Ratio
AlK	14.29	30.48	0.0504
SrL	51.45	33.80	0.2757
CrK	16.82	18.62	0.1493
NiK	17.44	17.10	0.1671
Total	100.00	100.00	

Cr dominating particles at inlet



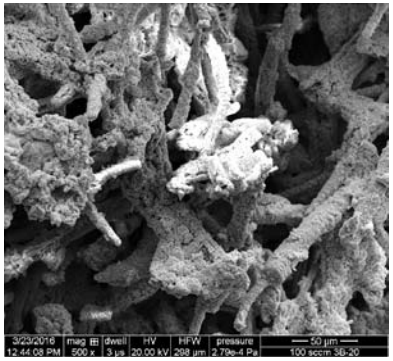
Element	Wt %	At %	K-Ratio
AlK	0.00	0.00	0.0000
SrL	66.69	54.36	0.5567
CrK	32.61	44.79	0.3186
NiK	0.70	0.85	0.0071
Total	100.00	100.00	

3mm



Element	Wt %	At %	K-Ratio
AlK	19.74	39.98	0.0982
SrL	48.04	29.96	0.2800
CrK	0.57	0.60	0.0055
NiK	31.65	29.46	0.3217
Total	100.00	100.00	

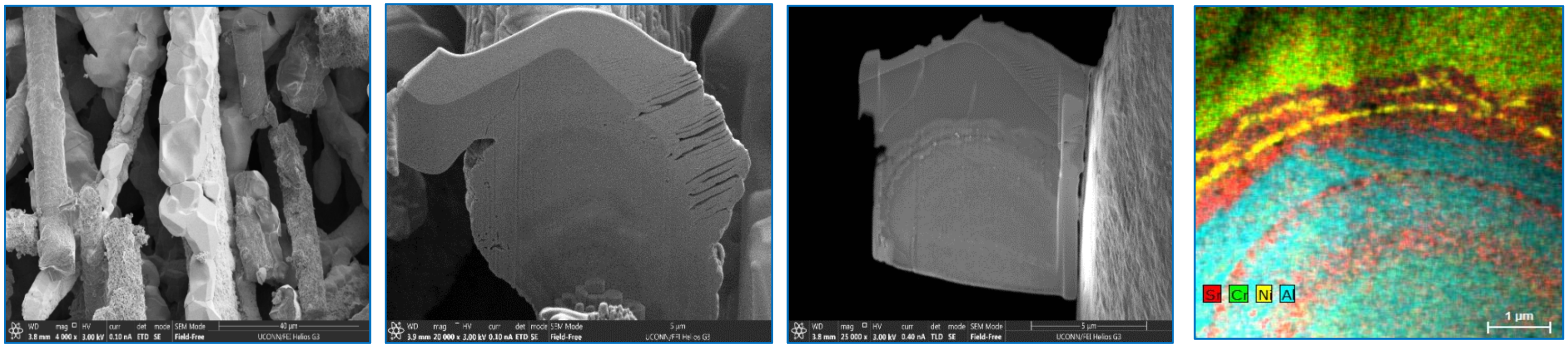
Outlet ~ 35mm

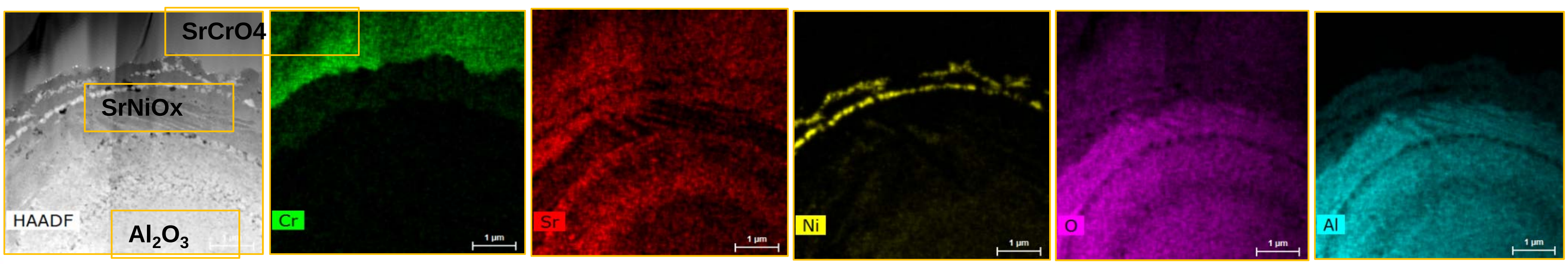


Element	Wt %	At %	K-Ratio
AlK	8.44	19.44	0.0363
SrL	47.11	33.42	0.2809
CrK	0.64	0.77	0.0064
NiK	43.81	46.37	0.4502
Total	100.00	100.00	

FIB-STEM Element Mapping of Posttest Getters

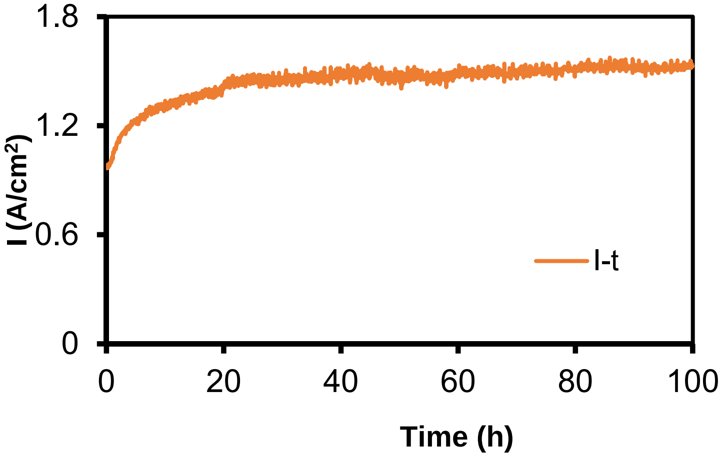
FIB X Section and elemental analysis



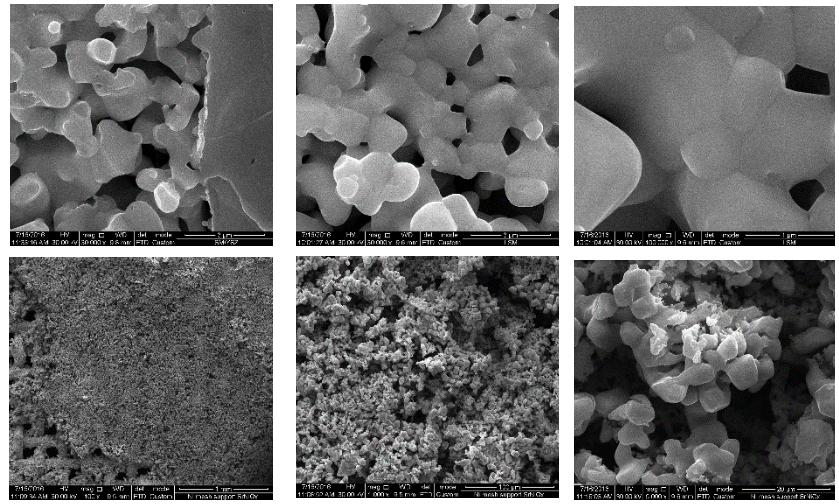


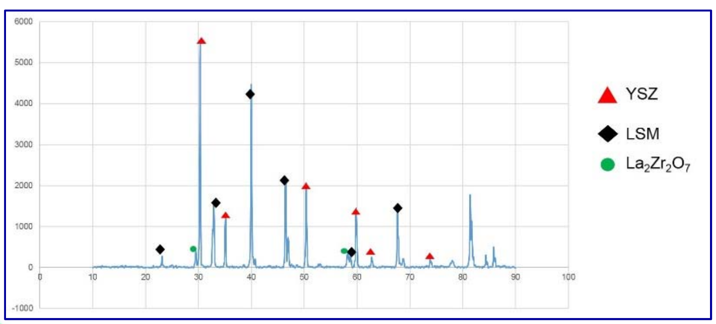
Interaction of strontium with chromium results in the formation of strontium chromate on the getter surface. Exolved NiO precipitates and serves as marker at the reaction interface.

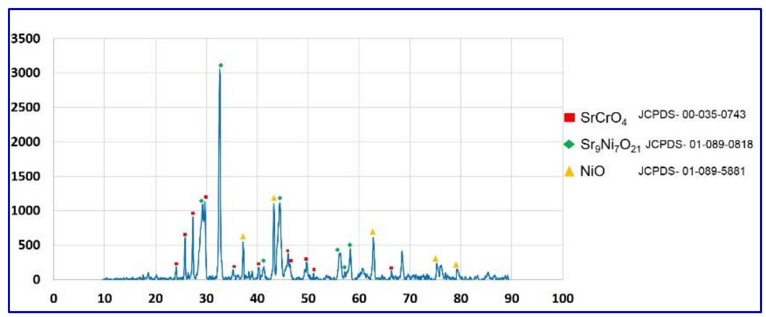
In- Cell Simulation



Air-3%H2O, 850C, LSM, 0.5 V bias







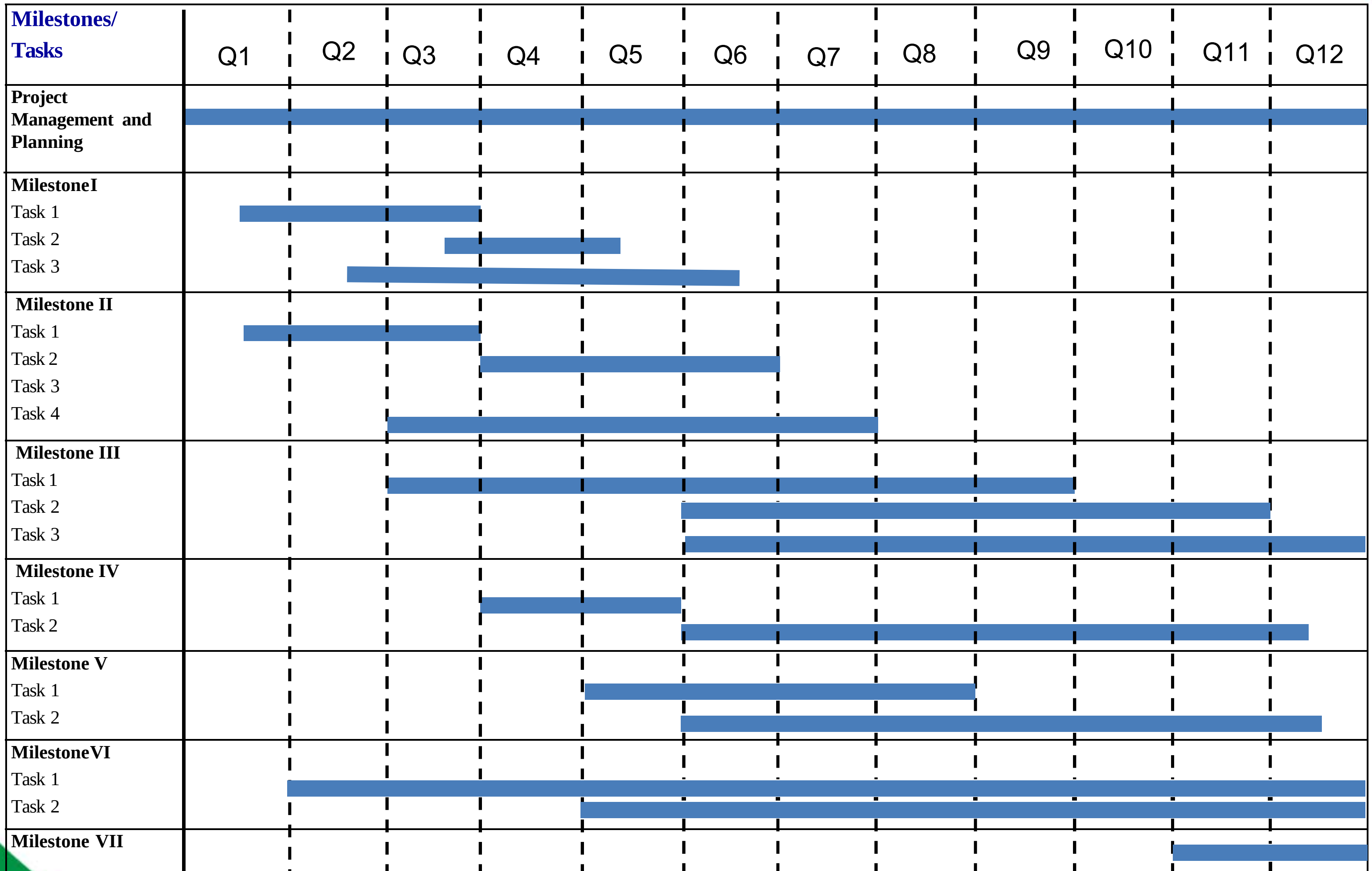
Further testing to simulate contact paste – In progress

Project Schedule/Milestones

Milestone Number and Task	Milestone Title	Planned Completion Date	Actual Completion Date
1	Development of Chromium Getter for BOP components by 'top-down' approach	Q6	Q6
2	Modification of cathode chemistry to tolerate moisture and chromium poisoning by 'top-down' approach	Q10	
3	Evaluation of the feasibility of the chromium getter and the modified cathodes	Q12	
4	Modification of cathode contact layer to reduce chromium poisoning	Q12	
5	Development of conductive coating to mitigate chromium evaporation from metallic interconnects	Q12	
6	Documentation, Reporting, and Publication	Q12	
7	Intellectual property and technology transfer	Q12	

- **Complete thermochemical assessment of Cr gettering (T, PH_2O, PO_2)** — **Q6**
- **Examine oxide systems and characterize surface reaction products** — **Q6-Q8**
- **Evaluate NiO, MnO and other additives and develop Cr capture profile** — **Q6-Q8**
  - **Transpiration experiments – f(PH_2O, T, t, Q)**
  - **Getter coating and utilization**
- **Design and conduct long term tests under systems operating conditions** — **Q8-Q12**
  - **Fiber / fiber-foam composites / blanket configuration**
- **Develop fabrication processes for large samples** — **Q8-Q12**
- **Qualify getters application in cell/stack for in the cell** — **Q8-Q10**
- **Work with industry in validating getters in the large systems** — **Q11-Q12**

Project Schedule/Milestones



Project Summary

Key technical accomplishments include:

- Laboratory experiments show that the getters successfully capture gas phase chromium and prevent cathode poisoning.
- Electrically tested cells with Cr show preferential deposition of Cr at the cathode –electrolyte interface. Presence of getter mitigated Cr deposition in the cathode.
- Getter materials and support configurations have been identified.
- Getter powder has been synthesized and characterized.

Lessons Learned:

- Alkaline earth and transition metal group oxides (solid solutions and compounds) show excellent tendency for the capture of Cr. Repeated experiments validate the observation.
- Ceramic honeycomb, foam and fibrous structures have been examined for getter support.
- Getter powder synthesis and getter fabrication and test techniques have been developed.

Outstanding issues:

- Getter design for optimum Cr capture / getter utilization
- Getter design to meet system requirements
- Long term test validation under simulated system conditions
- Support design and vendor

Plans for remaining key technical challenges:

- Initiate tests under SOFC system conditions
- Initiate scale up of getter fabrication
- Initiate in depth characterization of getter surface

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