Development of Chromium and Sulfur Getter for SOFC Systems

Prabhakar Singh

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

WORK PERFORMED UNDER AGREEMENT DE-FE-0027894

19th Annual SOFC Program Review Meeting
June 15, 2018

NATIONAL ENERGY TECHNOLOGY LABORATORY

UCONN UNIVERSITY OF CONNECTICUT

Technical Contributors

UConn

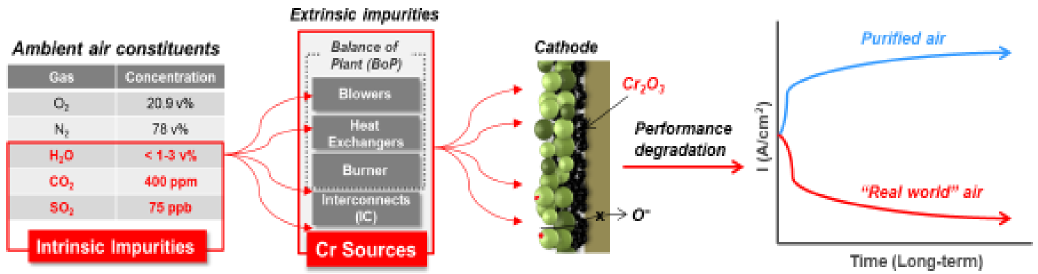
Prabhakar Singh	Professor
Boxun Hu	Assistant Research Professor
Steven L. Suib	Professor
Ashish Aphale	Post-doctoral Fellow
Su Jeong Heo	Graduate Student
Junsung Hong	Graduate Student
Michael Reisert	Graduate Student
Junkai He	Graduate Student
Yanliu Dang	Graduate Student
Seraphim Belko	Undergraduate Student

Program Manager: Dr. Rin Burke, National Energy Technology Laboratory

Innovation and Impact

- **We have developed hypothesis for the co-capture of both intrinsic (SO2) and extrinsic (CrOxHy) contaminants from ambient air has been validated.**
- **We have performed operando cell/getter tests confirmed performance stability with the use of co-getters.**
  - **Stable ohmic and non-ohmic polarization**
  - **Absence of contaminants in the cathode**
    - **Clean surface and interface**
- **We have synthesized getter materials and fabricated devices utilizing conventional ceramic processing techniques.**

- **Lessons learned from the Cr capture program capitalized for the selection, synthesis and testing of co-getters**
- **Lessons learned from the existing program provides a path forward for multi-impurity capture platform.**



Gas	Concentration
O_2	20.9 v%
N_2	78 v%
H_2O	< 1-3 v%
CO_2	400 ppm
SO_2	75 ppb

Impurity capture:
1. capture intrinsic impurities at the system inlet
2. Capture extrinsic impurities in BOP or in stack

- Chromium poisoning leading to the long term degradation in SOFC systems
- Permanent performance degradation
- High polarization losses
- Interfacial deposition limits the oxygen access at the triple phase boundary (TPB) sites

Program Objectives

The overall objective of the proposed research program is to develop cost effective co-getters for the combined capture of gaseous S and Cr species present in incoming air stream.

- **Validate co-capture process thermodynamically.**
- **Develop, synthesize and test validate co-getters under SOFC operating conditions.**
- **Develop underlying mechanisms.**
- **Explore design and integration opportunities for the getters in SOFC system.**

The developed approach will benefit high temperature electrochemical systems of interest to DOE in the field of power generation, gas separation and chemical conversion.

Outline

- Accomplishments
- Background
- Selection of Cr and S getter materials
- Experimental
    - Processes Development: High surface area (HSA) getter materials
    - Chromium Getter optimization: Computational Modeling
    - Evaluation of Co-getter performance
    - Characterization: SEM-EDX, XRD, EIS, FIB-TEM
- Results and Discussion
- Future Work
- Acknowledgements

Accomplishments-Technical

- Thermodynamic calculations based on Gibbs free energy change indicates co-capture of sulfur and chromium impurity in wide temperature range.
- SrMnO based getter has been synthesized and fabricated.
- Gas phase acidic airborne impurities react with basic air electrode constituents to form stable reaction products at the free surface and TPB.
- Getter has been validated electrochemically to demonstrate the successful capture of both Cr and S in gas phase at 850C.
- Posttest results from SEM indicates clean LSM/YSZ interface after 100 hrs of electrochemical test in presence of Cr and SO_2 vapor.
- SEM/EDS characterization of SMO getter reveals high concentration of S and Cr at the inlet of the getter and negligible concentrations at the center and the outlet of the getter, indicating complete capture.

- Graduate / Undergraduate students being trained - 3
- Post-doctoral fellows: 2
- Outreach: Middle and High School, Davinci Program, STEM
- Publications and presentations: Journal articles and technical society meetings

- ➢ Developed reaction mechanisms for the co-capture of Cr and S. Validated the getter operation by electrochemical and transpiration tests.
- ➢ Fabricated getters show excellent blockage of Cr and S species from entering into cathode electrode.

Ambient Air Constituents

Gas	Concentration
Oxygen	20.9 v%
Nitrogen	78 v%
Water	<1 to 3 v%
Carbon dioxide	350 ppm
Sulfur dioxide	<1 ppm
Noble gases	<1 v%
Particulate matter (PM)	<50 µg/m^3

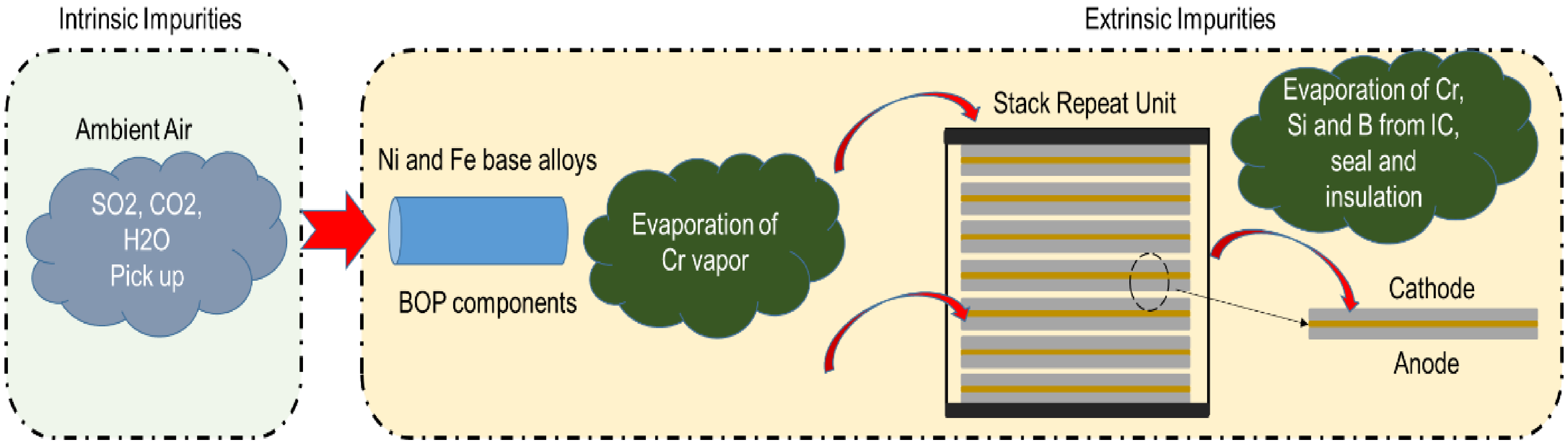
Air in fuel cell stack and system may also contain component derived impurities such as Cr (from metals and alloys) and Si, B, and alkali (from glass and insulation).

Presence of sulfur at the electrode/electrolyte interface leads to the formation of $SrSO_4$ and it can take place at the exposed surface or electrochemically active sites

$$SrO\,(s) + SO_2\,(g) + 0.5O_2\,(g) = SrSO_4\,(s)$$

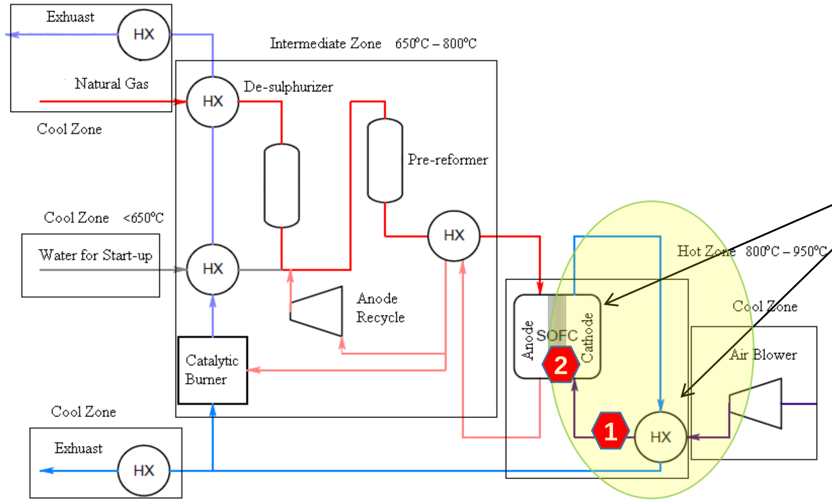
- Adsorption of SO_2 molecule takes place and it reacts with oxygen atom to form SO_4^{2-} ions in the lattice having high concentration of oxygen ion vacancy sites, leading to the rapid formation of $SrSO_4$ at the actives sites.
- The thermodynamic activity of SrO inside cathodes increases with decreasing oxygen potential near the interface and promotes the $SrSO_4$ formation leading to the reduction in the area of the active region thereby increasing the polarization resistance.
- The incorporation of SO_2 is difficult to eliminate due to strong chemical bond forces and this results in the overall irreversible performance degradation.

SOFC System : Intrinsic and Extrinsic Air Impurity Sources



Impurity capture:

1. capture intrinsic impurities at the system inlet
2. Capture extrinsic impurities in BOP or in stack



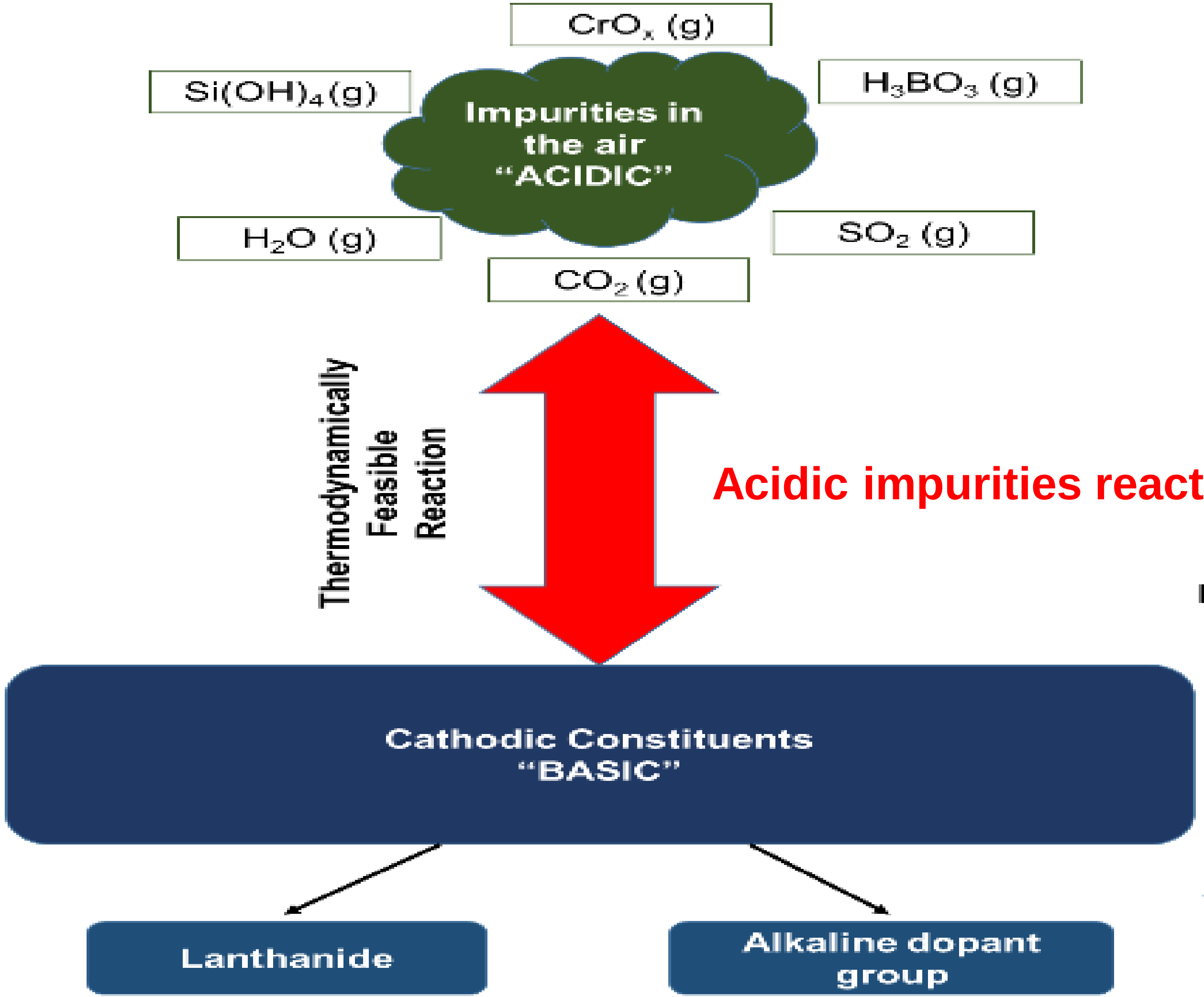
BOP components exposed to high temperature oxidizing atmosphere and prone to Cr evaporation & S interactions:

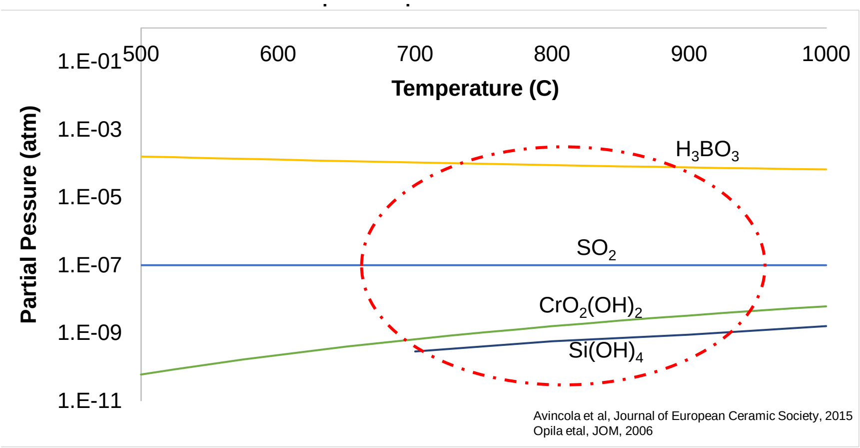
- Thermal Management system
- Air handling system
- Cathode manifold and ducting

Ambient air

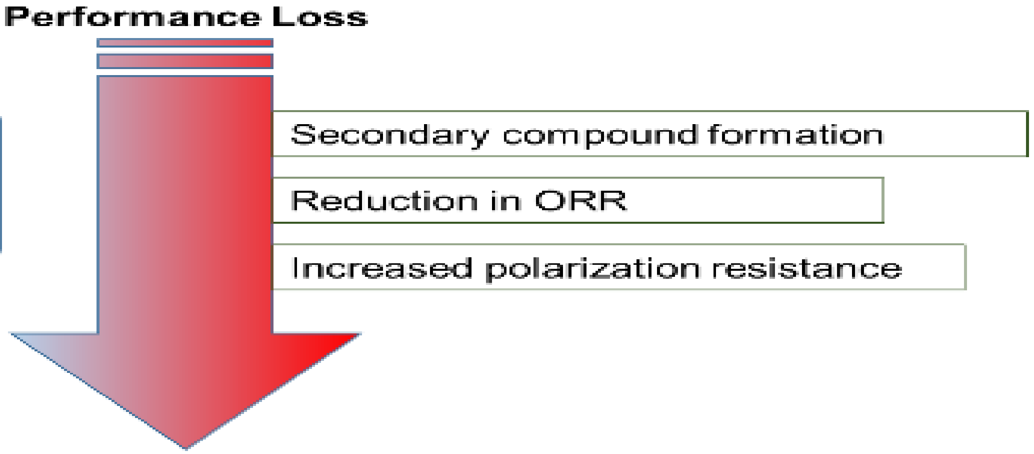
Gas	Concentration
Oxygen	20.9 v%
Nitrogen	78v%
Water	<1-3v%
CO2	350ppm
SO2	<1ppm
Noble gases	<1v%
PM's	<50 µ

Chemical Nature of Impurities

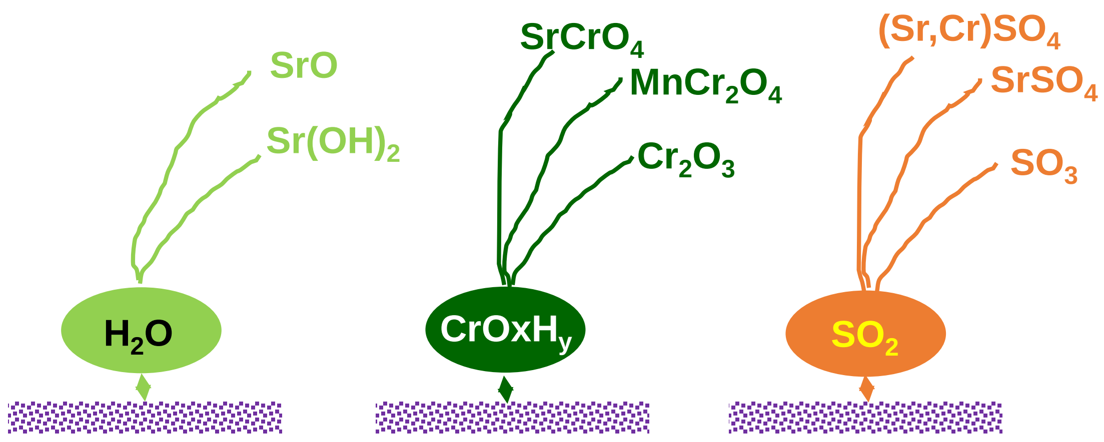


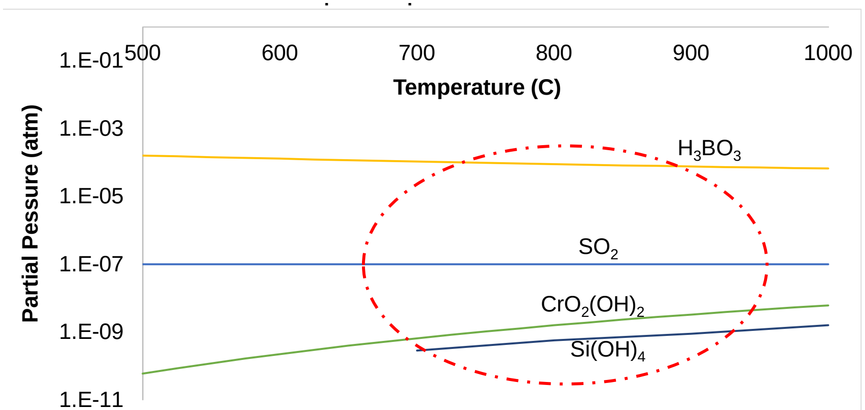


Acidic impurities react with basic cathode (Host and dopant)

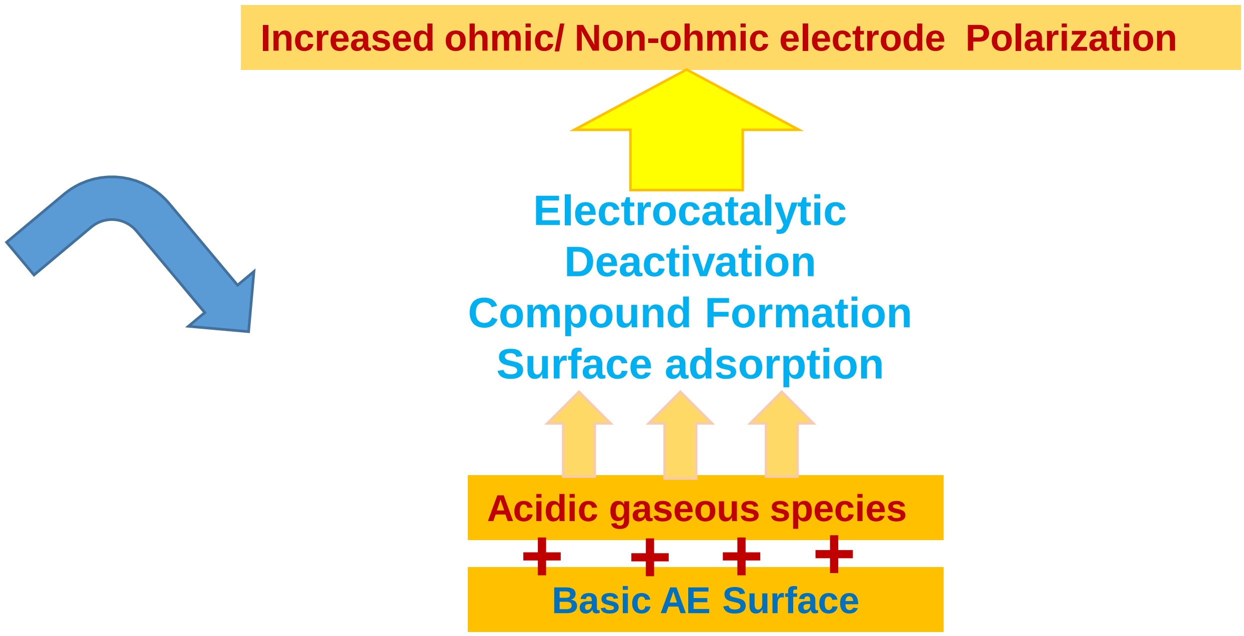


Airborne Gaseous Impurities interacting with SOFC Cathode

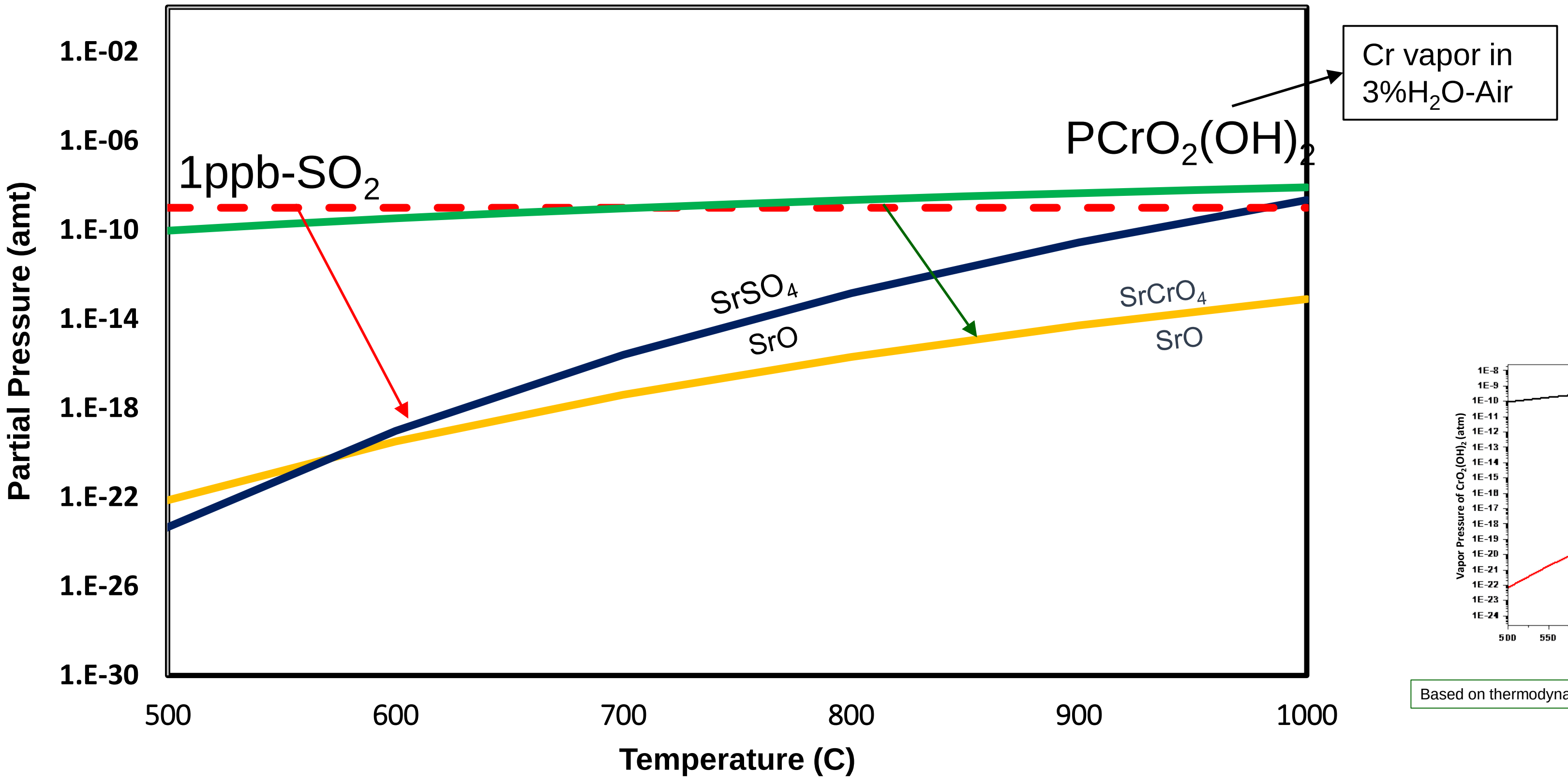


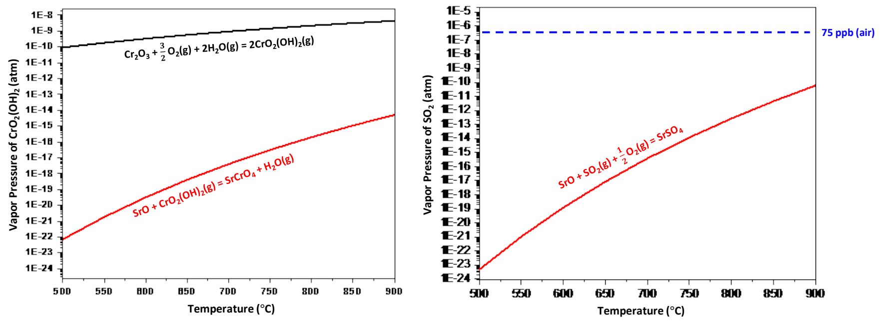


Avincola et al, Journal of European Ceramic Society, 2015
Opila etal, JOM, 2006



Gas Phase SO_2 and Cr Species: Reaction Products Stability

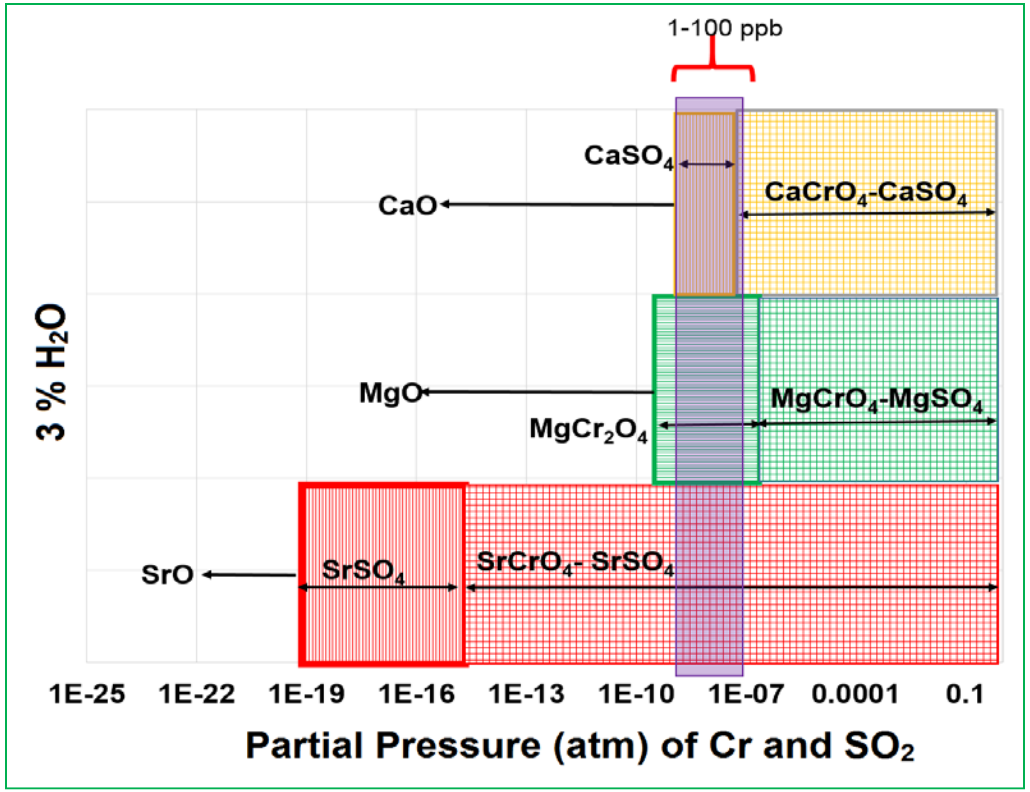




Based on thermodynamic calculations, it is assumed that SrO is capable of absorb Cr vapor (CrO2(OH)2(g)) and SO_2(g).

- Thermodynamic calculations show that SrO based getter is capable to capture both Cr (extrinsic) and SO_2 (intrinsic) impurities in gas phase in wide temperature range.
- Significant reduction in Cr and SO_2 vapor pressure is observed in presence of SrO.

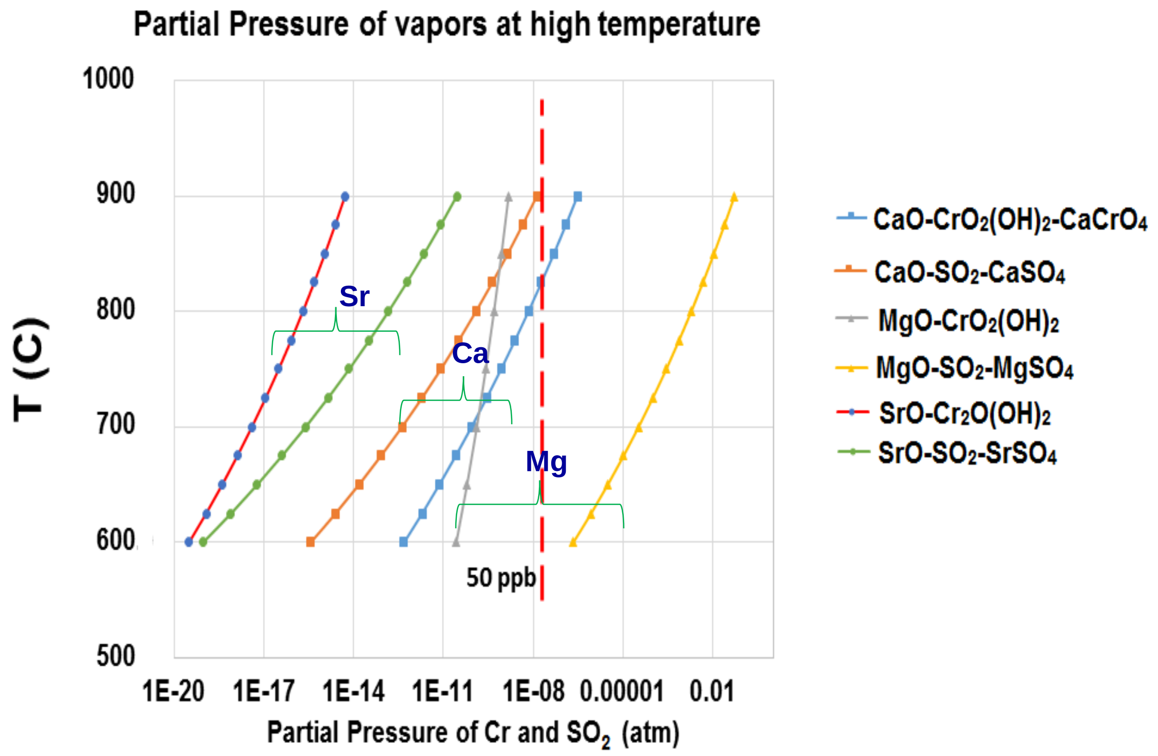
Co-Capture of Cr and SO_x on Metal Oxides



- Sr-Ni-O, Sr-Mn-O, Sr-Fe-O perovskite type compounds with relatively high electrical conductivity are the potential coating materials for getter application.
- CaO and MgO are considered.
- The oxidation of both Cr vapor and SO_2 occurs the most by SrO getter material over a wide temperature range.

Co-stability calculated based on Gibbs free energy and equilibrium constant

Thermodynamic Calculations: Vapors at High Temperatures



- SrO is better than CaO, and MgO as a getter material for Cr and S capture.
- SrO is capable of forming $SrCrO_4$ and $SrSO_4$ compounds at extremely low concentrations of Cr and SO_2 vapors, even below 1 ppb.

Fabrication of SMO Getter

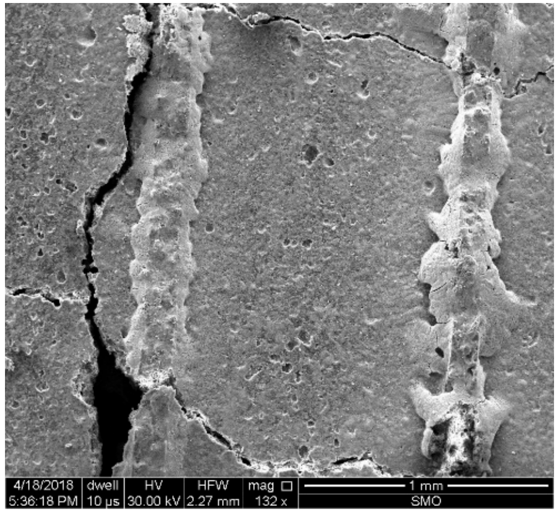
Fabrication process

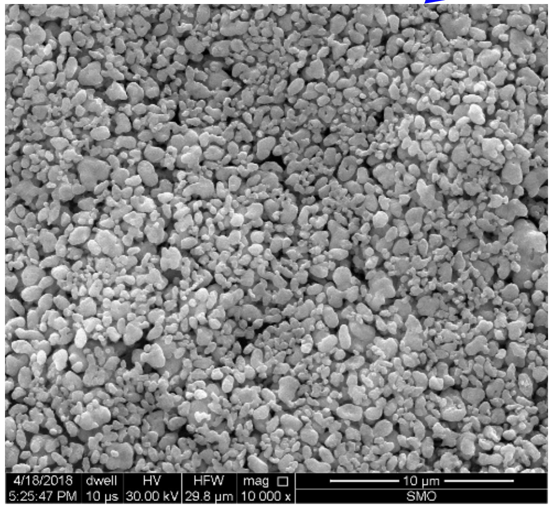
- Preparation of aqueous solution (strontium nitrate + manganese carbonate)
- Dip coating of cordierite substrate
- Vacuum infiltration
- Heat-treatment at 1200ºC for 3 hours in air
- Repetition of the process to have thick coating layer

Cordierite substrate coated with the suspension

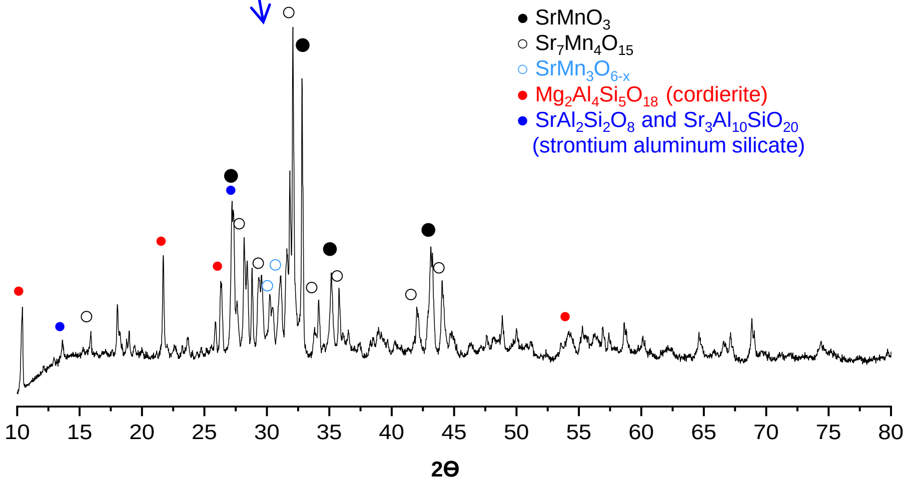
Heat-treated at 1200 C

SEM





XRD



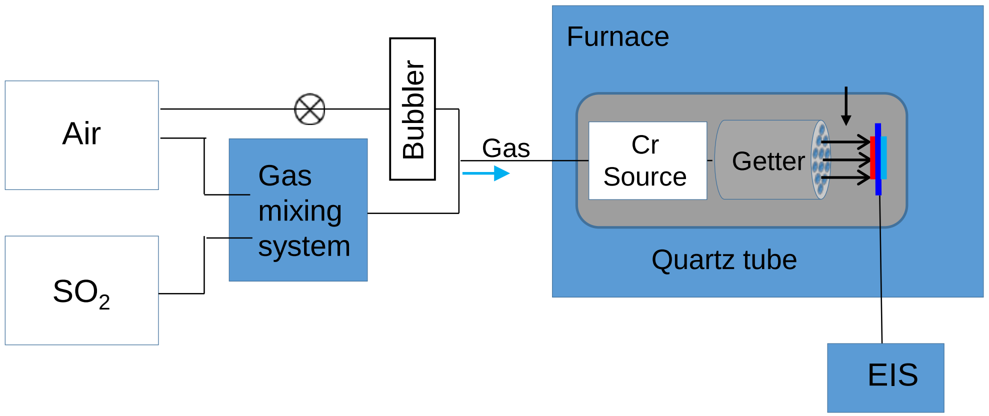
Fabrication of SMO getter composed of $SrMnO_3$ and $Sr_7Mn_4O_{15}$

NATIONAL ENERGY TECHNOLOGY LABORATORY

UCONN UNIVERSITY OF CONNECTICUT

Getter Validation Using Half-Cells

Schematic of Experimental Test Setup

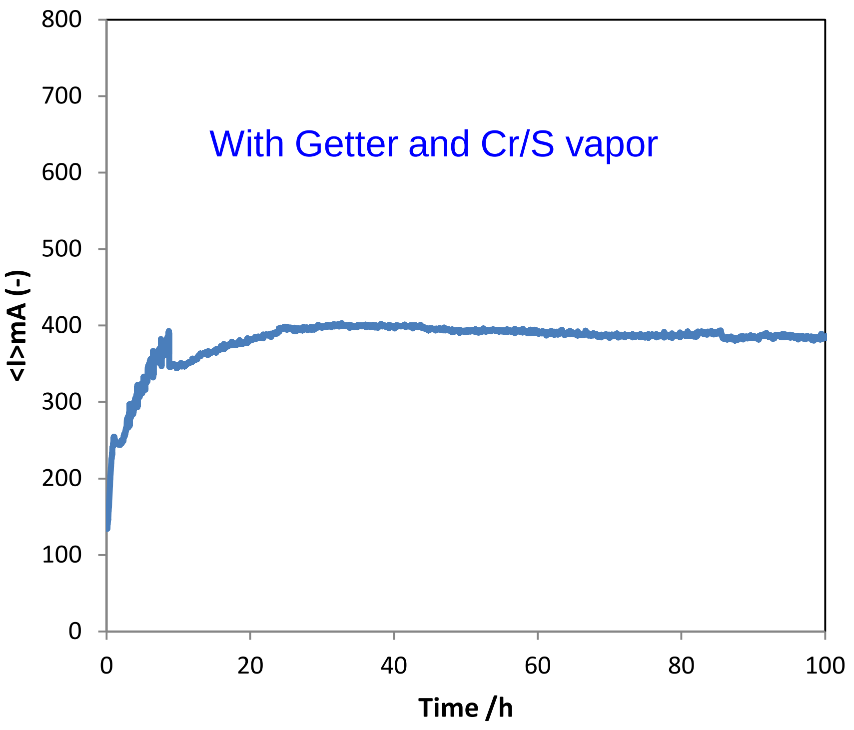


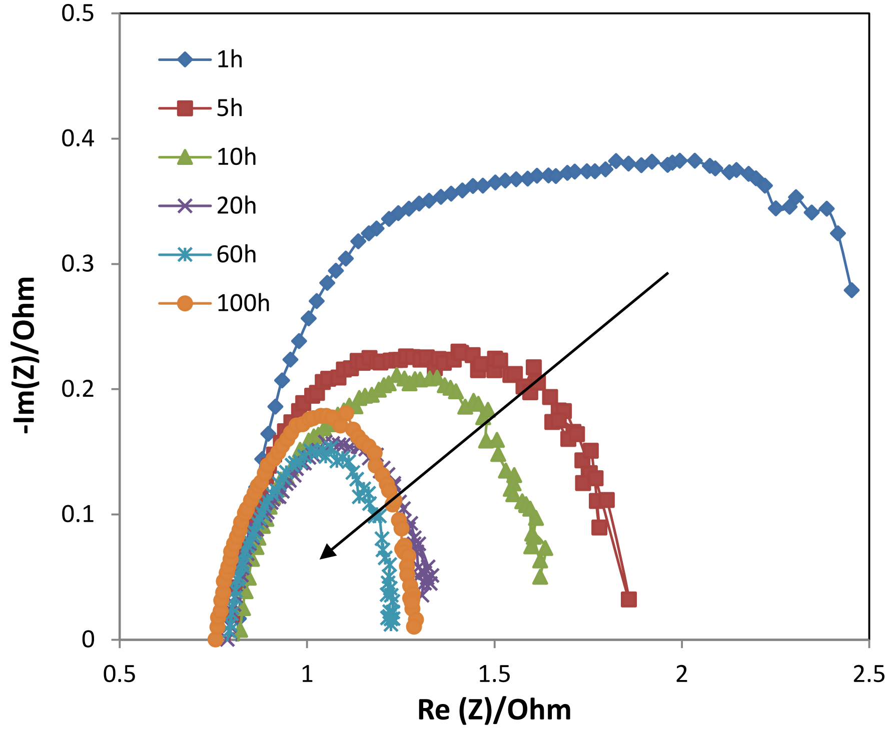
Experimental Matrix

Test #	SMO getter (with S & Cr)	With S & Cr	With S only
Materials	LSM/YSZ/Pt	LSM/YSZ/Pt	LSM/YSZ/Pt
Getter	With SMO getter	No getter	No getter
Cr Source	Cr_2O_3 pellets	Cr_2O_3 pellets	-
S Source	Various SO_2 concentration	Various SO_2 concentration	Various SO_2 concentration
Atmosphere	Air + 3% H_2O	Air + 3% H_2O	Air + 3% H_2O
Flow rate	150 sccm (C) / 50 sccm (A)	150 sccm (C) / 50 sccm (A)	150 sccm (C) / 50 sccm (A)
Temp.	750 °C	750 °C	750 °C
Applied bias	- 500 mV	- 500 mV	- 500 mV

Electrochemical Performance

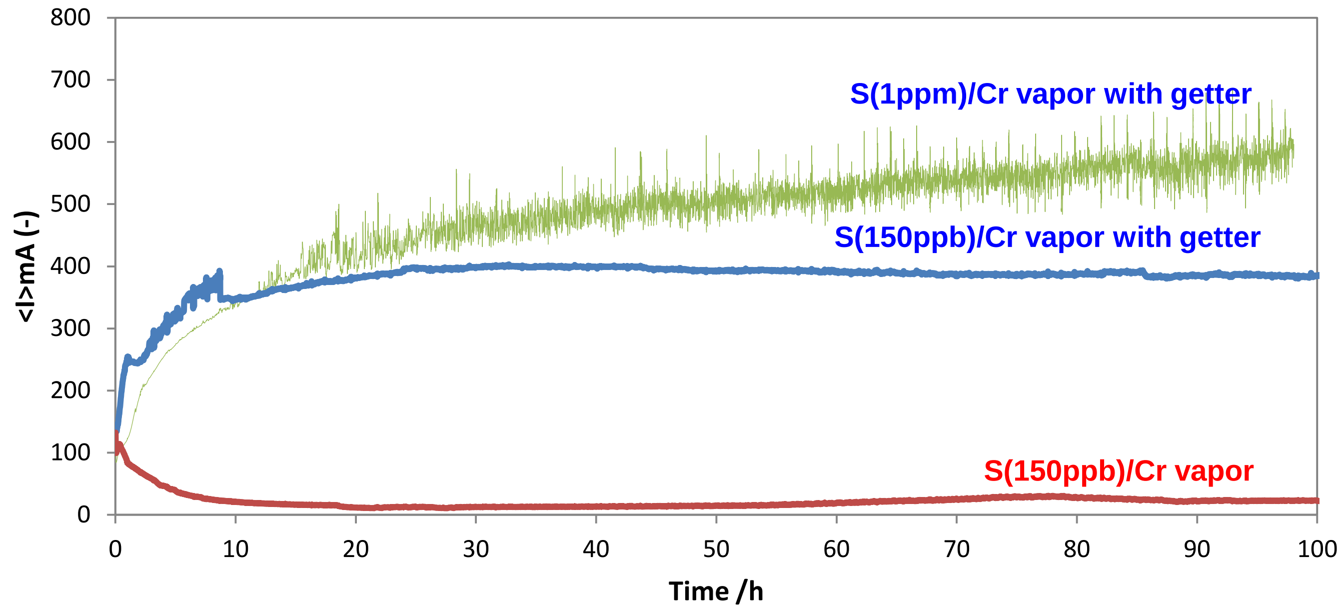
Test #	SMO getter (with S & Cr)
Materials	LSM/YSZ/Pt
Getter	With SMO getter
Cr Source	Cr_2O_3 pellets
S Source	150 ppb SO_2
Atmosphere	Air + 3% H_2O
Flow rate	150 sccm (C) / 50 sccm (A)
Temp.	750 °C
Applied bias	- 500 mV

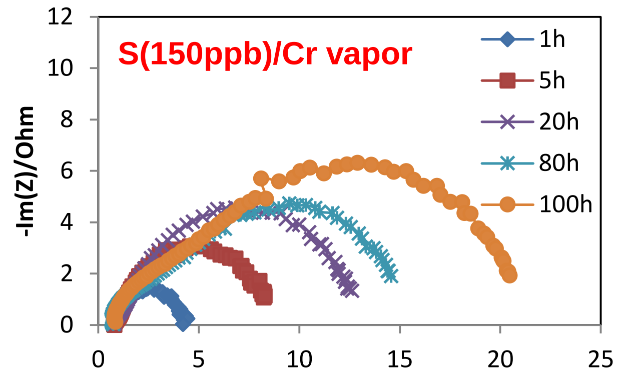


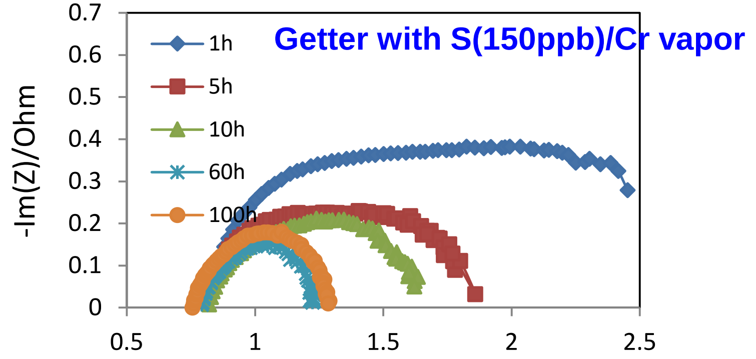


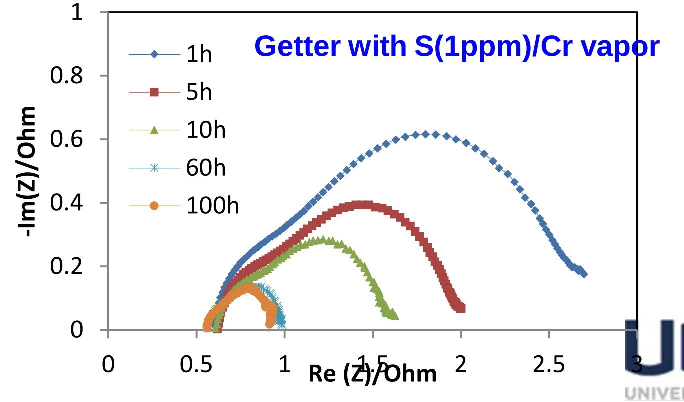
- The LSM/YSZ/Pt half-cell exposed to 3% H_2O/air in the presence of Cr & SO_2 vapor with SMO getter shows a stable performance in I-t curve.
- Nyquist spectra shows reduction in the polarization resistance over the time with constant ohmic resistance.

Electrochemical Performance







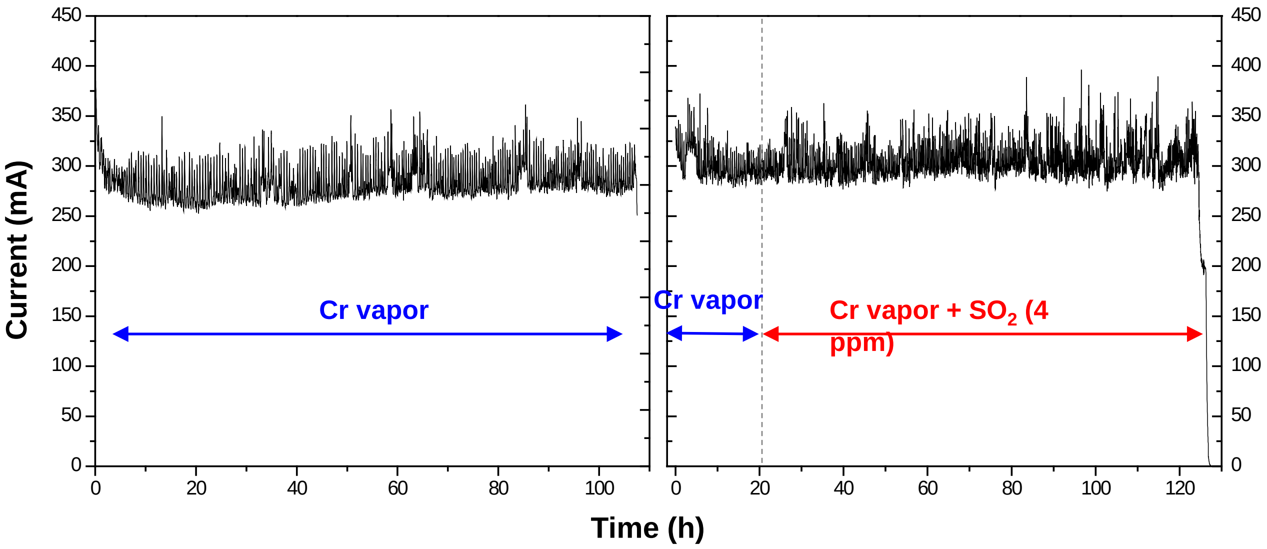


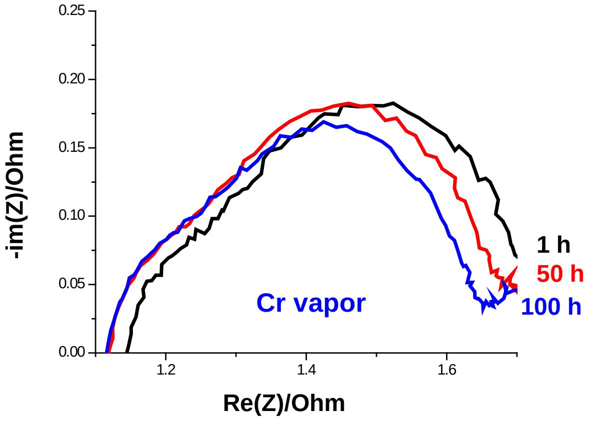
Test #	With S & Cr	With S & Cr	With S & Cr
Materials	LSM/YSZ/Pt	LSM/YSZ/Pt	LSM/YSZ/Pt
Getter	No getter	SMO getter	SMO getter
Cr Source	Cr_2O_3 pellets	Cr_2O_3 pellets	Cr_2O_3 pellets
S Source	150 ppb SO_2	150 ppb SO_2	1 ppm SO_2
Atmosphere	Air + 3% H_2O	Air + 3% H_2O	Air + 3% H_2O
Flow rate	150 sccm (C) / 50 sccm (A)	150 sccm (C) / 50 sccm (A)	150 sccm (C) / 50 sccm (A)
Temp.	750 °C	750 °C	750 °C
Applied bias	- 500 mV	- 500 mV	- 500 mV
Time	100 h	100 h	100 h

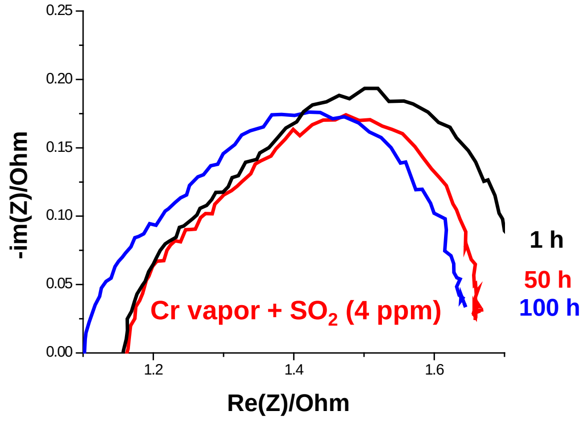
The LSM/YSZ/Pt half-cell exposed to 3% H_2O/air in the presence of Cr & SO_2 vapor with SMO getter shows a stable performance in I-t curve.

Electrochemical Performance

Test #	SMO getter (with S & Cr)
Materials	LSM/YSZ/Pt with SMO getter
Cr Souce	Cr_2O_3 pellets
Base atmosphere	Air + 3% H_2O
Atmosphere 1 Atmosphere 2	Cr_2O_3 pellets (120h) 4 ppm SO_2 + Cr_2O_3 pellets (100 h)
Flow rate	120 sccm (C) /50 sccm (A)
Temp.	700 °C
Applied bias	- 500 mV





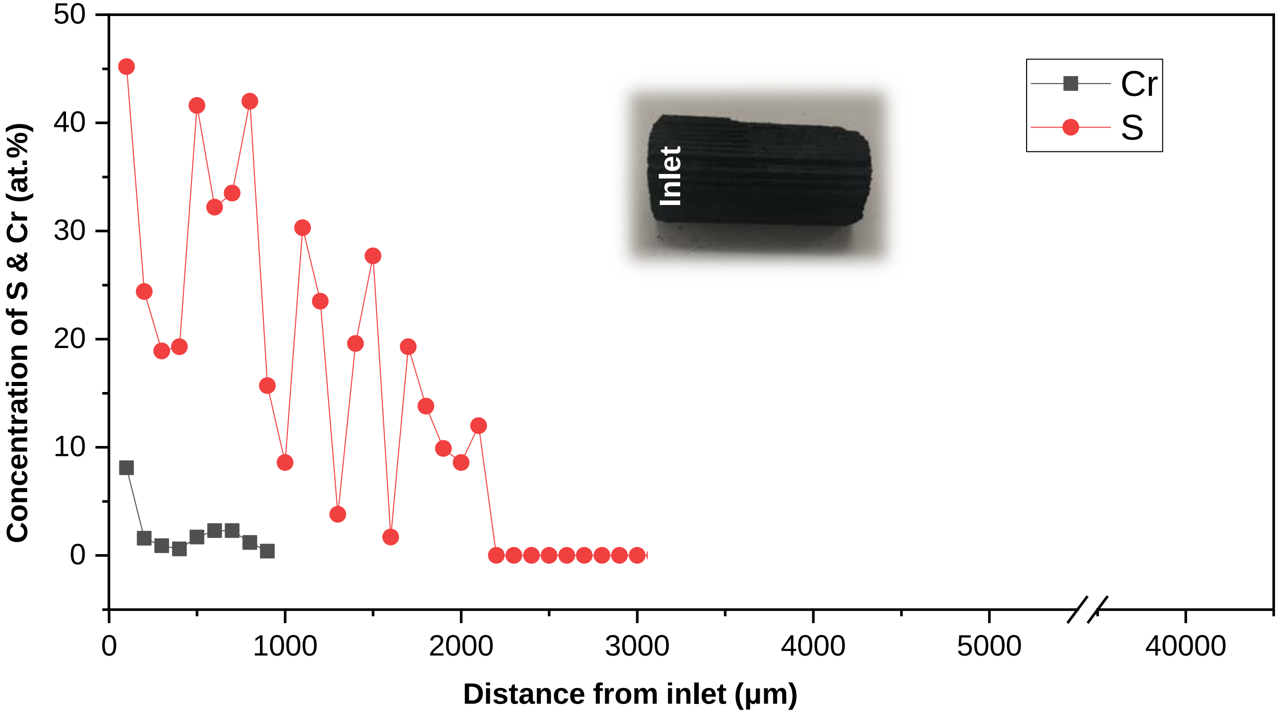


For the test with SMO getter, there was no degradation in the electrochemical performance.

Posttest Characterization of SMO Getter by EDS

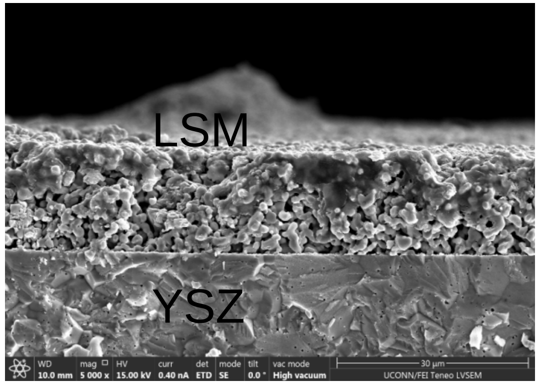
- EDS analysis on the getter along the hole

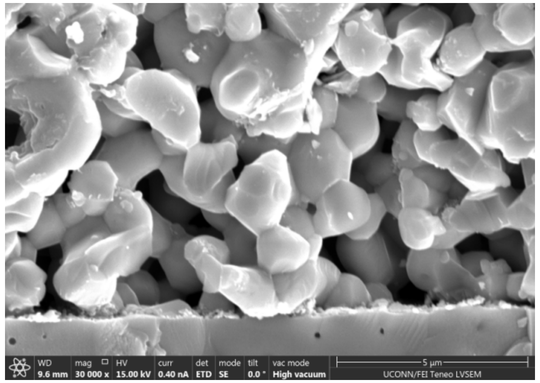
Test #	SMO getter (with S & Cr)
Materials	LSM/YSZ/Pt with SMO getter
Cr Souce	Cr_2O_3 pellets
Base atmosphere	Air + 3% H_2O
Atmosphere 1 Atmosphere 2	Cr_2O_3 pellets (120h) 4 ppm SO_2 + Cr_2O_3 pellets (100 h)
Flow rate	120 sccm (C) /50 sccm (A)
Temp.	700 °C
Applied bias	- 500 mV

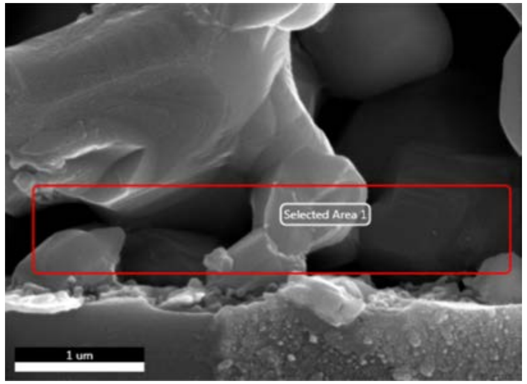


- Sulfur and chromium were detected within first 4500 μm from inlet, based on EDS analysis.
- There found no S and Cr at the outlet of the getter.

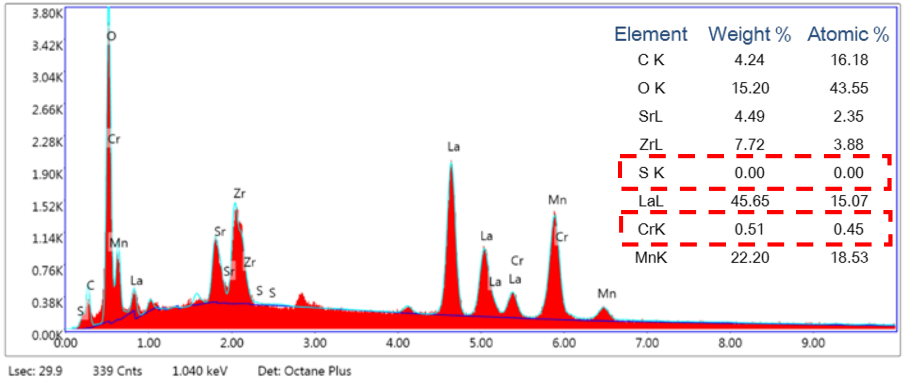
Posttest Characterization – LSM/YSZ Interface







Test #	With S & Cr
Materials	LSM/YSZ/Pt
Getter	SNO getter
Cr Source	Cr_2O_3 pellets
S Source	150 ppb SO_2
Atmosphere	Air + 3% H_2O
Flow rate	150 sccm (C) / 50 sccm (A)
Temp.	750 °C
Applied bias	- 500 mV
Time	100 h



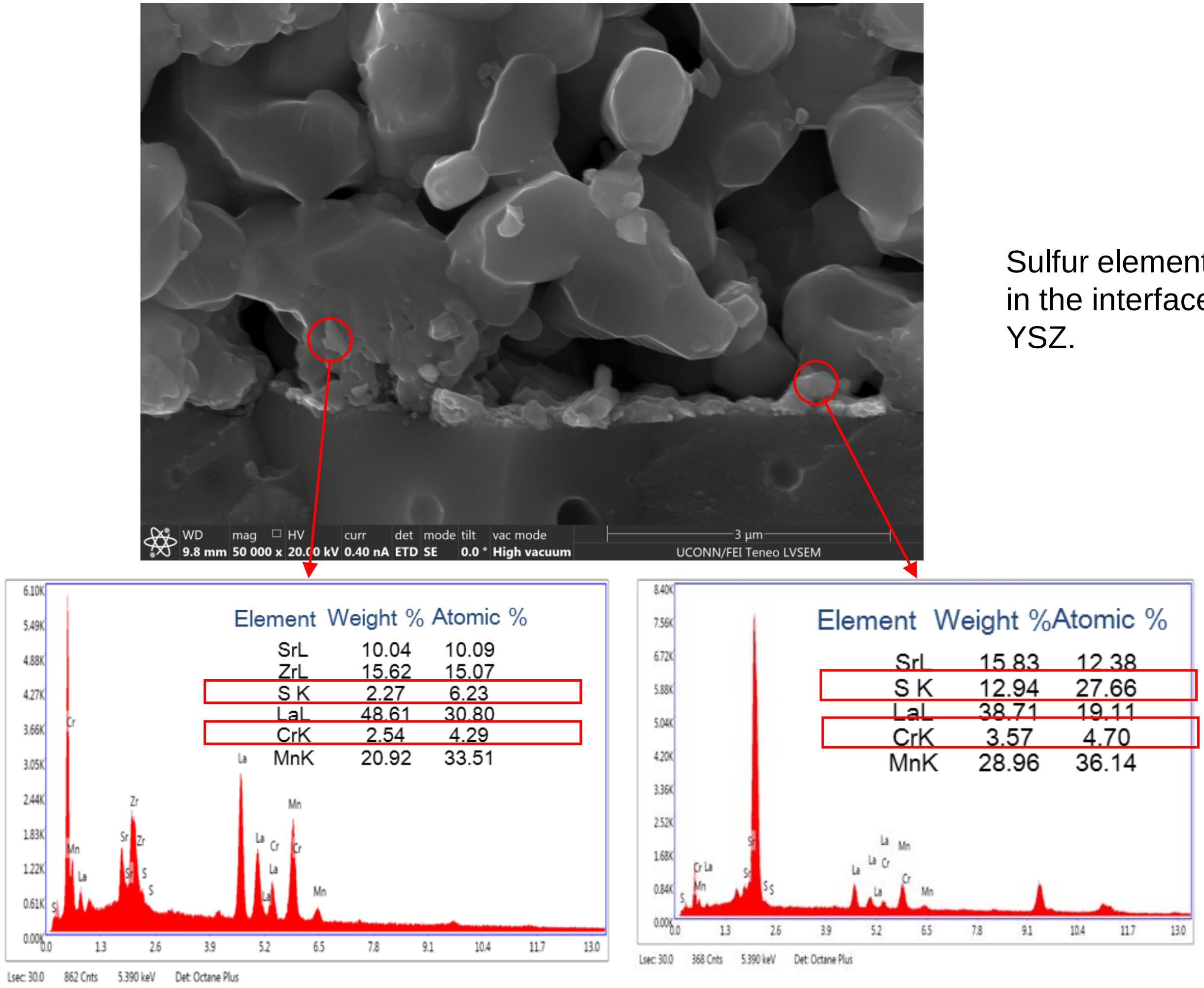
SEM/EDS of posttest LSM/YSZ interface shows no/ negligible concentration of S and Cr.

NATIONAL ENERGY TECHNOLOGY LABORATORY

UCONN UNIVERSITY OF CONNECTICUT

Cell Exposure to Cr/S vapor - Interface

Test #	With S & Cr
Materials	LSM/YSZ/Pt
Getter	**No getter**
Cr Source	**Cr_2O_3 pellets**
S Source	**150 ppb SO_2**
Atmosphere	Air + 3% H_2O
Flow rate	150 sccm (C) / 50 sccm (A)
Temp.	750 °C
Applied bias	- 500 mV
Time	100 h



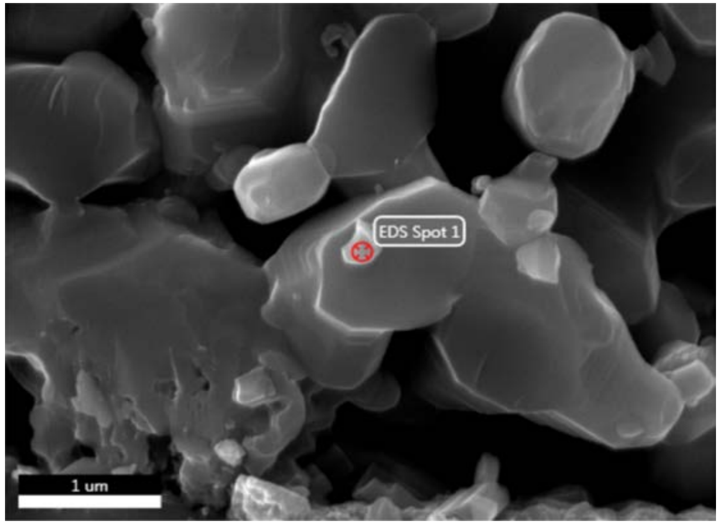
Sulfur elements are also deposited in the interface between LSM and YSZ.

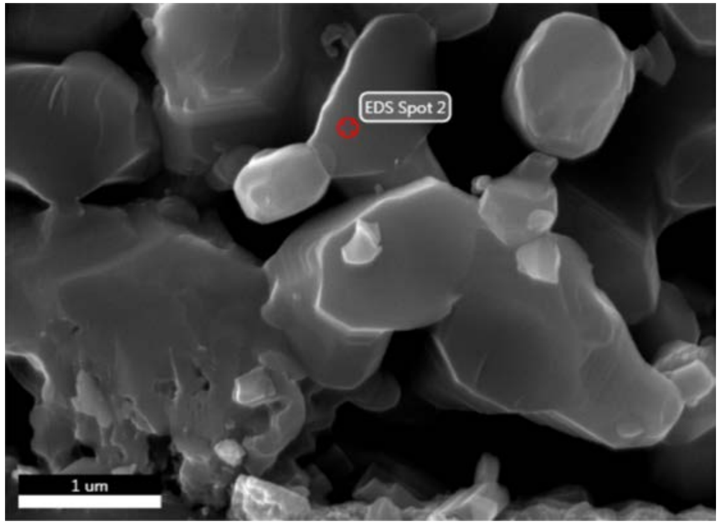
NATIONAL ENERGY TECHNOLOGY LABORATORY

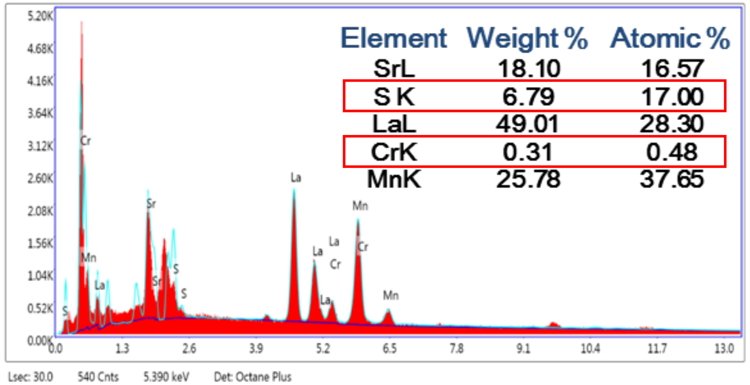
UCONN UNIVERSITY OF CONNECTICUT

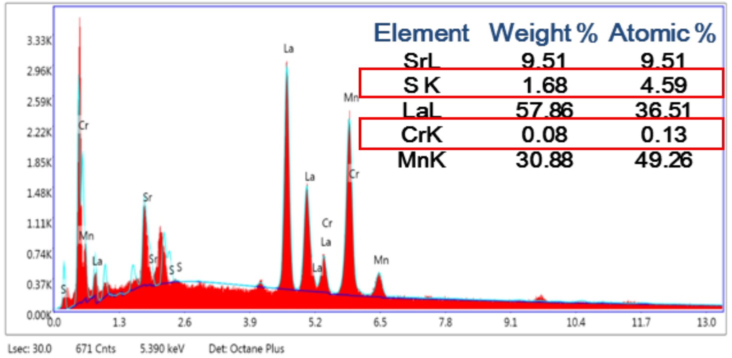
Cell Exposure to Cr/S vapor - Surface

Test #	With S & Cr
Materials	LSM/YSZ/Pt
Getter	No getter
Cr Source	Cr_2O_3 pellets
S Source	150 ppb SO_2
Atmosphere	Air + 3% H_2O
Flow rate	150 sccm (C) / 50 sccm (A)
Temp.	750 °C
Applied bias	- 500 mV
Time	100 h





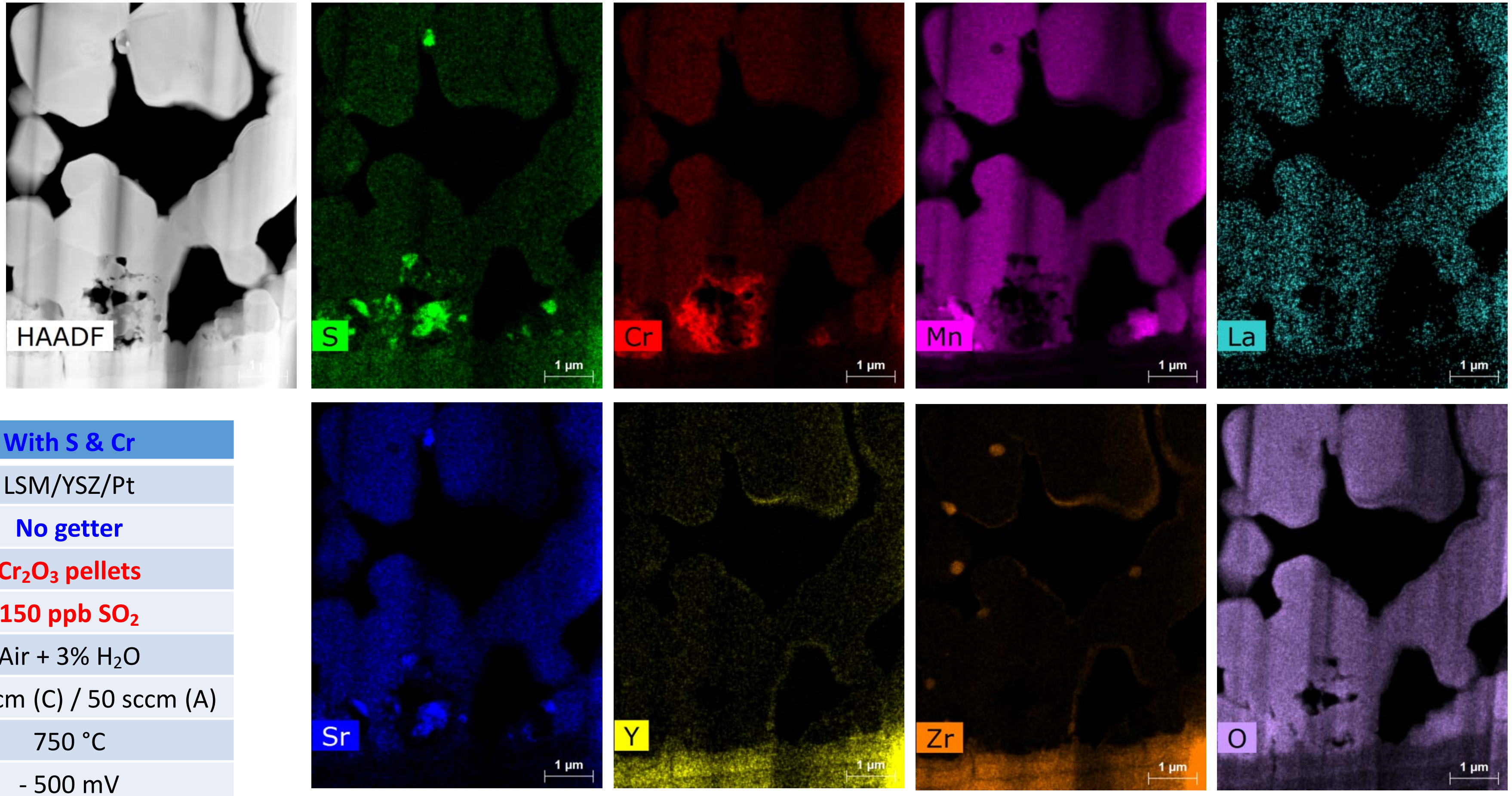




- SEM/EDS shows the Sulfur elements are detected on the small particle.

Cell Exposure to Cr/S Vapors - EDS mapping

Cr/S vapor (No getter)



Test #	With S & Cr
Materials	LSM/YSZ/Pt
Getter	No getter
Cr Source	Cr_2O_3 pellets
S Source	150 ppb SO_2
Atmosphere	Air + 3% H_2O
Flow rate	150 sccm (C) / 50 sccm (A)
Temp.	750 °C
Applied bias	- 500 mV
Time	100 h

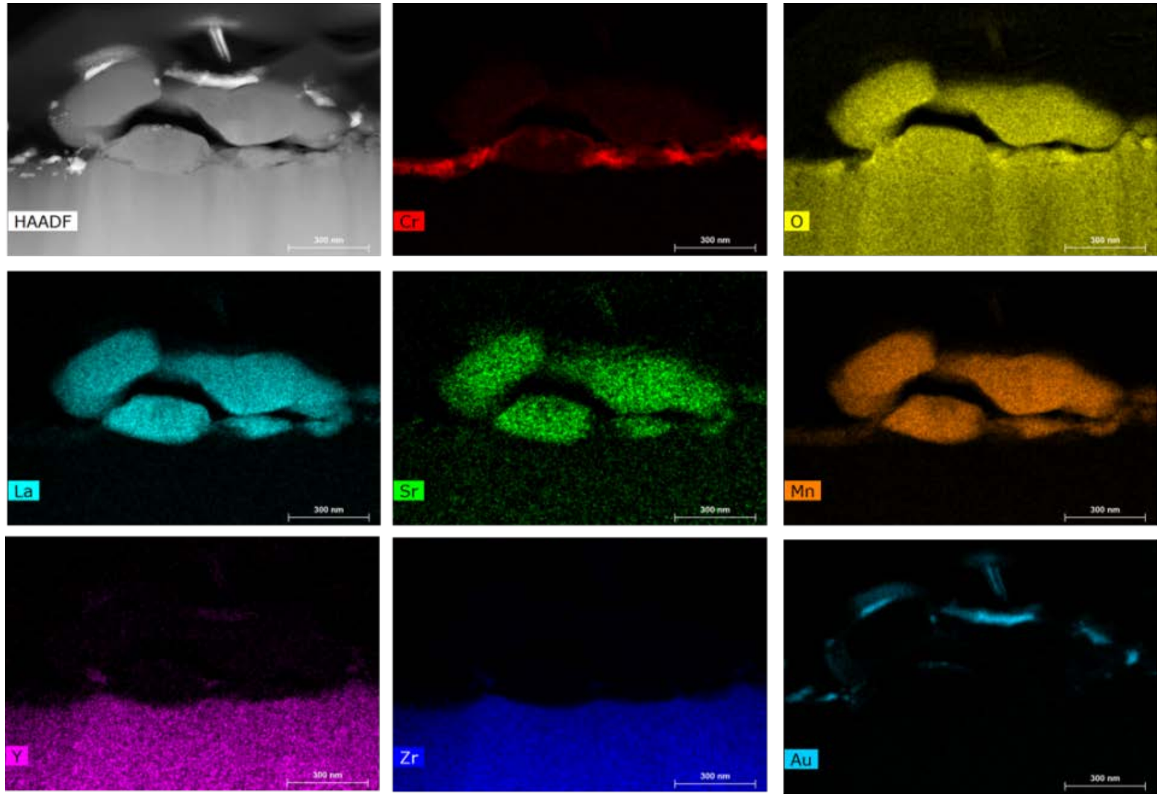
TEM/EDS mapping shows sulfur elements are detected on the surface as well as interface between LSM and YSZ. Cr elements are dominated in the interface.

NATIONAL ENERGY TECHNOLOGY LABORATORY

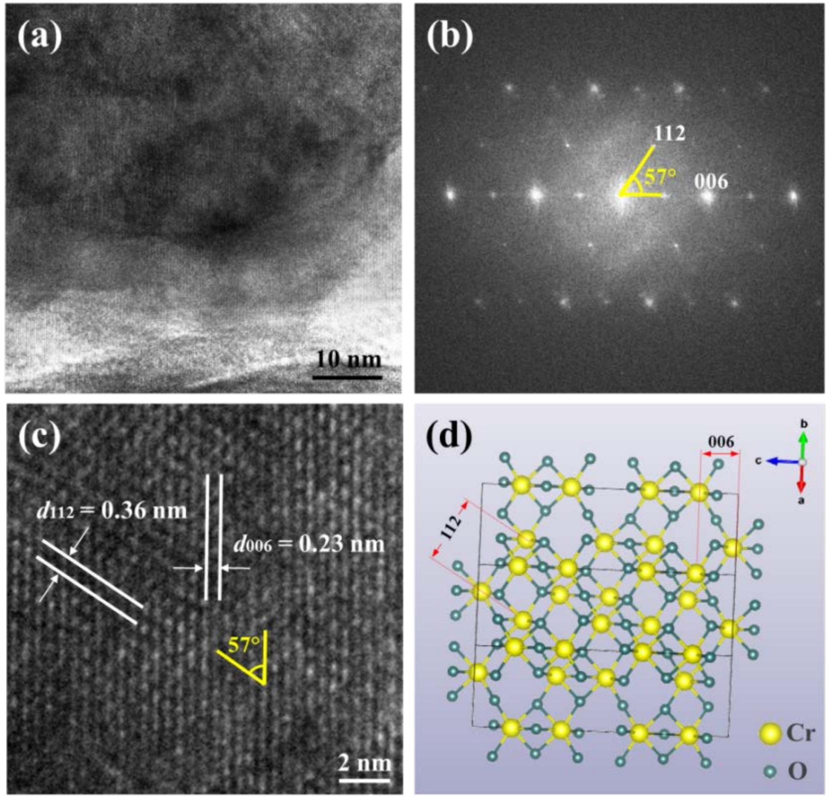
UCONN UNIVERSITY OF CONNECTICUT

Cr Deposition in LSM/YSZ Interface

Only Cr vapor (No S, No getter)



Cross sectional FIB-STEM micrograph and mapping of LSM/YSZ interface after Cr poisoning at 650C



(a) TEM image of region of the chromium deposition taken along [110], (b) The corresponding FFT pattern (c) HRTEM image of the crystalline and (d) the atomic model illustrated.

Test #	With Cr
Materials	LSM/YSZ/Pt
Getter	No getter
Cr Source	Cr_2O_3 pellets
Atmosphere	Air + 3% H_2O
Flow rate	150 sccm (C) 50 sccm (A)
Temp.	650 °C
Applied bias	- 500 mV
Time	100 h

- FIB-STEM and mapping reveals deposition of chromium at LSM/YSZ interface
- HRTEM results show it is rhombohedral Cr_2O_3 (space group R-3c, no. 167)

NATIONAL ENERGY TECHNOLOGY LABORATORY

UCONN UNIVERSITY OF CONNECTICUT

Conclusions

- Gas phase acidic airborne impurities react with basic air electrode constituents to form stable reaction products at the free surface and TPB.
- Gr II Alkaline earth and transition metal oxides have been selected as potential getter materials as they offer oxide basicity and ability to capture acidic impurities.
- Thermodynamic calculations based on Gibbs free energy change indicates co-capture of sulfur and chromium impurity in wide temperature range.
- SrMnO based getter has been synthesized and fabricated.
- Getter has been validated electrochemically to demonstrate the successful capture of both Cr and S in gas phase at 850C.
- Posttest results from SEM indicates clean LSM/YSZ interface after 100 hrs of electrochemical test in presence of Cr and SO_2 vapor.
- SEM/EDS characterization of SMO getter reveals high concentration of S and Cr at the inlet of the getter and negligible concentrations at the center and the outlet of the getter, indicating complete capture.

Acknowledgements

- Financial support from the US DOE under federal grant DE-FE 0023385
- Dr. Rin Burke for guidance
- UConn for providing laboratory support

Thank you

Background: Getter

A list of Cr getter properties against the state of the art Cr poisoning mitigation and getter materials

Cr getter critical property	Performance of new Cr getter against baseline state of the art Cr getter	Test conditions (Temp, time, atm)
Phase Stability	Superior: New Cr getter shows no phase changes and interaction with humidity and CO2 present in air.	RT-980C, Ambient air
Reaction products	As processed getters consist of several oxide phases containing Sr and Ni ($Sr_9Ni_7O_{21}$, $Sr_4Ni_3O_9$ and $Sr_2Ni_4O_5$).	Powder synthesis process and transpiration, electrochemical testing at 850C for up to 500 hrs in Air -3%H2O
Microstructures	Stable powder, coating and substrate microstructures obtained New Cr getter retains its microstructure after high temperature exposures (850C) in humidified air. Literature review does not provide background information on the SOTA.	During processing up to 980C in air During bench top testing at 850C for up to 500 hrs in humid air
Thermochemistry	Similar or Superior: Based on thermochemical models developed	
Physical Properties	Similar or Superior: Based on resistance to ambient air (NAAQS)	
Product morphology	Porous powder coating on ceramic substrates	During processing up to 980C in air During bench top testing at 850C for up to 500 hrs in humid air
Cr Conc. profile	Superior: Capture Cr in the first 1500 - 3000 micron. Reproducible results	During bench top testing at 850C for up to 500 hrs in humid air
Substrate	Configuration include honeycomb, foam and fibrous structure, Substrate materials include Cordierite, Mullite, zirconia and alumina.	
Ease of fabrication	Conventional powder preparation and coating techniques	

Long term SOFC Degradation – Role of Cathode

A Universal Degradation Phenomena for HT Electrochemical Systems

- SOFC
- SOEC
- OTM

Cathode Degradation

- Ohmic losses
- Non-ohmic losses
- Mechanical changes

Gas phase constituents and contaminants → Gas – Solid Reactions

Solid state reaction and Inter-diffusion → Solid – Solid Reactions

Dopant exolution, Compound Formation, Surface Morphology Changes, Interface Diffusion

Intrinsic + system generated extrinsic air impurities