Multi-Constituent Airborne Contaminants Capture with Low Cost Oxide Getters and Mitigation of Cathode Poisoning in SOFCs

Prabhakar Singh

Department of Materials Science and Engineering
University of Connecticut, CT

WORK PERFORMED UNDER AGREEMENT DE-FE 0023385, 0027894 and 0031182

FE SOFC program at the 2020 AMR meeting, Crystal City
May 20, 2020

NATIONAL ENERGY TECHNOLOGY LABORATORY

UCONN
UNIVERSITY OF CONNECTICUT

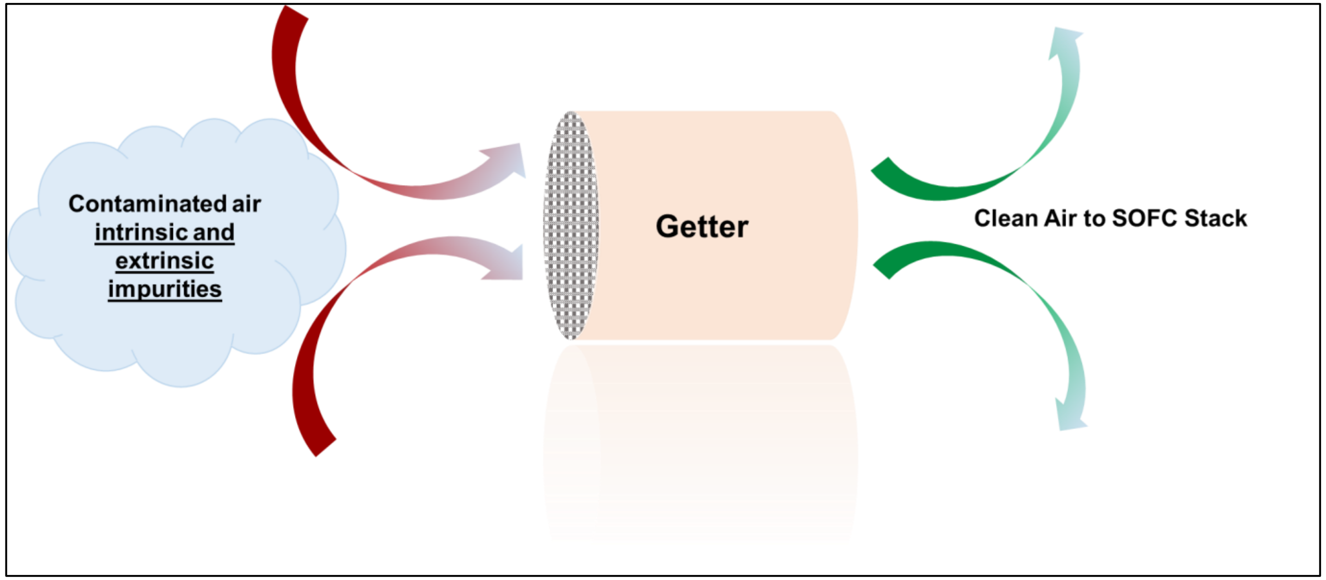
Technical Contributors

UConn	Prabhakar Singh	Professor
	Steven Suib	Professor
	Avinash Dongare	Associate Professor
	Boxun Hu	Assistant Research Professor
	Ashish Aphale	Post-doctoral research associate
	Pawan Kumar Dubey	Post-doctoral fellow
	Junsung Hong	Graduate Student
	Michael Reisert	Graduate Student
	Su Jeong Heo	Graduate Student
	Junkai He	Graduate Student
	Yanliu Dang	Graduate Student
	Seraphim Belko	Graduate Student
Alfred University	Scott Misture	Professor
UAlabama	Manoj Mahapatra	Assistant Professor

Program Manager: Dr. Patcharin N. Burke, NETL

Outline

- Accomplishments
- Program objectives
- Technical Approach
- Experimental
    - Getter materials synthesis and stability evaluation
    - Long-term validation of getter performance for multi-contaminant capture
    - In-situ validation using electrochemical tests and transpiration tests.
    - Posttest characterizations
- Results
- Discussion
- Acknowledgements
- Publications



Benefits of Technology to the Programs

Potential benefits of this project :

- The programs remain significant to the commercialization of SOFC systems by improving the TRL.
- Mitigation of cathode poisoning and highly durable anode enables increased performance stability and long-term reliability of SOFC systems thus accelerating demonstration and deployment of the technology.

Impact

- Mechanistic understanding of the degradation processes in pure electronic and mixed electronic and ionic conducting (MEIC) cathodes.
- Development of mitigation process utilizing low cost getters to capture trace levels of airborne contaminants.
- Reduction in oxide evaporation by developing surface pretreatment conditions.
- Mitigation of carbon deposits in the cell anode.
- Improved cell and stack temperature distribution.
- Eliminated external reformer by using DIR solid oxide fuel cells.
- Improved cell and stack electrochemical performance and durability.
- Reduced materials cost.

Program Objectives

- **The overall objective of the proposed research programs is to develop and validate reliable, cost-effective getter approaches for mitigation of SOFC cathode degradation through incorporation of reliable materials and architectures to inhibit detrimental solid-solid and solid-gas interactions.**
- **It is also the objective of the program to development of low-cost alloy anodes for distributed internal reforming of fuels to potentially increase the flue-flexibility, reliability and long-term endurance of SOFCs.**

Approaches:

- **Develop mechanistic understanding of cathode degradation in "real world" air atmosphere.**
- **Develop materials and architectures of cost-effective getters for application in stacks and BOP.**
- **Develop alloy surface pretreatment conditions to minimize chromium evaporation.**
- **Validate and demonstrate getter performance to capture trace levels of airborne multi-components impurities.**
- **Independent validation of getter performance has been performed by industrial partners and national laboratories under their systems operating conditions.**
- **Fundamental thermodynamic calculations complemented the experimental observations.**

Outcome

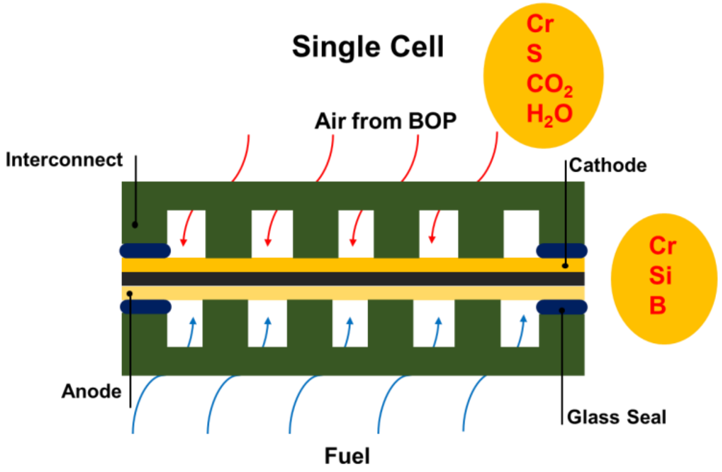
- **Proposed approaches successfully developed, validated and implemented.**
- **Proposed program milestones have been met.**
- **Conducted materials and technology transfer.**

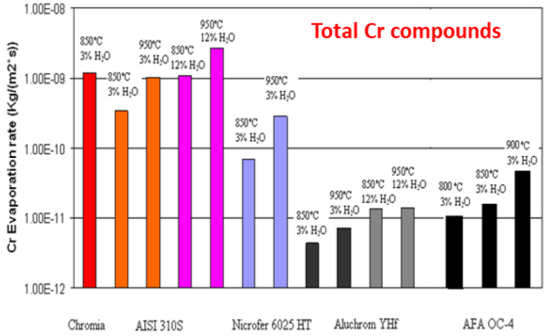
Program Accomplishments

- Developed getter for the capture of trace levels of multi-components impurities present in ambient and process air.
- Develop mechanistic understanding of cathode degradation under ambient air atmosphere
- Group II Akaline earth and transition metal oxide based low cost getter offers excellent capture of trace airborne contaminants
- Getter performance has been validated for the capture of single (Cr or S) and multiple (Cr and S) contaminants in their trace concentrations in ppm-ppb range.
- Electrochemical tests indicates stable cathode performance under SOFC systems conditions.
- Getter posttest characterization indicates high concentration of both Cr and S at the inlet, while no/negligible concentrations at the outlet indicating complete capture of contaminants.

Background: Sources of Contaminants

- 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).
- Air electrodes remain prone to degradation due to acid-base interactions with contaminants.
- Dopant exolution, Compound formation, Surface/Interface morphology changes and Interdiffusion.





NAAQS (US EPA)

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

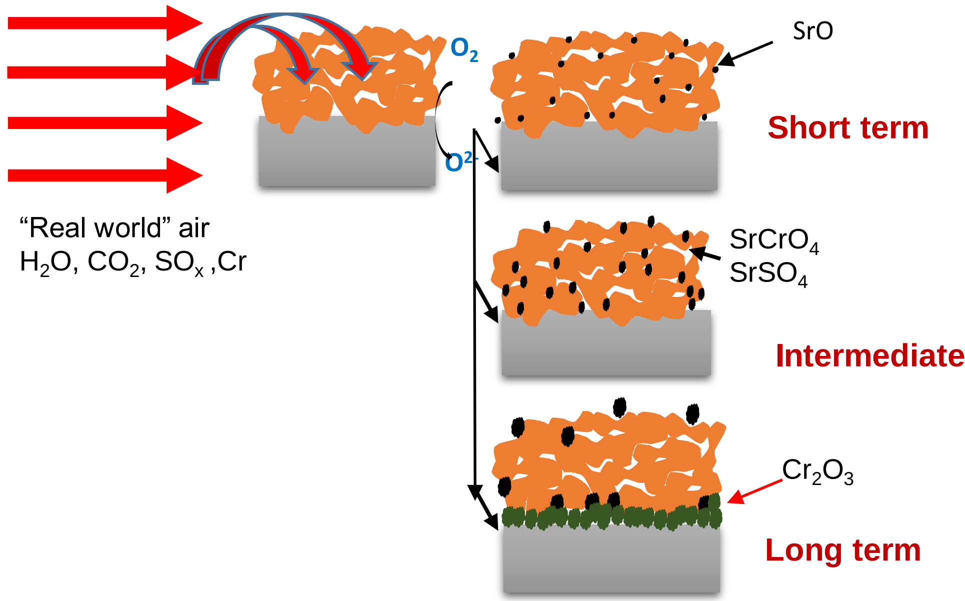
Acidic gaseous species

\+ + + +

Basic AE Surface

- Electrocatalytic Deactivation
- Compound Formation
- Surface adsorption

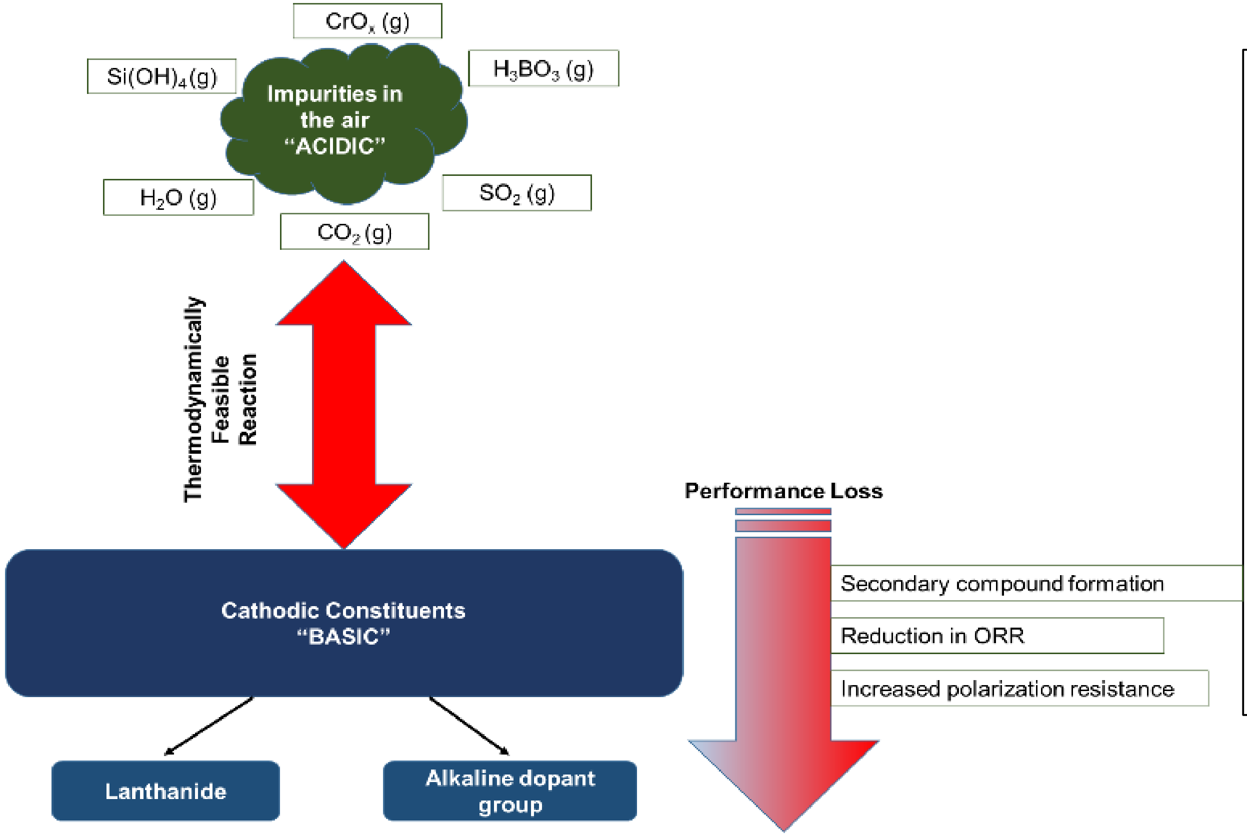
Long-term Degradation



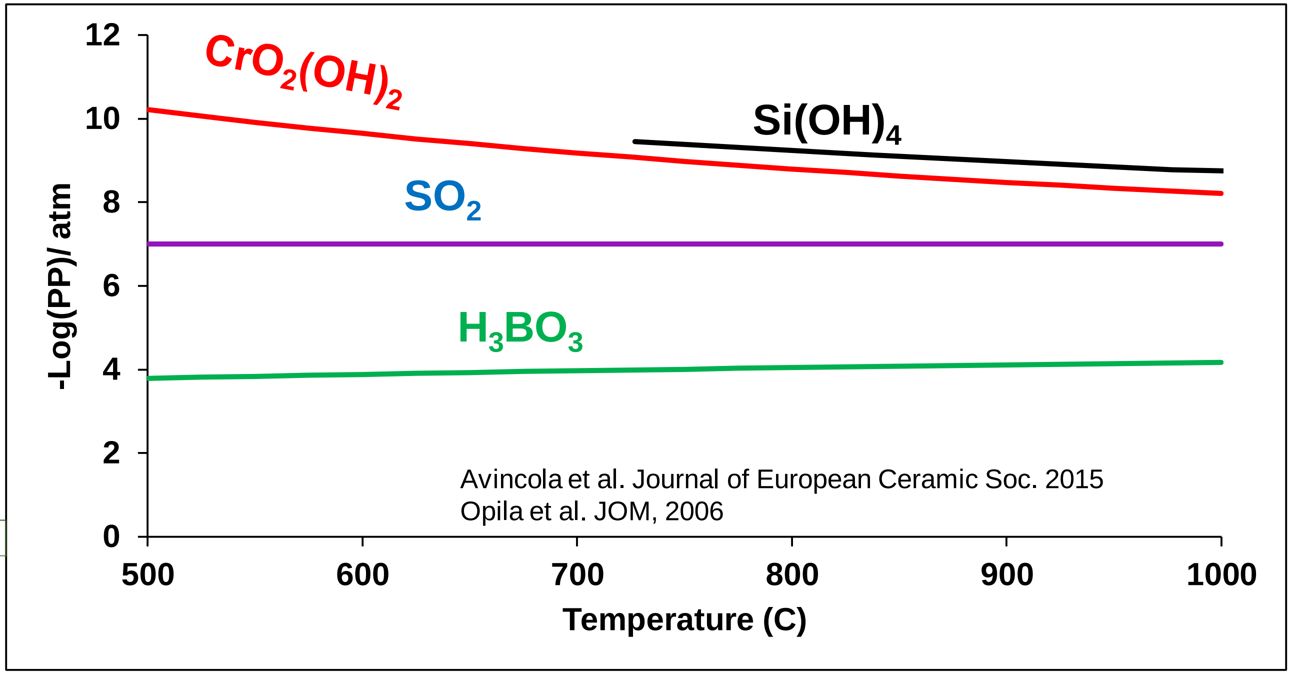
NATIONAL ENERGY TECHNOLOGY LABORATORY

UCONN
UNIVERSITY OF CONNECTICUT

Background: Technical Approach



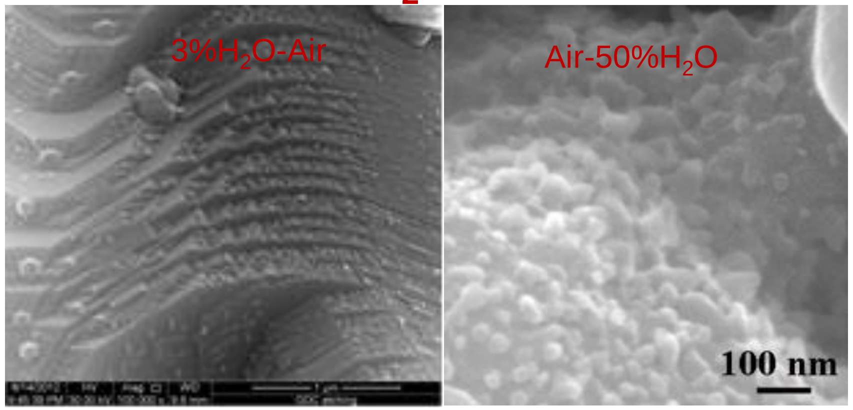
Thermodynamic Calculations

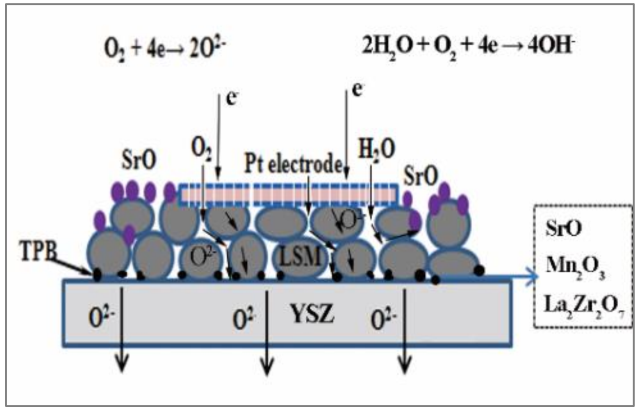


- Cathode poisoning leading to the long-term degradation in SOFC systems
- Permanent performance degradation leading high polarization losses
- Interfacial deposition limits the oxygen access at the triple phase boundary (TPB) sites

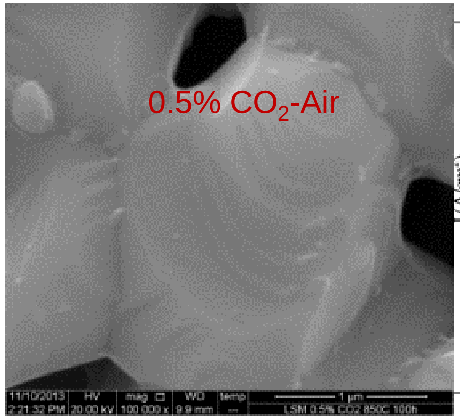
Prior work: Cathode Poisoning in "Real World" Air

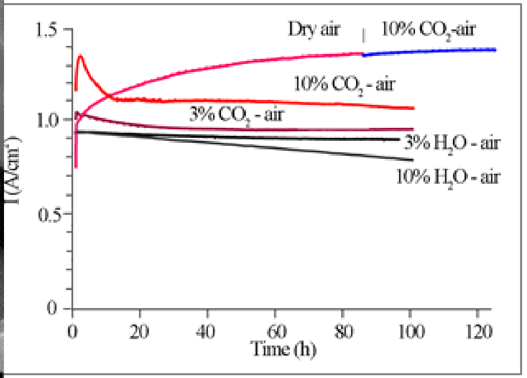
H_2O-Air



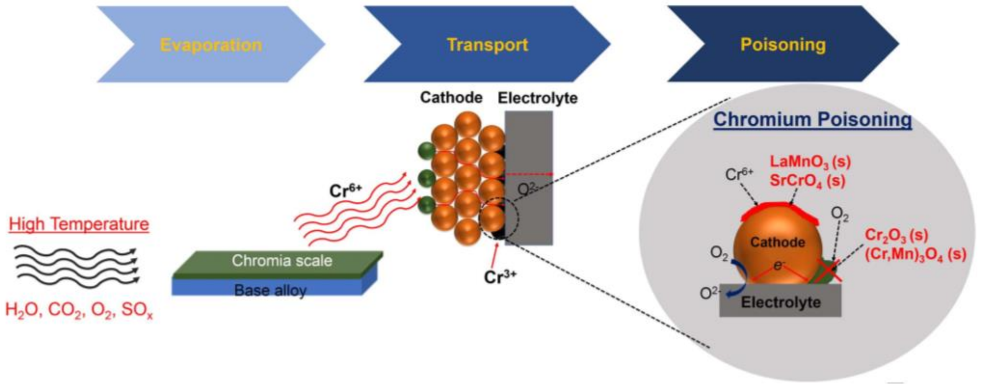


CO_2-Air

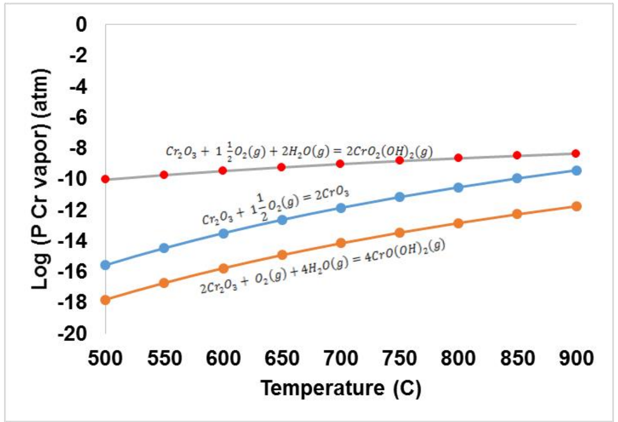




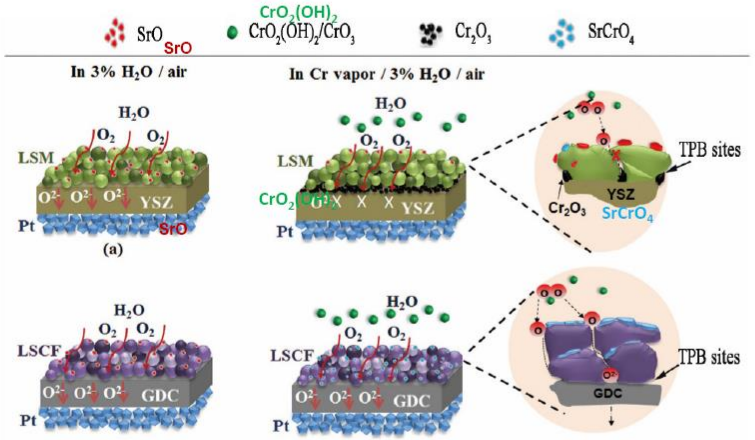
Cr-Air



Thermodynamic calculations



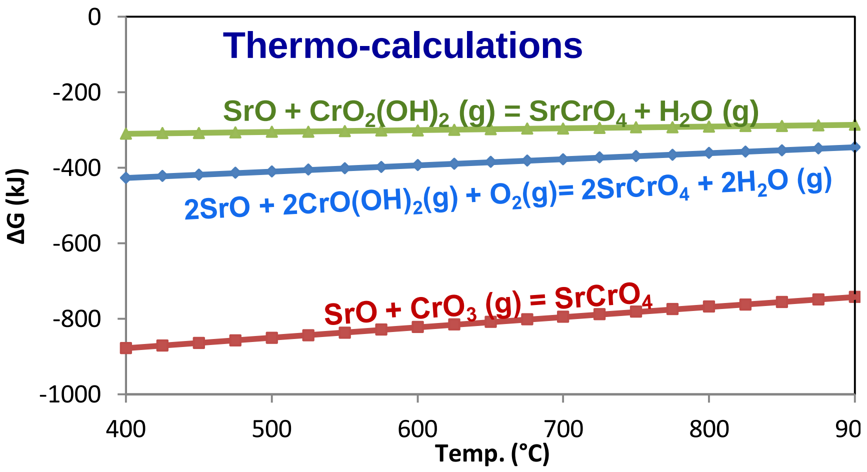
Cathode degradation mechanism



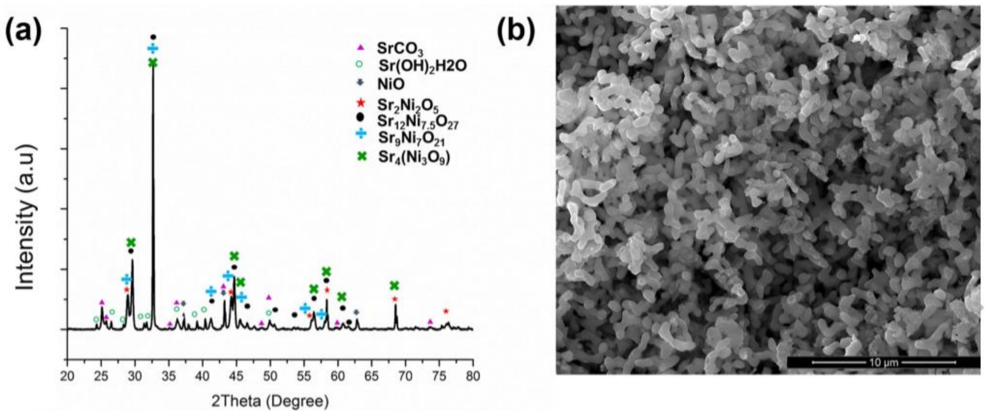
Cathode undergoes significant morphological and chemical changes in ambient air atmosphere

- Boxun Hu, Michael Keane, Manoj K. Mahapatra, Prabhakar, Journal of Power Sources 248, 196-204, 2014
- Boxun Hu, Manoj Mahapatra, Michael Keane, Heng Zhang and Prabhakar Singh, Journal of Power Sources, 268, 404-413, 2014
- Ashish Aphale, Aman Uddin, Boxun Hu, Su Jeong Heo, Junsung Hong and Prabhakar Singh, ECS, 2018

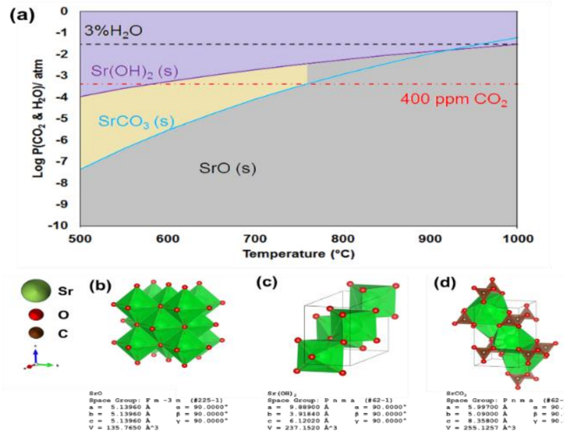
Getter Synthesis and Stability



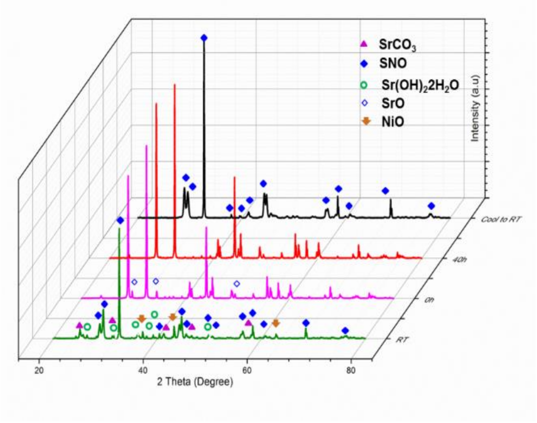
Getter powder phase and morphology



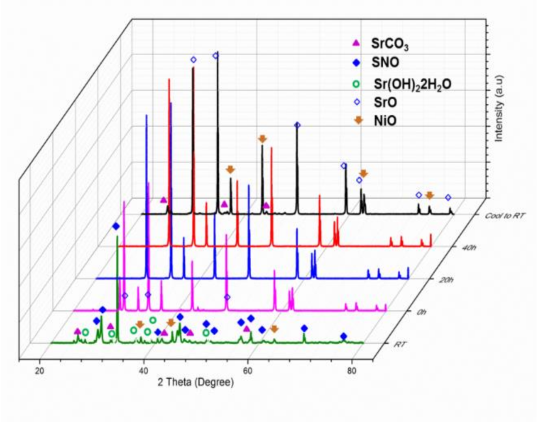
Phase stability diagram



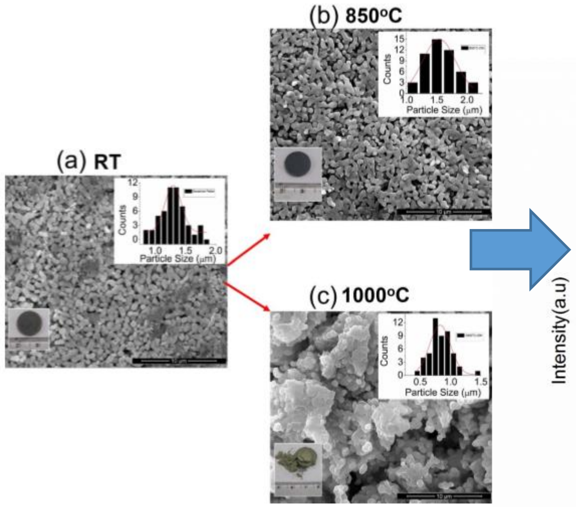
High temperature *in-situ* XRD performed on SrNiOx powder for 40h



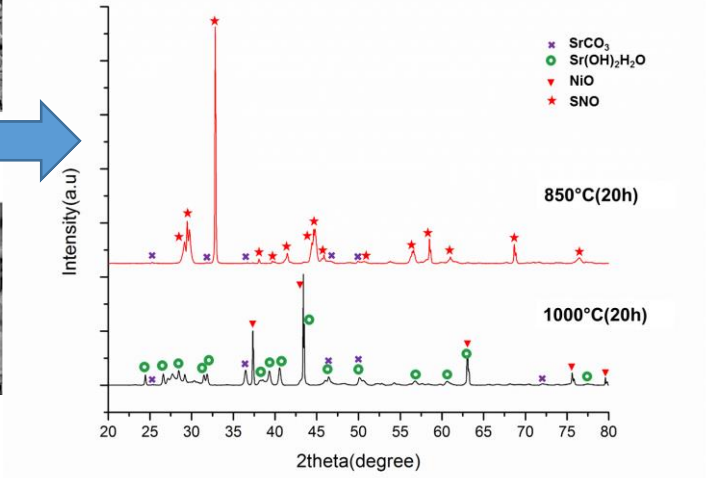
850˚C



1000˚C



XRD analysis after sintering



Getter powder remains stable under SOFC operating conditions

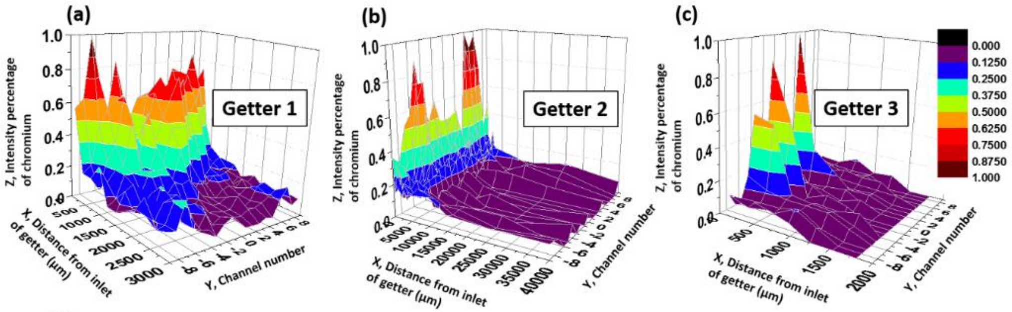
Ashish Aphale, Aman Uddin, Boxun Hu, Su Jeong Heo, Junsung Hong and Prabhakar Singh, Synthesis and Stability of SrxNiyOz Chromium Getter for Solid Oxide Fuel Cells", ECS, 2018

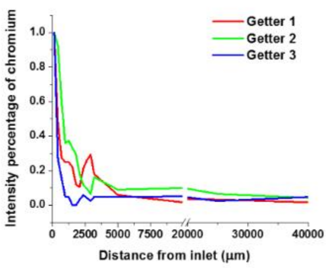
Chromium Capture Validation

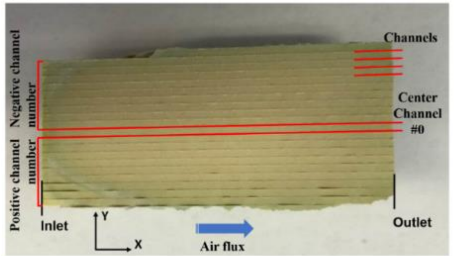
Transpiration Tests

Without getter

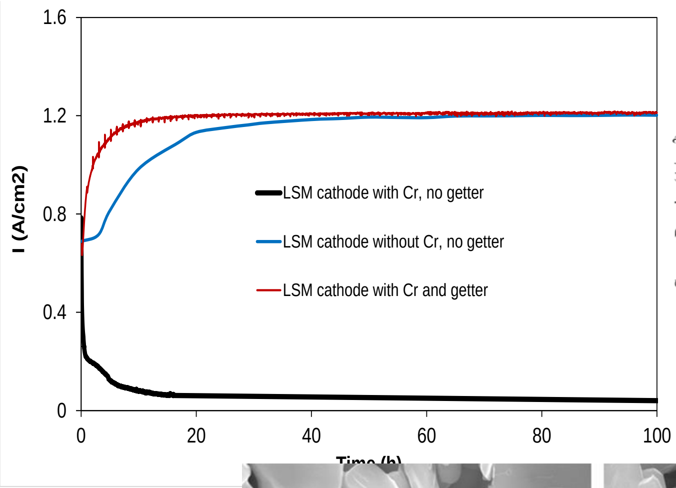
With getter

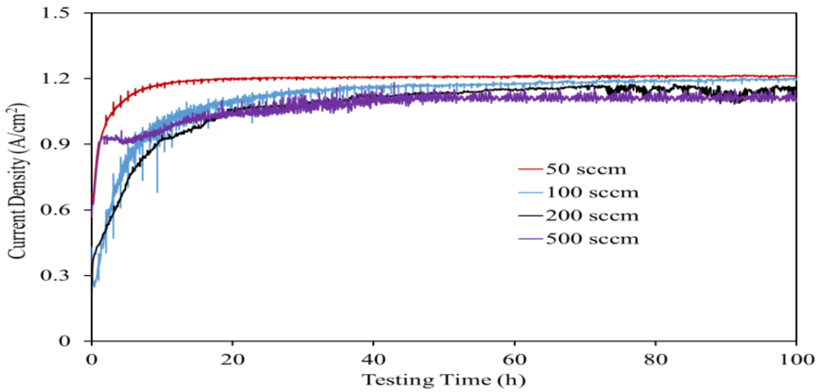






Electrochemical Tests





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

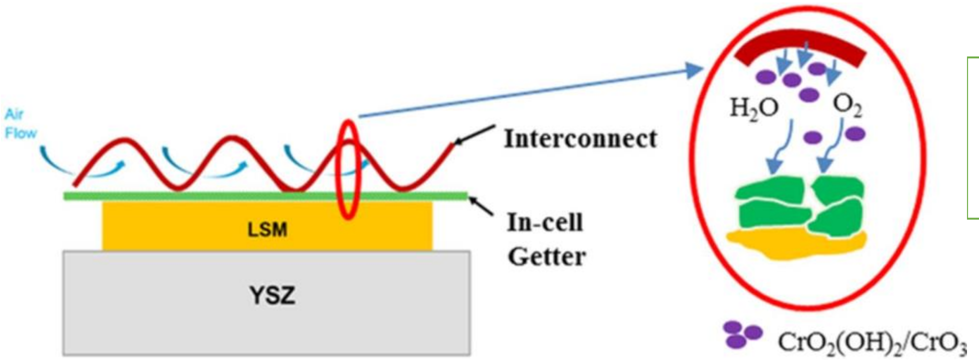
Successful capture of gas phase Cr vapors and mitigation of cathode poisoning is demonstrated

B Hu, S Krishnan, C Liang, SJ Heo, AN Aphale, R Ramprasad, P Singh, International Journal of Hydrogen Energy 42 (15), (2017)

NATIONAL ENERGY TECHNOLOGY LABORATORY

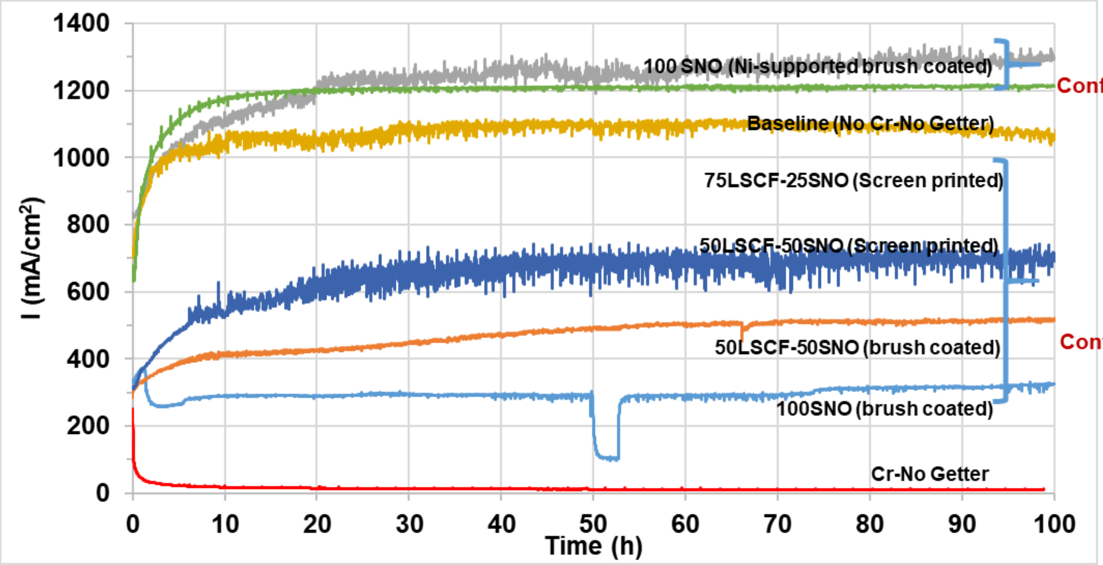
UCONN UNIVERSITY OF CONNECTICUT

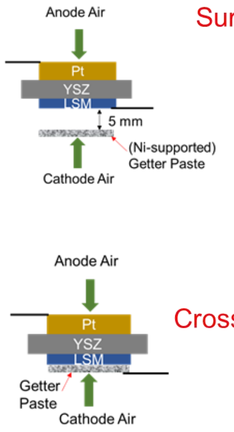
Chromium Capture Validation



- Half-cell fabrication procedure was maintained for all the half-cell fabrication
- LSM was screen printed and sintered at 1200 ˚C for 1h
- SNO or LSCF/SNO getter was brush coated and sintered at 850 ˚C for 20h
- Config-1: Getter paste is 5 mm apart form LSM and Config-2: Getter paste is in direct contact with LSM

I-t data

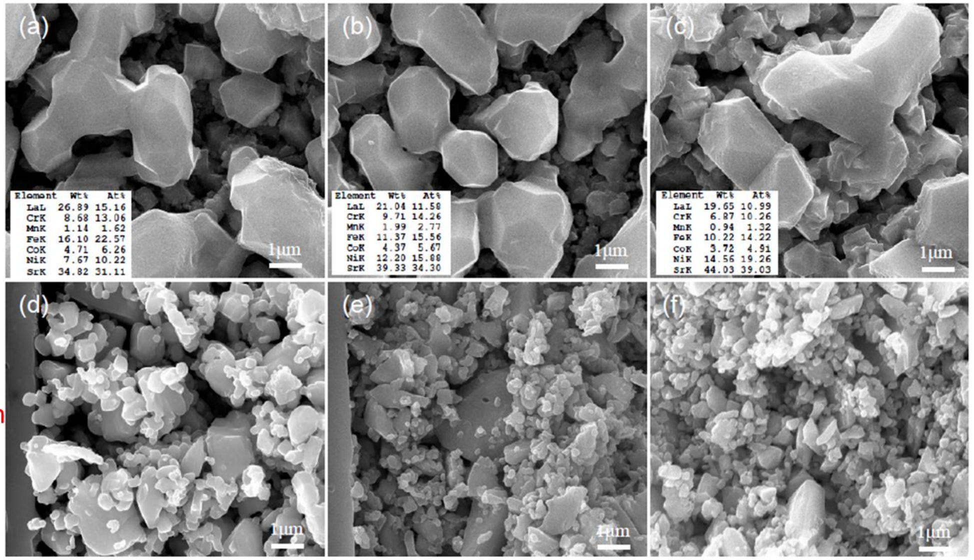




Surface

Cross-section

75LSCF-25SNO (screen printed) | 50LSCF-50SNO (screen printed) | 50LSCF-50SNO (brush coated)

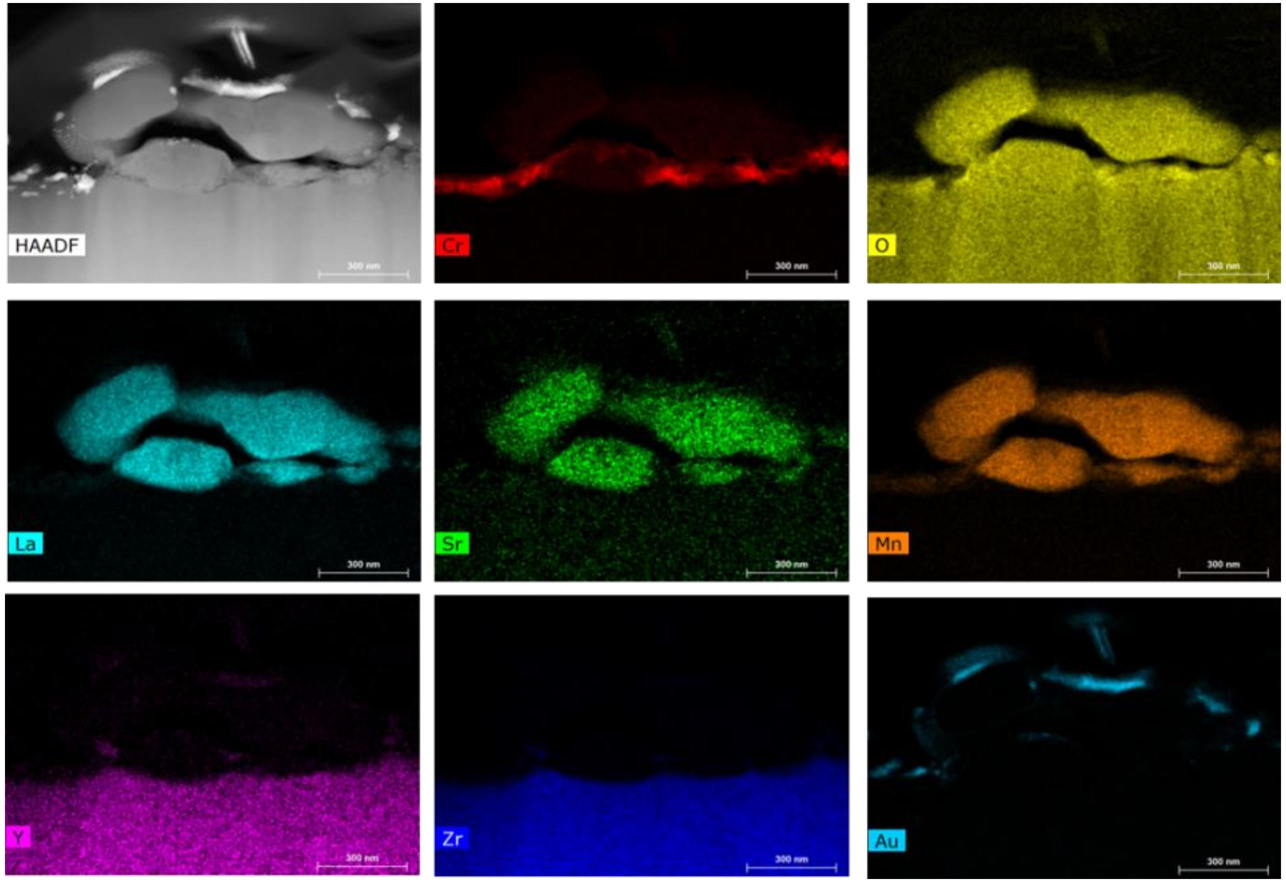


Md Aman Uddin, Ashish Aphale, Boxun, Hu, Su Jeong HeO, Ugur Pasaogullari and Prabhakar Singh, J. Electrochem. Soc. 2017

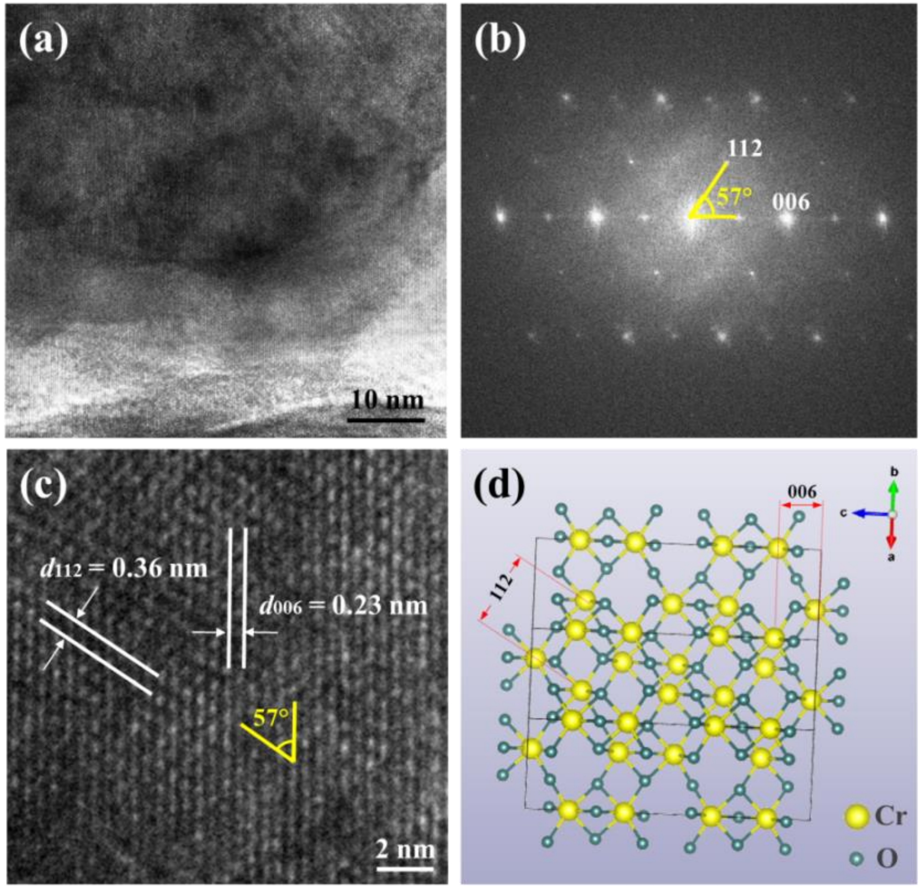
NATIONAL ENERGY TECHNOLOGY LABORATORY

UCONN UNIVERSITY OF CONNECTICUT

Cr Poisoning of TBP Sites



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.

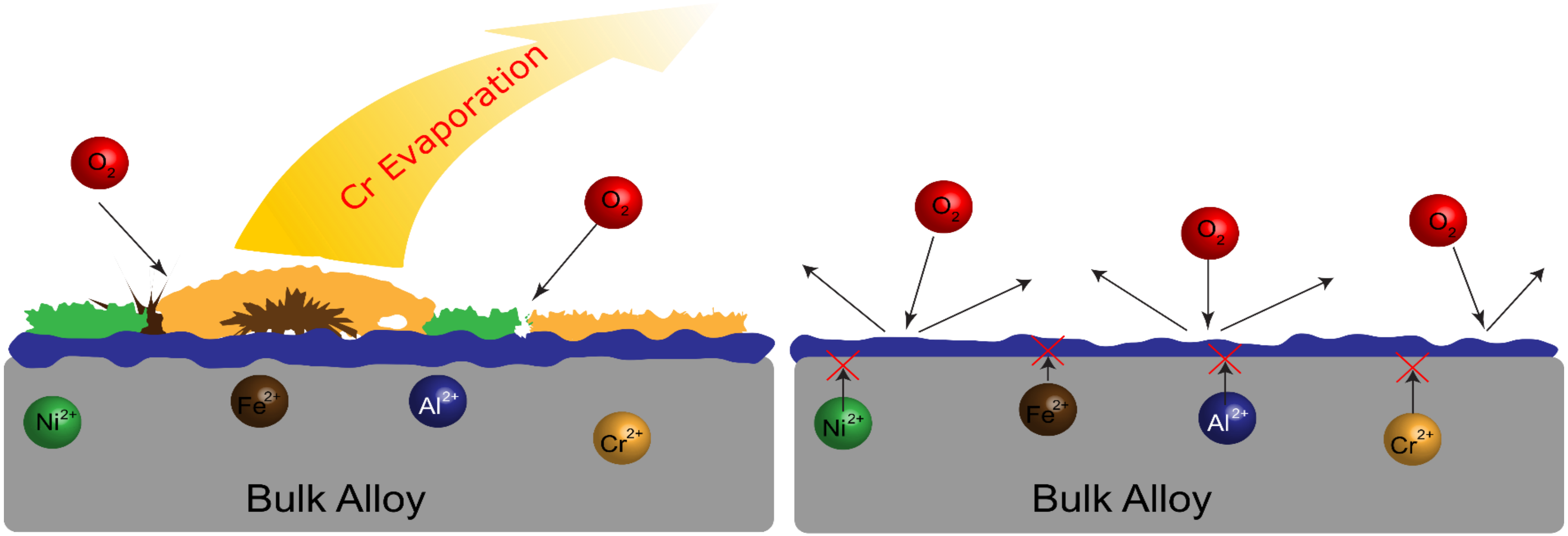
- **FIB-STEM and mapping reveals deposition of chromium at LSM/YSZ interface**
- **HRTEM results show it is rhombohedral Cr_2O_3 (space group R-3c, no. 167)**

NATIONAL ENERGY TECHNOLOGY LABORATORY

SJ Heo, J Hong, A Aphale, B Hu, P Singh, Journal of The Electrochemical Society 166 (13), F990-F995

UCONN
UNIVERSITY OF CONNECTICUT

Surface Morphology: Pretreatment V/s of Conventional Alloy



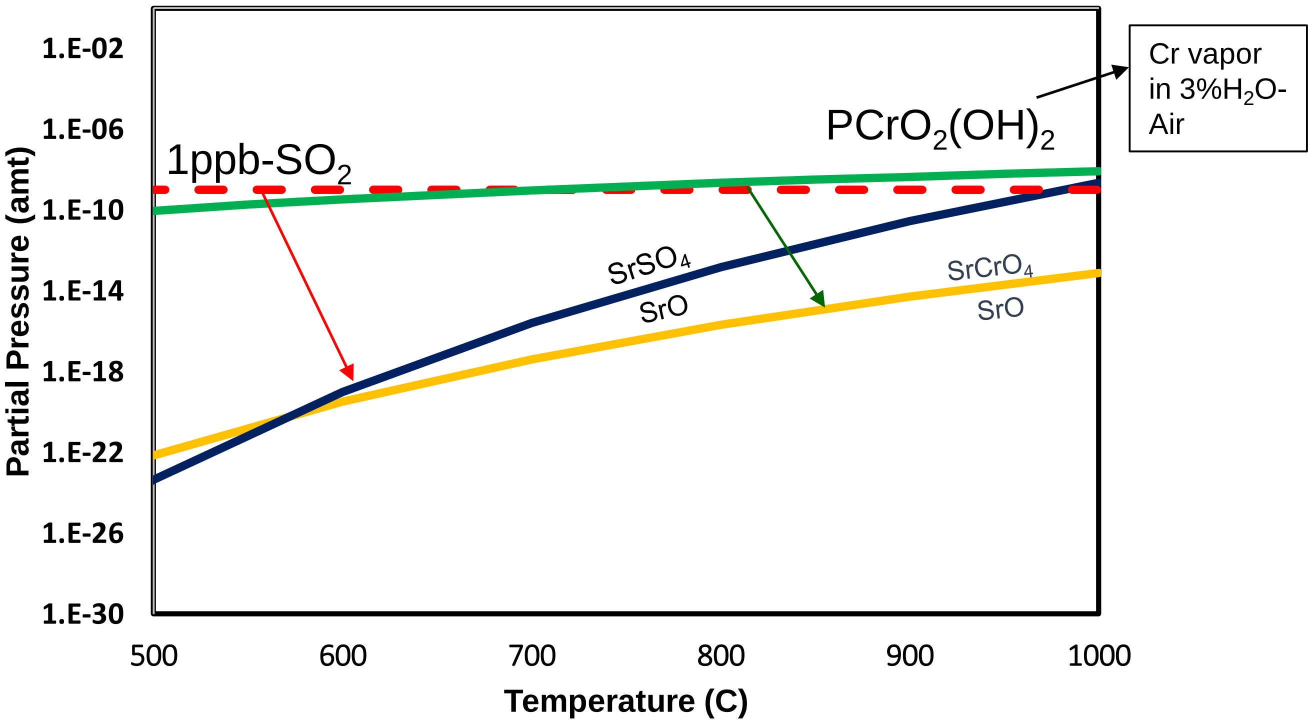
Conventional
Alumina forming Alloy

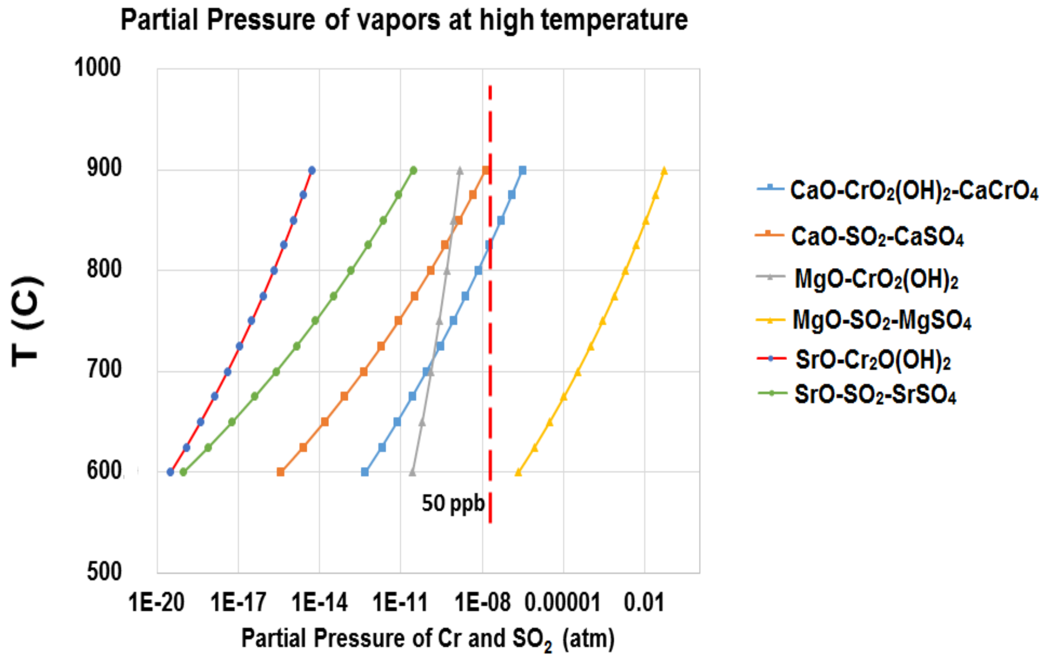
Surface Pretreated
Alumina forming Alloy

- Oxidation of alumina forming alloy leads to formation of mixed oxide scales and alumina subscale.
- Surface pretreatment leads to the formation of exclusive alumina scale only.

Ashish Aphale, Michael Reisert, Su Jeong Heo, Boxun Hu, Junsung Hong and Prabhakar Singh, 2020 (Manuscript ready to be submitted)

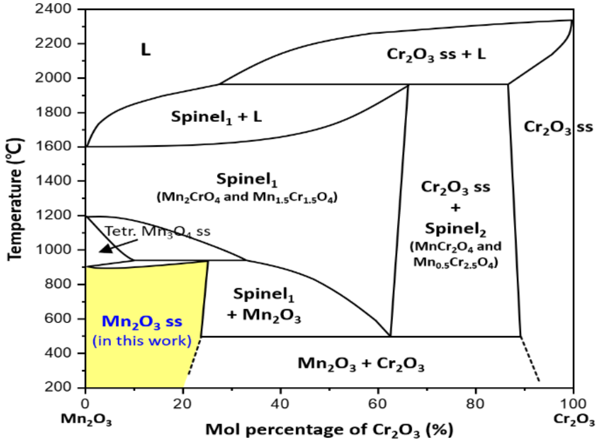
Capture of Gas phase SO_2 and Cr Species

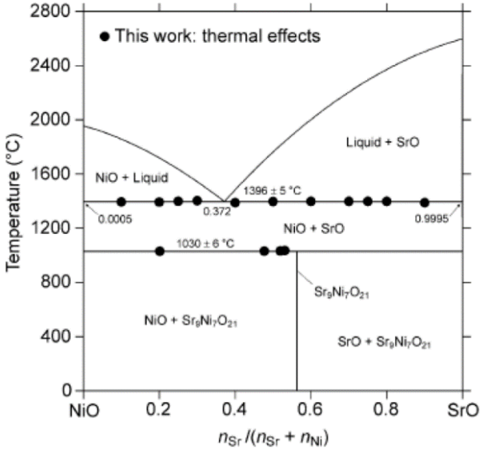


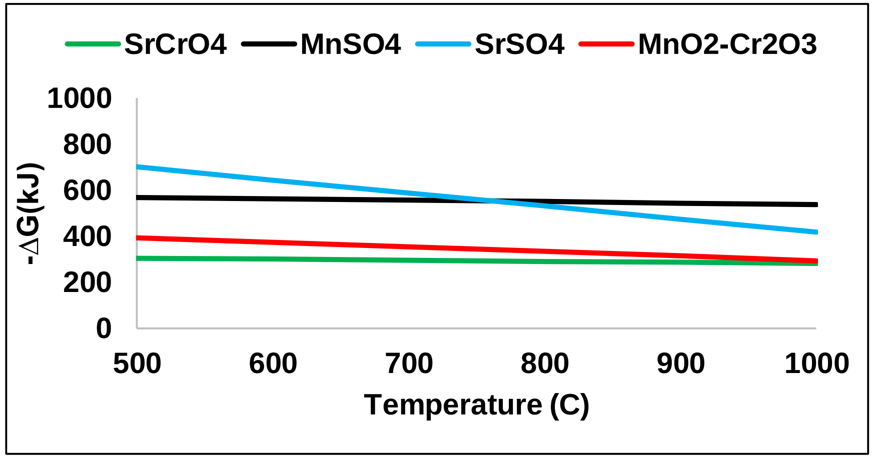


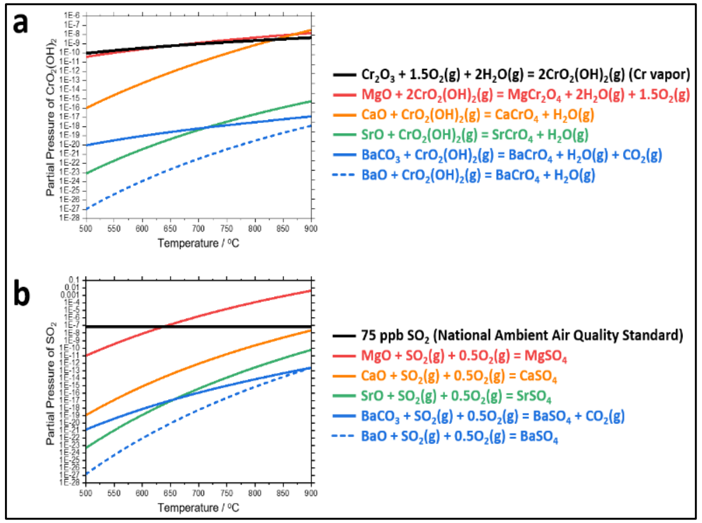
- **SrO is better than CaO, and MgO as a getter material for Cr and S capture.**
- **SrO can form $SrCrO_4$ and $SrSO_4$ compounds at extremely low concentrations of Cr and SO_2 vapors.**
- **Operational feasibility under wide temperature ranges.**

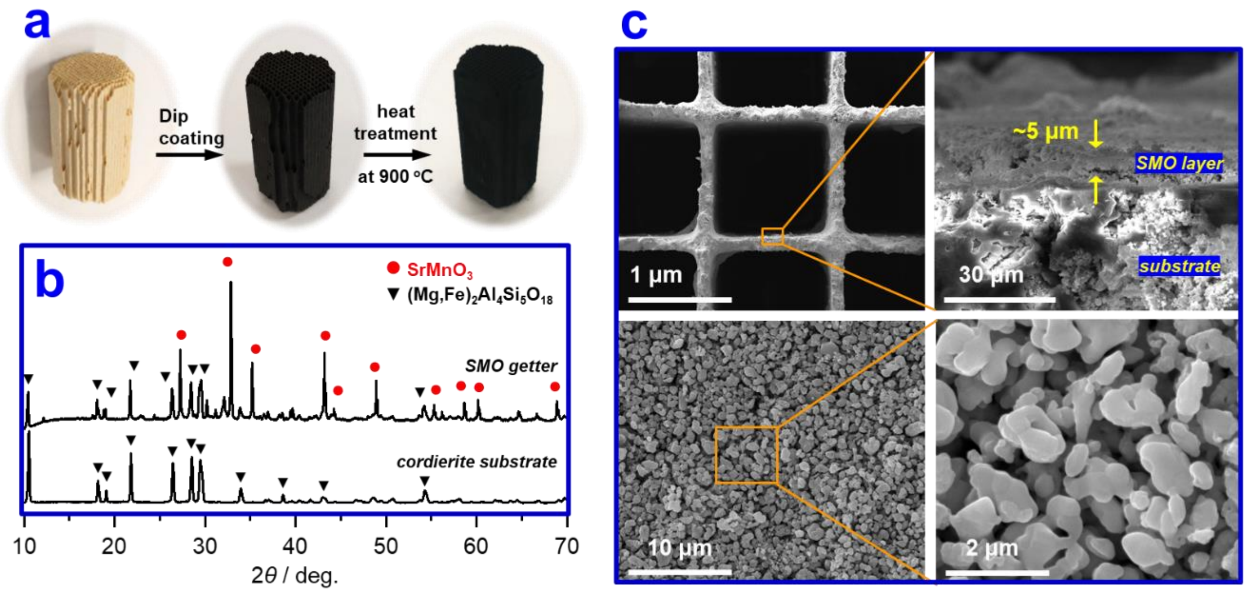
Advanced Getter: Materials Section and Fabrication







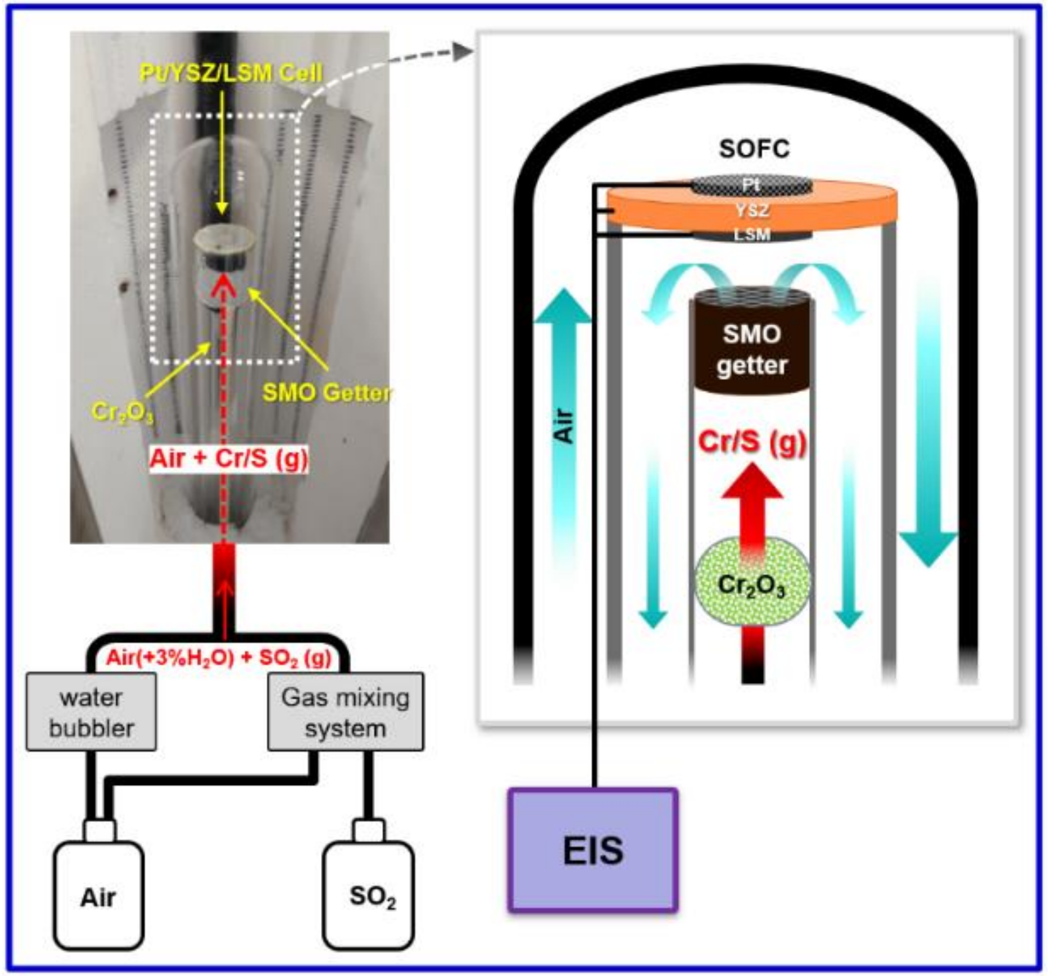




- ➢ Thermodynamic reaction feasibility (-ΔG) for capture of both S and Cr on select getter
- ➢ 5 um thick getter layer coating achieved on cordierite substrate

J Hong, AN Aphale, SJ Heo, B Hu, M Reisert, S Belko, P Singh, ACS applied materials & interfaces 11 (38), 34878-34888 (2019)

Getter Performance Validation



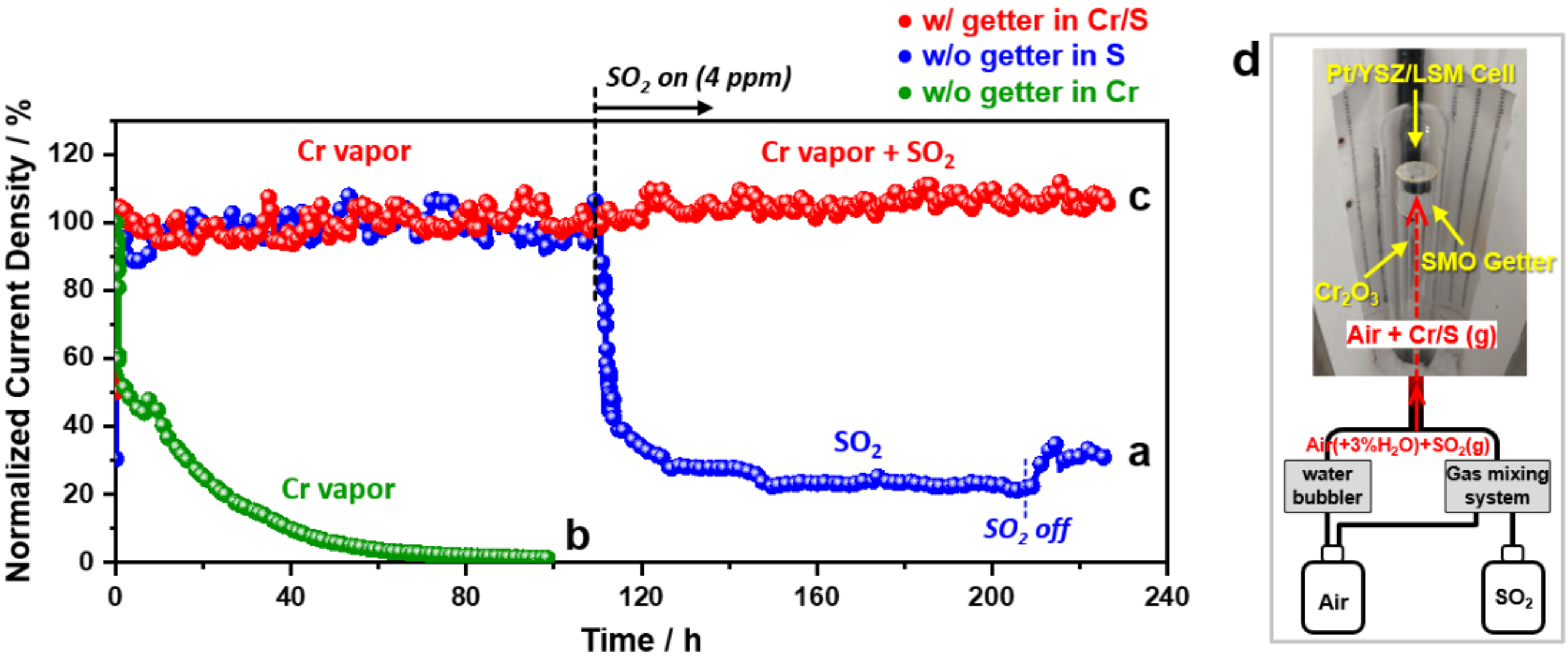
Experimental Matrix

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

Getter performance validated at 150 ppb-4 ppm range of SO_2 concentration

Long-term Electrochemical Validation of SMO Getter

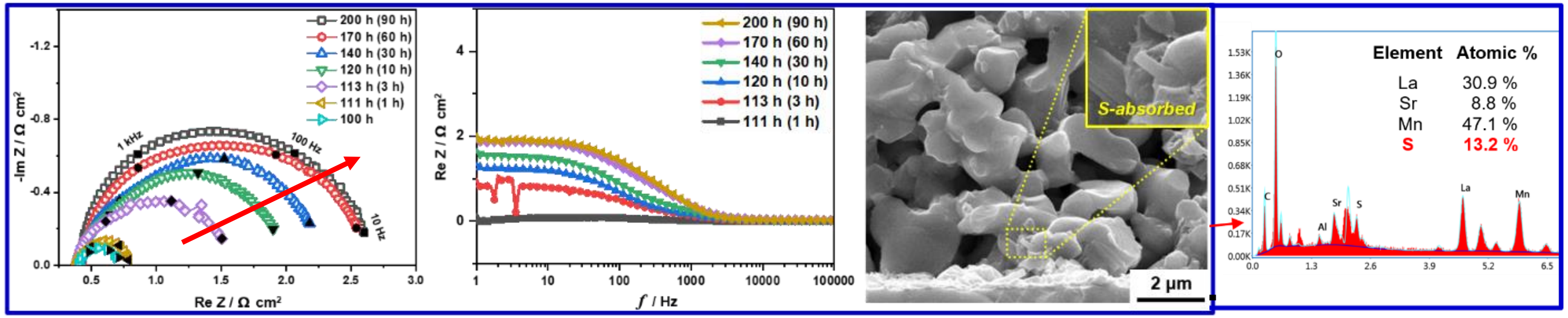
LSM performance when exposed to 4 ppm SO_2 and Cr containing air at 700C for 230 hrs.



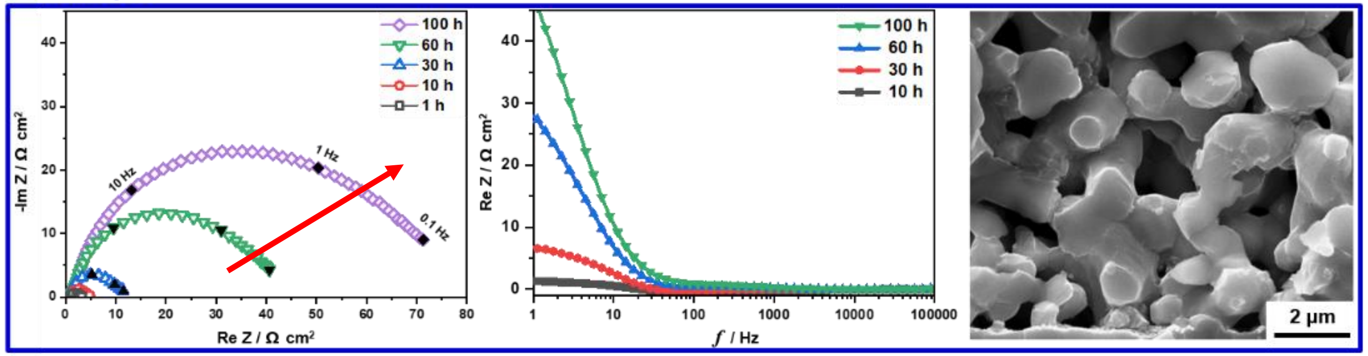
- Stable performance of LSM cathode observed in presence of SMO Getter
- Rapid degradation of cathode in Cr containing air observed.
- Exposure to only SO_2 (4 ppm) also leads to significant degradation of cathode in air. Partial recovery of the cathode is observed after removing SO2.

Electrochemical Performance and Morphology

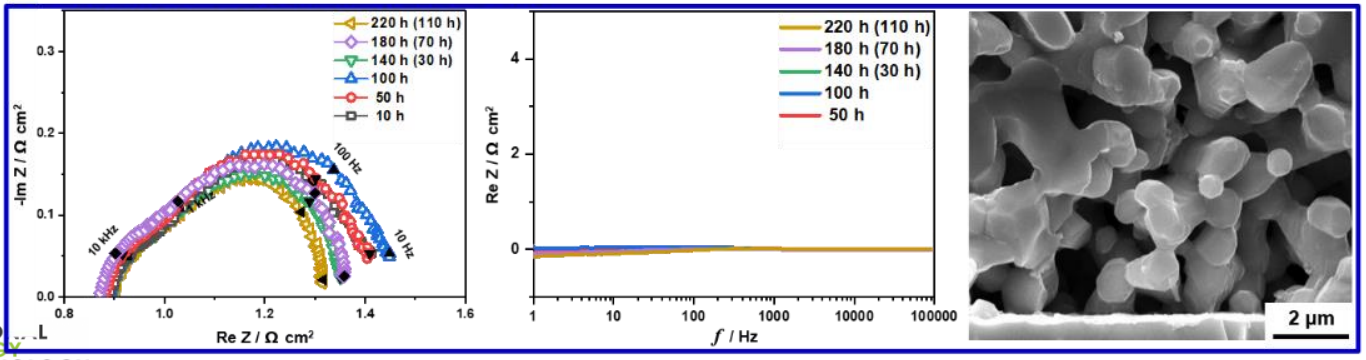
a. SO_2 gas



b. Cr vapor

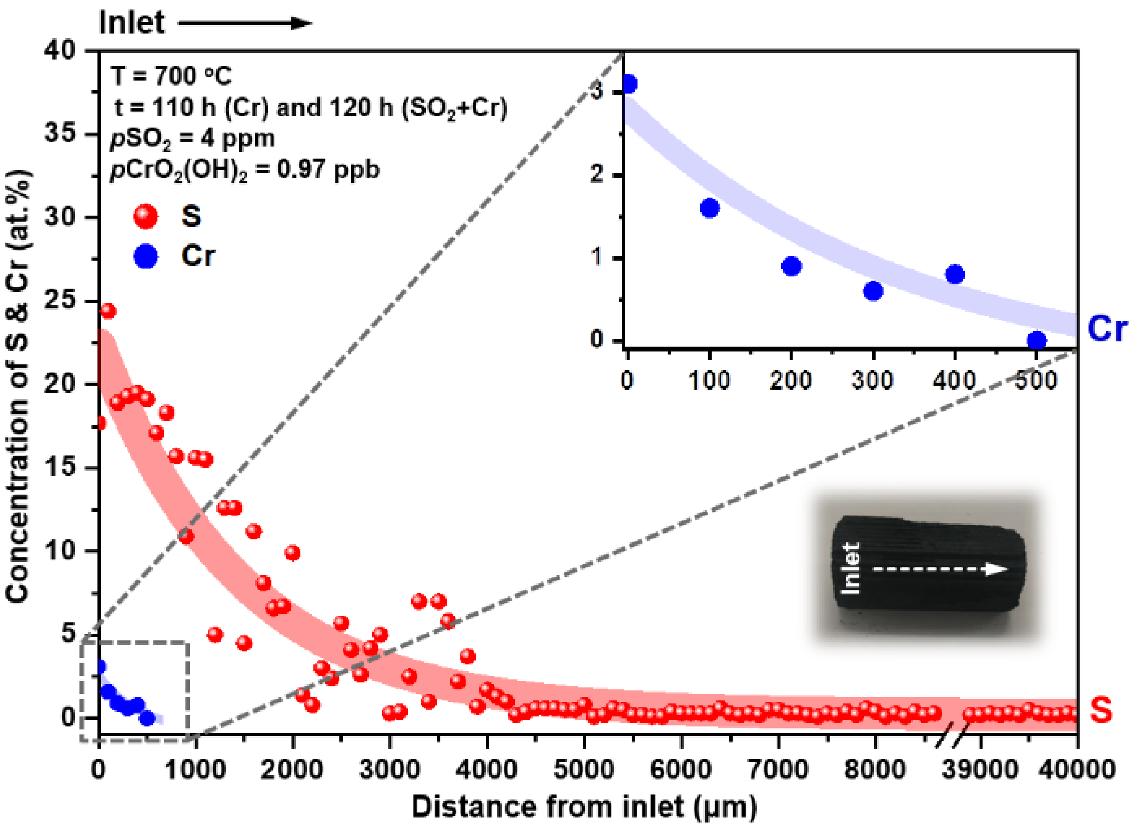


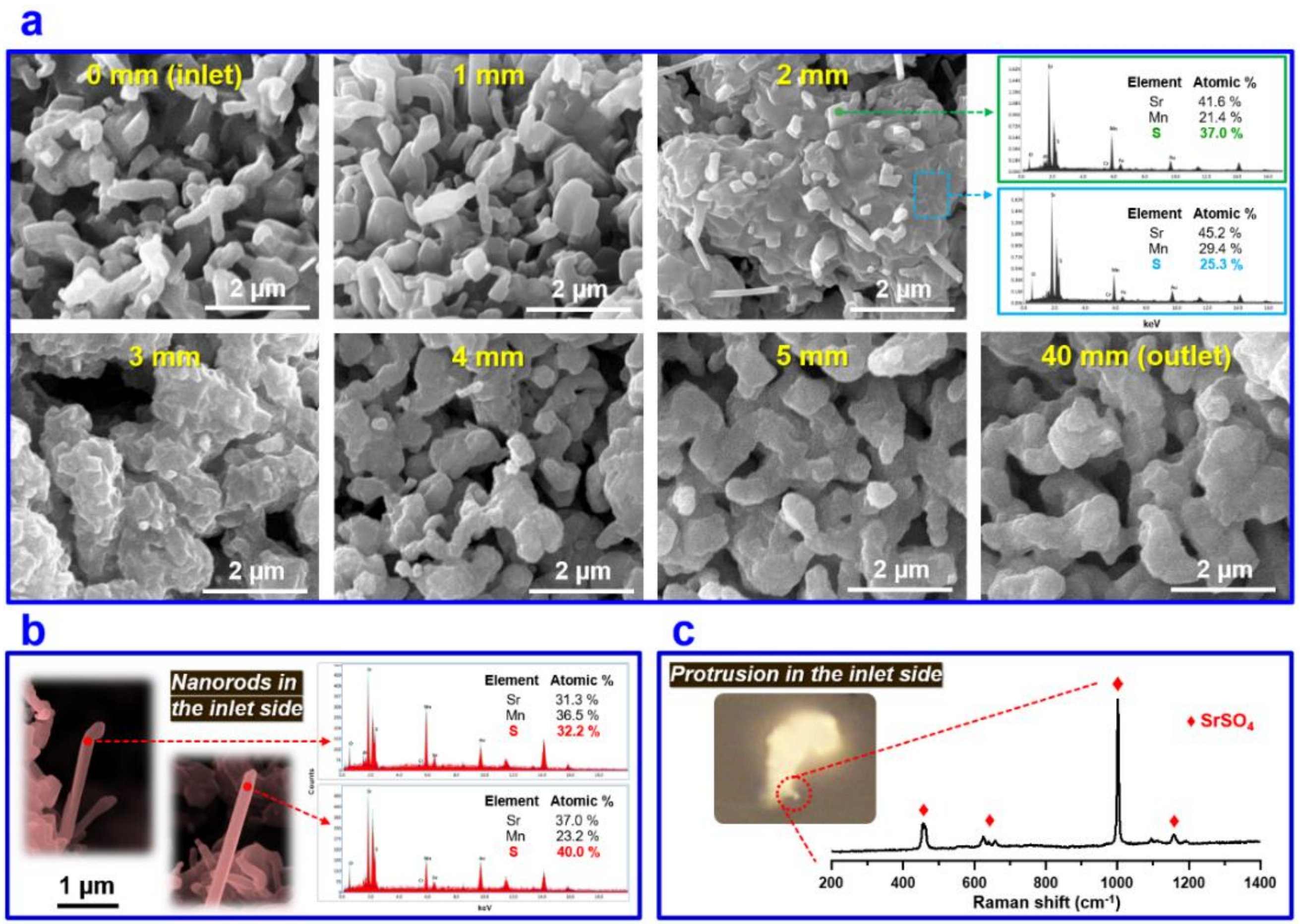
c. Cr vapor and SO_2 gas with SMO Getter



- Nyquist plot shows significant increase in polarization resistance for LSM when exposed to Cr and S containing air.
- Significant S concentration is observed at the LSM/YSZ interface.
- Presence getter demonstrates stable cathode performance and clean interface.

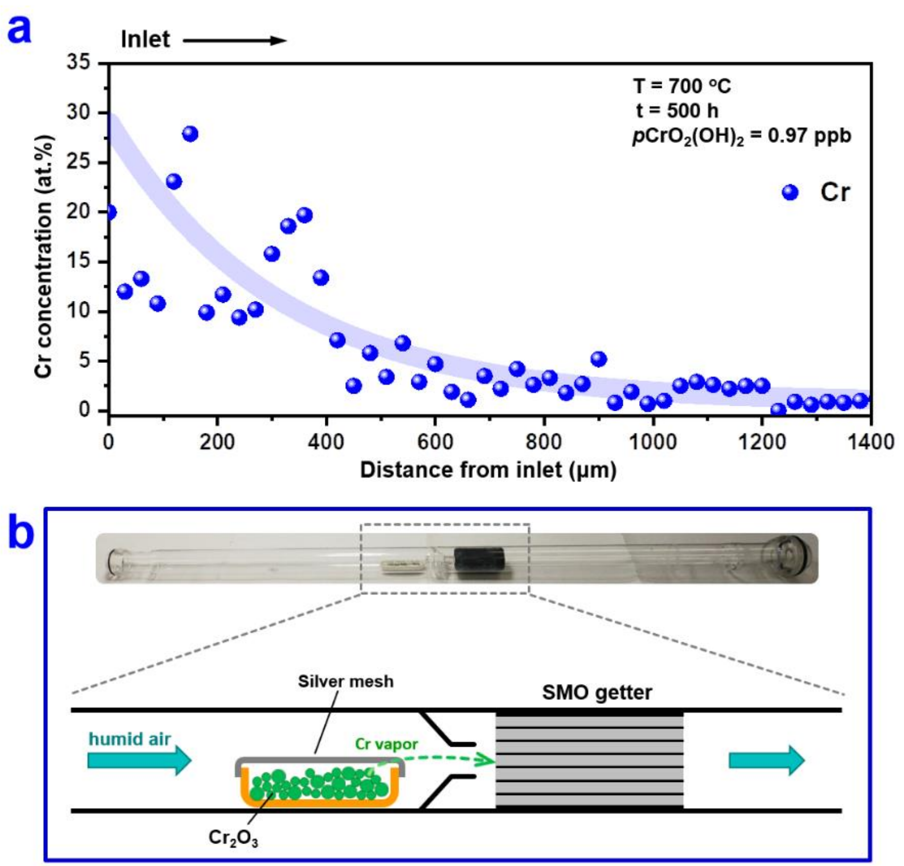
Cr and S Capture Profile on Posttest Getter

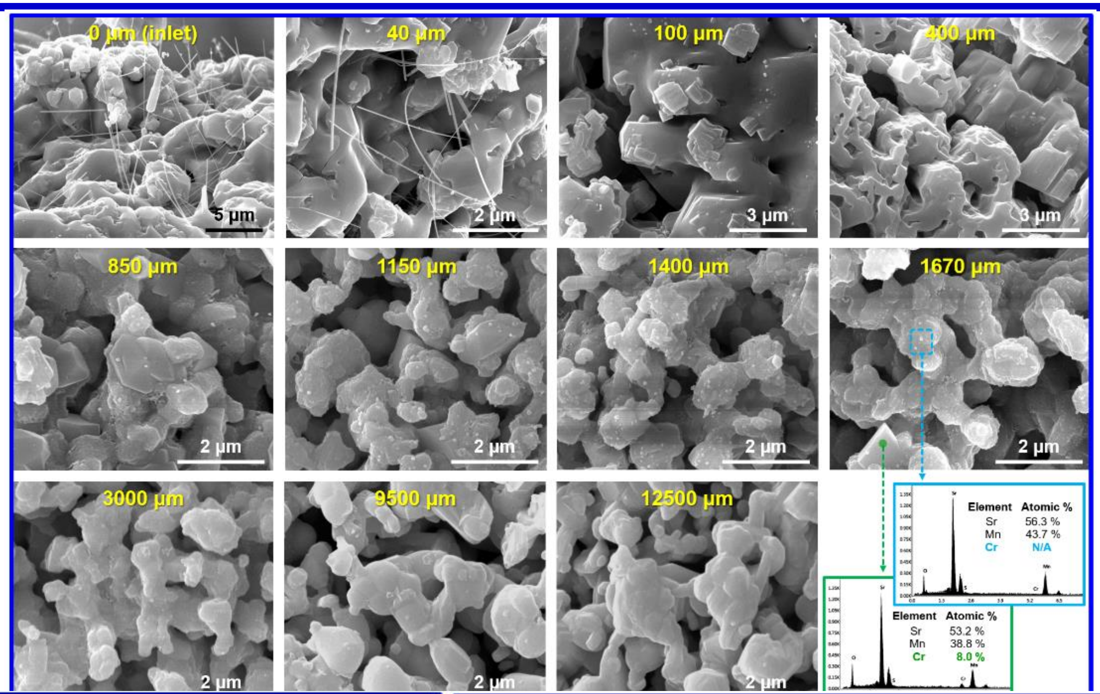


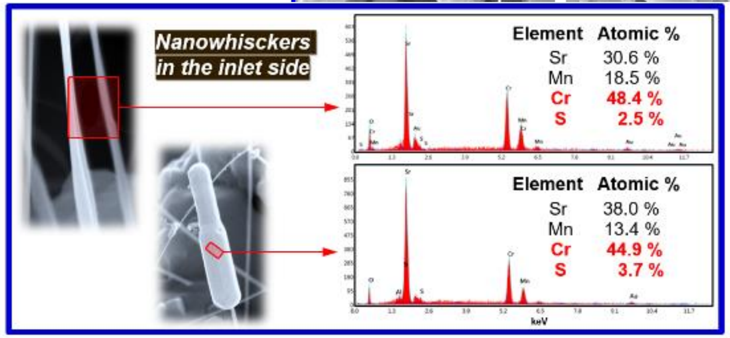


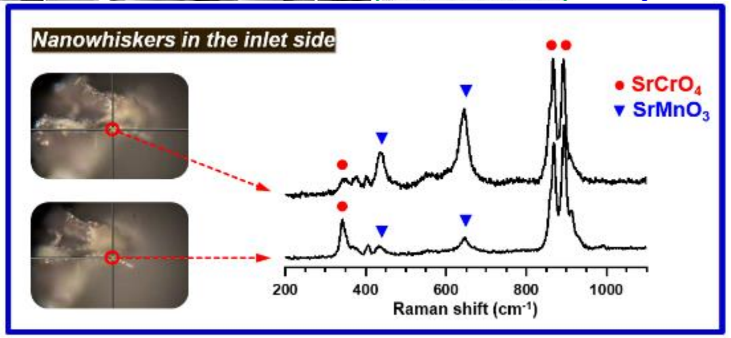
- Large concentrations of Cr and S appear at the getter inlet with no/negligible concentrations at the outlet.
- Raman spectroscopy reveals presence of SrSO4 formation on SMO getter.

Cr Capture Profile on SMO Getter (Transpiration)



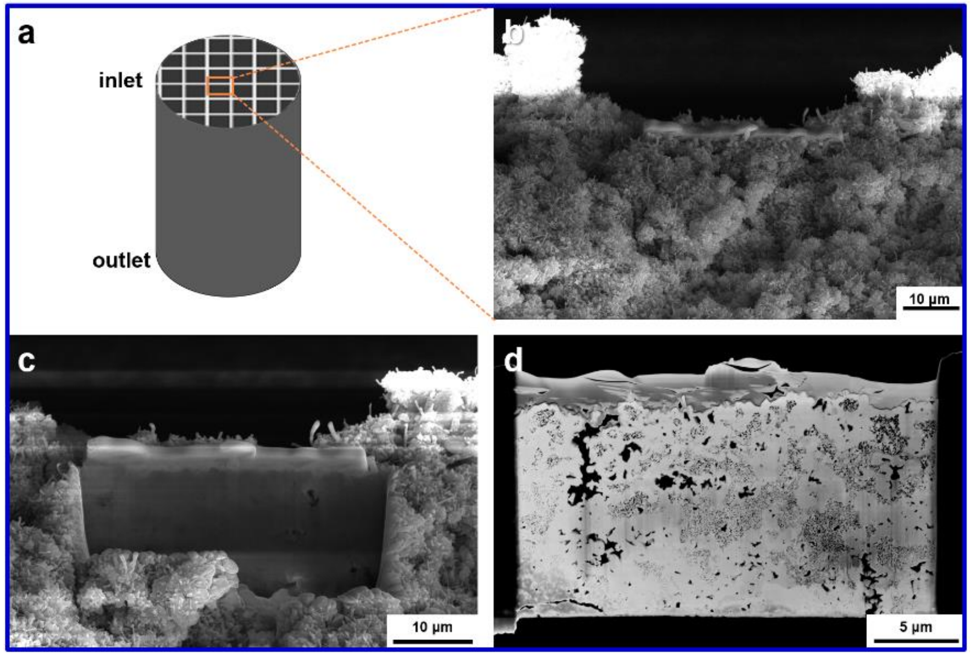


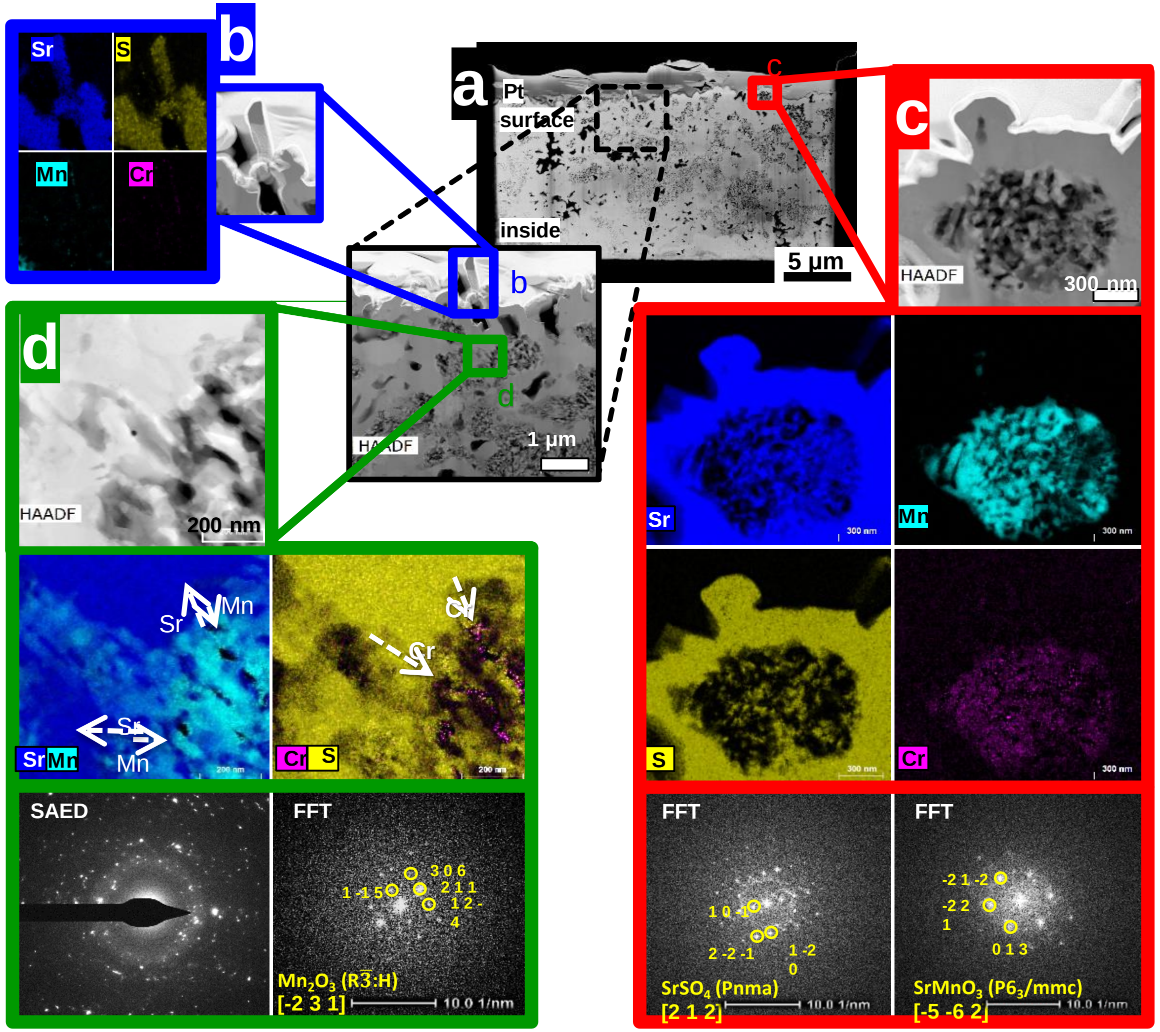


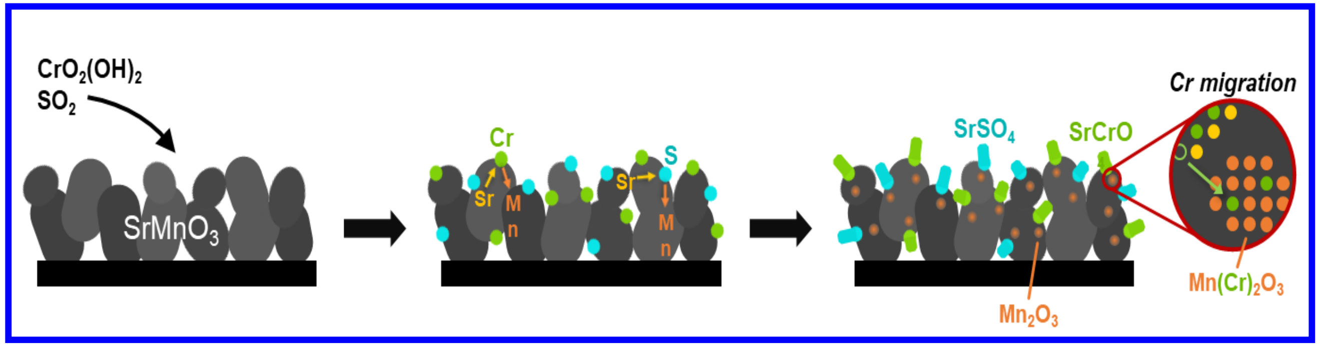


- Capture of Cr vapor demonstrated on SMO getter at 700C for 500 hrs.
- SEM-EDS spectra indicated significant concentrations of Cr (at.%) at the getter inlet.
- SEM micrographs show Cr capture at the inlet of getter
- Raman spectroscopy reveals formation of SrCrO4 on SMO getter.

FIB/STEM Analyses and Elemental Mapping of Posttest Getter

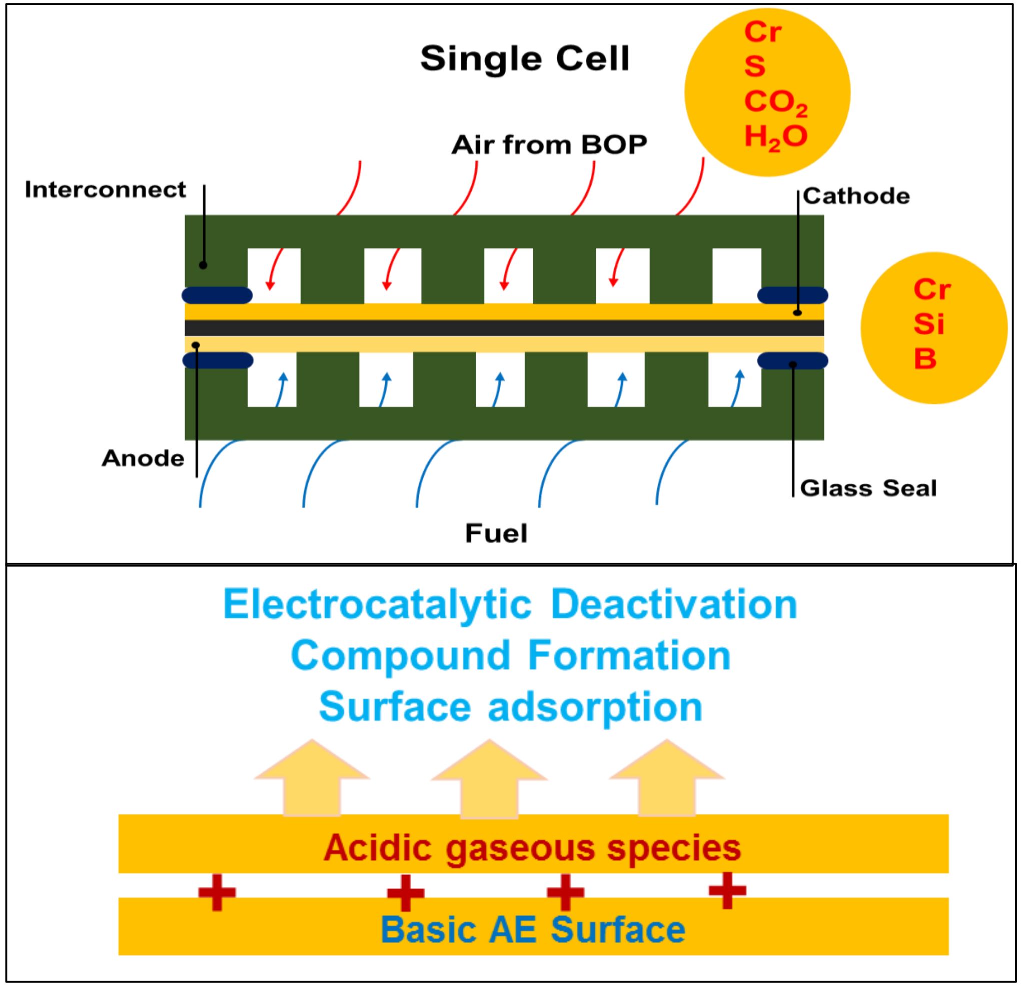




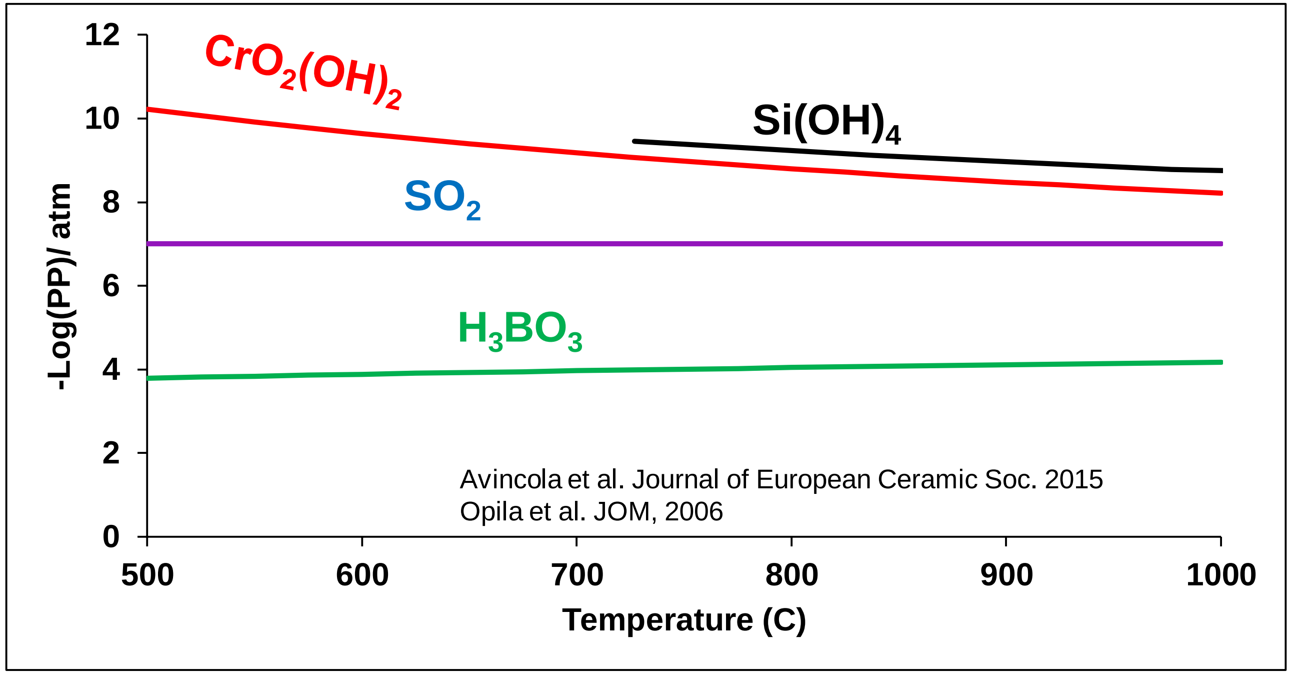


- Co-capture of Cr and S is observed from FIB/TEM analyses.
- Elemental mapping confirms presence of S and Cr with in SrMnOx getter.
- SMO getter provides continues absorption of contaminants by morphology elongation.

Multi-contaminant (trace) Cathode Air



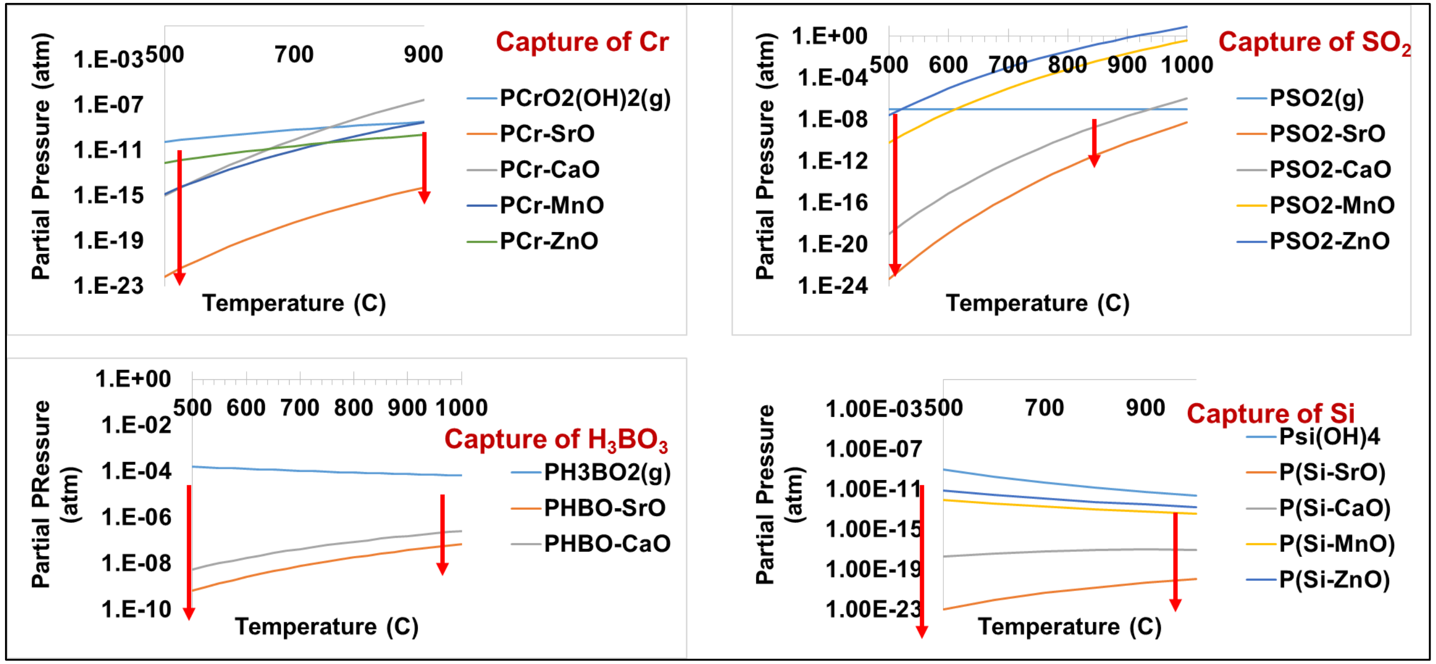
Thermodynamic Calculations

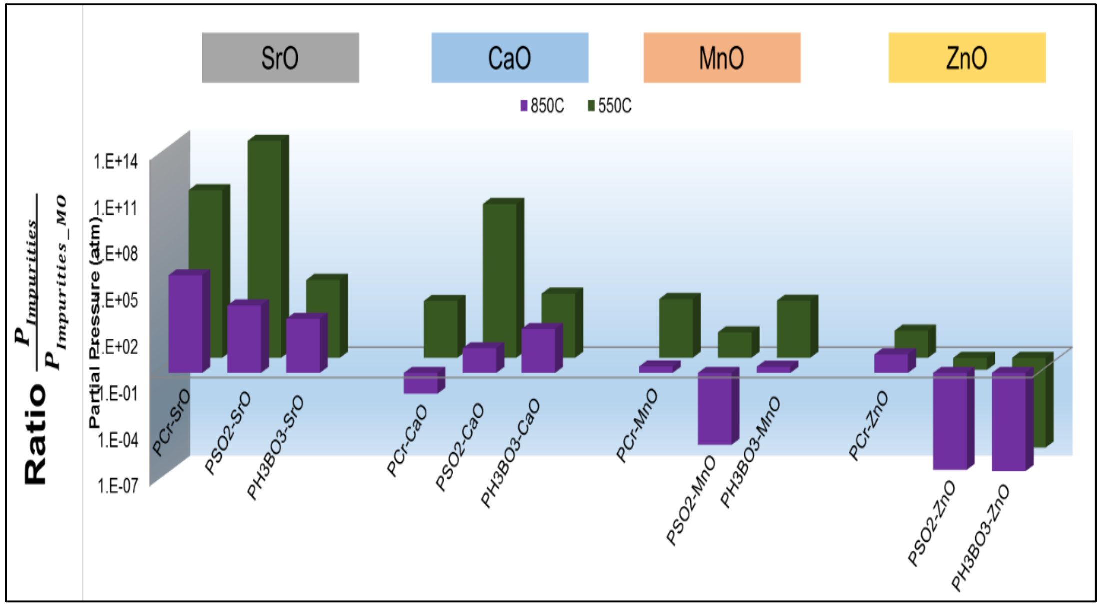


Air in fuel cell stack and system may also contain component derived impurities such as Cr (from metals and alloys) and Si, B, and alkali (from glass and insulation).

Getter selection for multi-contaminant systems

Capture of gas phase impurities by 'Getters' based on Gibbs free energy and equilibrium constant k. Unit solid phase activity assumed





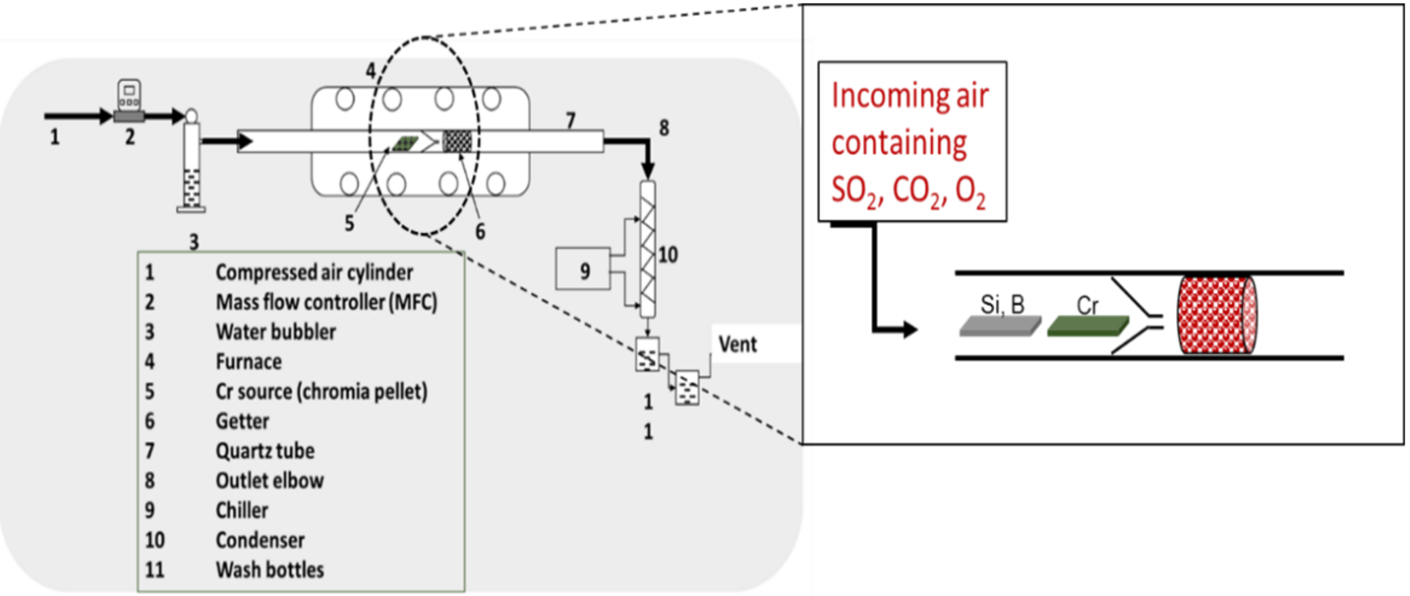
- **Significant vapor pressures exists from contaminants in ambient air as well as ones evaporating from alloys and glass based seals.**
- **Select oxides have shown potential to capture these contaminants under wide operating temperature range of 500-1000C in humidified air atmosphere.**
- **Transpiration and electrochemical validation tests setups have been established to understand multi-capture of contaminants under SOFC operating conditions.**

NATIONAL ENERGY TECHNOLOGY LABORATORY

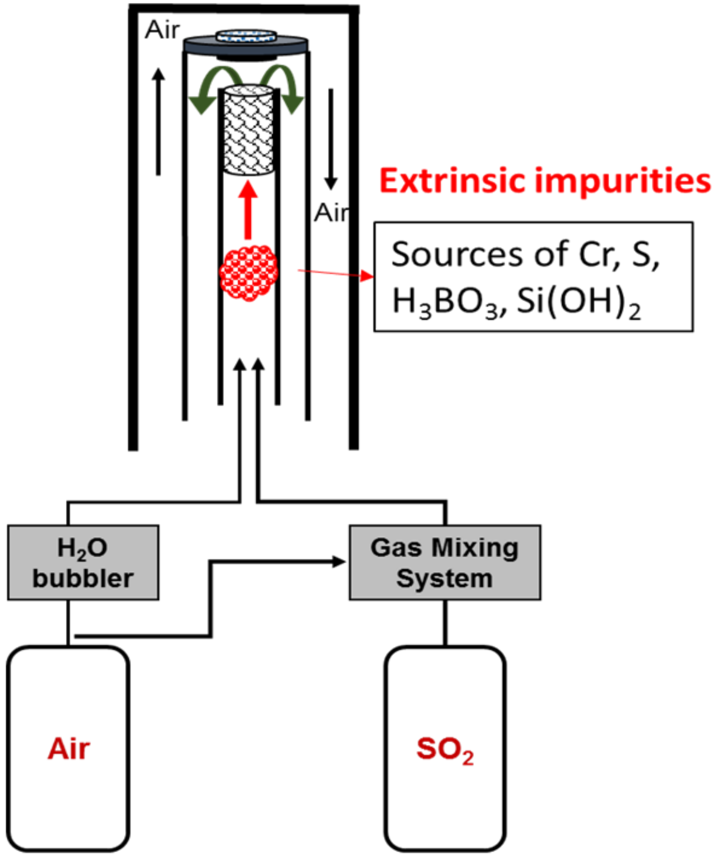
UCONN UNIVERSITY OF CONNECTICUT

Getter Validation Test: Multi-contaminant Capture

Transpiration tests

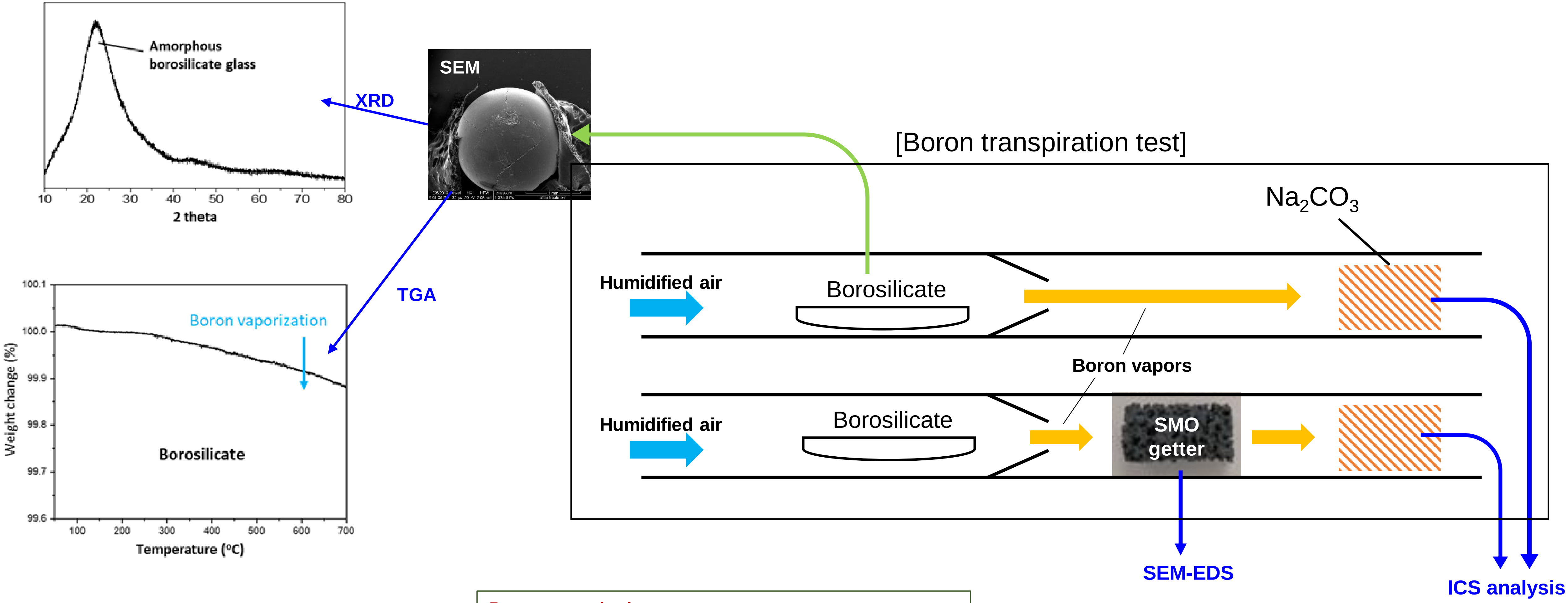


Electrochemical tests



Response parameters:
- Contaminants vapor pressure
- Getter validations
- Posttest getter morphology and chemistry
- Cathode performance: surface and cross section

Getter Validation Test: Boron Transpiration



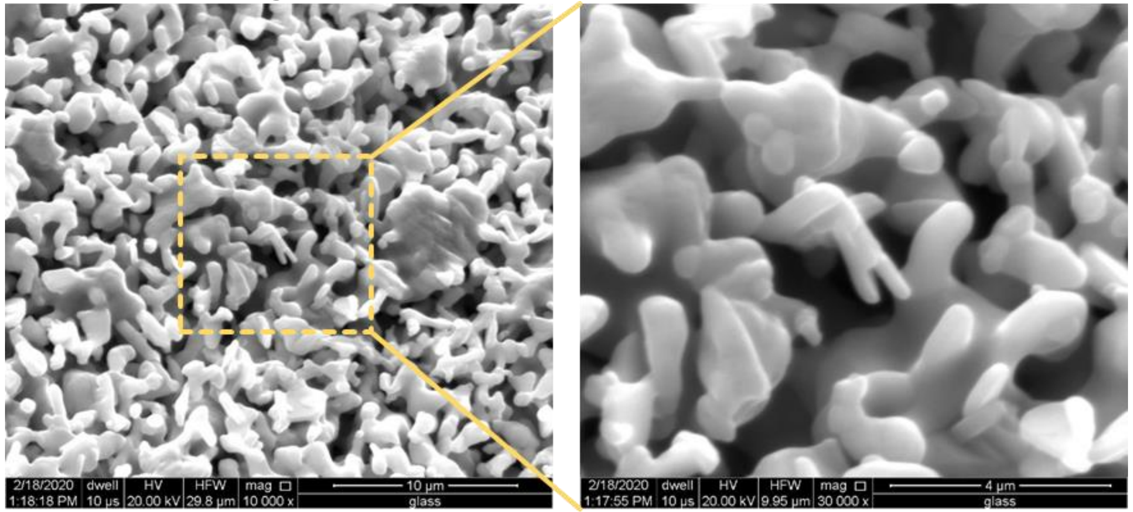
Boron transpiration test:
- **Borosilicate crystal structure**
- **Borosilicate vaporization over temperature**
- **Evaluation of boron getter ability of SMO**

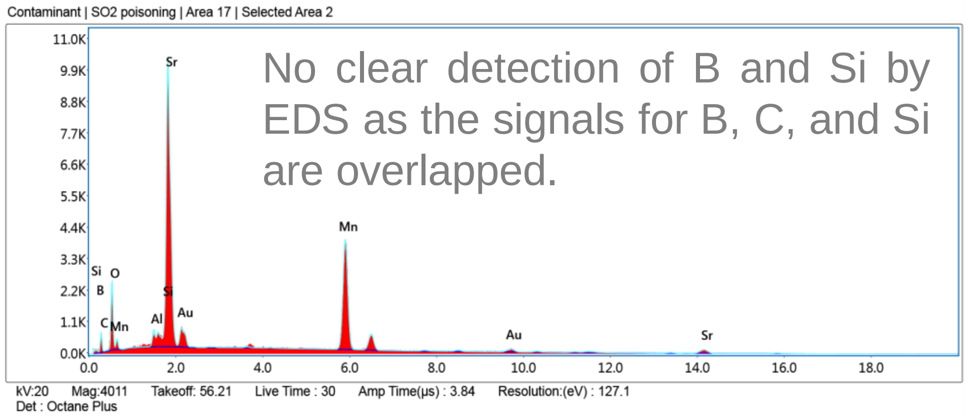
NATIONAL ENERGY TECHNOLOGY LABORATORY

UCONN UNIVERSITY OF CONNECTICUT

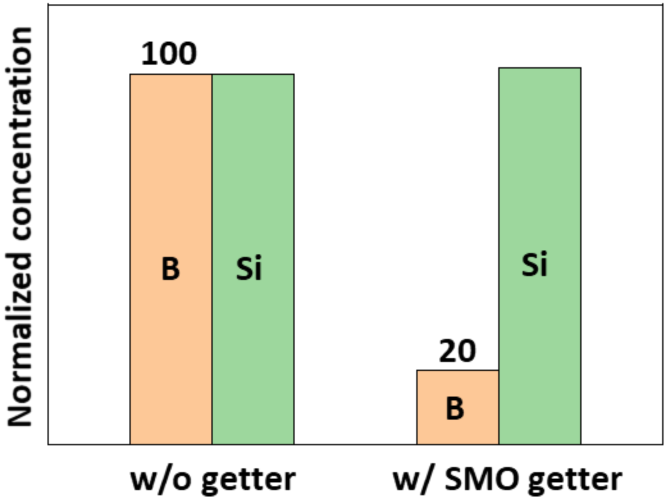
Getter Validation Test: Boron Vapor Capture

Inlet of the getter





No clear detection of B and Si by EDS as the signals for B, C, and Si are overlapped.



Boron getter ability of SMO:

- **No significant morphology change**
- **Not clear signals for B and Si by EDS**
- **Though, ICP showed the B concentration decrease with the SMO getter**
- **Further tests will be needed to clarify the result.**

NATIONAL ENERGY TECHNOLOGY LABORATORY

UCONN UNIVERSITY OF CONNECTICUT

Publications (Papers)

- Ashish Aphale, Michael Reisert, Su Jeong Heo, Junsung Hong, Boxun Hu, Amit Pandey and Prabhakar Singh, " Surface pretreatment of H214 alloy for minimization of Cr evaporation in SOFC power systems", Manuscript to be submitted, (2020).
- J Hong, A Aphale, SJ Heo, B Hu, M Reisert, S Belko, P Singh, "Strontium Manganese Oxide Getter for Capturing Airborne Cr and S Contaminants in High-Temperature Electrochemical Systems", ACS applied materials & interfaces, (2019), https://doi.org/10.1021/acsami.9b09677
- SJ Heo, J Hong, A Aphale, B Hu, P Singh, " Chromium Poisoning of La1-xSrxMnO3±δ Cathodes and Electrochemical Validation of Chromium Getters in Intermediate Temperature-Solid Oxide Fuel Cells", Journal of The Electrochemical Society 166 (13), F990-F995.
- Ashish Aphale, Junsung Hong, Boxun Hu and Prabhakar Singh, "Development and Validation of Chromium Getters for Solid Oxide Fuel Cell Power Systems", *J. Vis. Exp.* (147), e59623 (2019).
- J Hong, SJ Heo, AN Aphale, B Hu, P Singh, "H_2O Absorption Assisted Sr-Segregation in Strontium Nickel Oxide Based Chromium Getter and Encapsulation with SrCO3", *Journal of The Electrochemical Society* 166 (2), F59-F65, (2019).
- Ashish Aphale, B Hu, P Singh, "Low-cost Getters for Gaseous Chromium Removal in High-temperature Electrochemical Systems, *JOM*, 1-7 (2018)
- M Reisert, A Aphale, P Singh, "Solid Oxide Electrochemical Systems: Material Degradation Processes and Novel Mitigation Approaches", *Materials* 11(11), 2169 (2018)
- AN Aphale*, B Hu, M Reisert, A Pandey, P Singh, "Oxidation behavior and chromium evaporation from Fe and Ni base alloys under SOFC systems operation conditions, *JOM*, 1-8 (2018)
- A Aphale, MA Uddin, B Hu, SJ Heo, J Hong, P Singh, "Synthesis and stability of $Sr_xNi_yO_z$ chromium getter for solid oxide fuel cells", *Journal of Electrochemical Society*, 165(9), (2018)
- Hu, B.; Aphale, A. N.; Reisert, M.; Belko, S.; Marina, O. A.; Stevenson, J. W.; Singh, P. Solid Oxide Electrolysis for Hydrogen Production: From Oxygen Ion to Proton Conducting Cells. *ECS Trans.* 2018, *85* (10), 13–20. - published April 2018
- MA Uddin, AN Aphale, B Hu, U Pasaogullari, P Singh, "In-Cell Chromium Getters to Mitigate Cathode Poisoning in SOFC Stack", ECS Transactions 78 (1), 1039-1046, 2017
- B Hu, AN Aphale, C Liang, SJ Heo, MA Uddin, P Singh, "Carbon Tolerant Double Site Doped Perovskite Cathodes for High-Temperature Electrolysis Cells", ECS Transactions 78 (1), 3257 (2017)
- Yeong-Shyung Chou, Jung Pyung Choi, Jeffry W Stevenson, Chiying Liang, Boxun Hu, Weyshla Rodriguez, Ashish N Aphale, Prabhakar Singh "Performance and Microstructure of a Novel Cr-Getter Material with LSCF-Based Cells in a Generic Stack Test Fixture" ECS Transactions 78 (1), 1047-1054 (2017)
- B Hu, S Krishnan, C Liang, SJ Heo, AN Aphale, R Ramprasad, P Singh, "Experimental and thermodynamic evaluation of La1− xSrxMnO3±δ and La1− xSrxCo1− yFeyO3− δ cathodes in Cr-containing humidified air", International Journal of Hydrogen Energy 42 (15), 10208-10216, 2017
- C Liang, B Hu, A Aphale, M Venkataraman, MK Mahapatra, P Singh, "Mitigation of chromium assisted degradation of LSM cathode in SOFC", ECS Transactions 75 (28), 57, 2017
- MA Uddin, A Aphale, B Hu, SJ Heo, U Pasaogullari, P Singh, "Electrochemical validation of In-cell chromium getters to mitigate chromium poisoning in SOFC stack" Journal of The Electrochemical Society 164 (13), F1342-F1347, 2017
- 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 268, 404-413, 2014
- 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, 2014

Publications (Books and Presentations)

- **Book Chapter:** M Reisert, A Aphale*, P Singh, “Observations on Accelerated Oxidation of a Ferritic Stainless Steel Under Dual Atmosphere Exposure Conditions”, in book Energy Technology, 273-281, (2019).
- **Book Chapter:** Ashish Aphale, Chiying Liang, Boxun Hu and Prabhakar Singh, “Cathode Degradation from Airborne Contaminants in Solid Oxide Fuel Cells: A Review”, in book: Solid Oxide Fuel Cell Lifetime and Reliability, pp 101-119 (2017). DOI: 10.1016/B978-0-08-101102-7.00006-4
- Prabhakar Singh, Boxun Hu, Ashish Aphale, Junsung Hong, Su Heo, PACRIM 13, 2019, Okinawa, Japan (Invited talk)
- Junsung Hong, Ashish Aphale, Su Jeong Heo, Boxun Hu, Michael Reisert, and Prabhakar Singh, “Capture of Trace Airborne Impurities and Mitigation of Electrode Poisoning in SOFC" US DOE SOFC Review Meeting, Washington 2019
- Boxun Hu, Seraphim Belko, Ashish Aphale, Na Li, Junsung Hong, and Prabhakar Singh. “Carbon Resistant High Entropy Alloy Anode for Internal Reforming of Hydrocarbons in SOFC" US DOE SOFC Review Meeting, Washington 2019
- Michael Reisert, Ashish Aphale, Nilesh Dale, Motoki Yaginuma, Takeshi Shiomi, and Prabhakar Singh, “Hydrogen-assisted Corrosion of Stainless Steels in Dual Atmosphere Exposure Conditions" US DOE SOFC Review Meeting, Washington 2019
- Rajesh Kumar, Boxun Hu, Ashish N. Aphale, Prabhakar Singh, and Avinash M. Dongare "ENERGETICS OF CARBON DEPOSITION ON METALLIC SURFACES" US DOE SOFC Review Meeting, Washington 2019
- Ashish Aphale, Md Aman Uddin, Junsung Hong, Justin Webster, Su Jeong Heo, Boxun Hu, Prabhakar Singh, “Chromium Evaporation from Metallic Components and Cathode Poisoning in SOFC”, TMS Annual Meeting & Exhibition, Phoenix, Arizona (2018)
- Ashish Aphale, Md Aman Uddin, Boxun Hu, Justin Webster, Su Jeong Heo, Junsung Hong and Prabhakar Singh, “Role of Select Minor Airborne Impurities on SOFC Cathode Degradation: Computational Simulation and Experimental Studies”, 42nd ICACC, Daytona, FL Jan 2018
- Junsung Hong, Su Jeong Heo, Ashish N. Aphale, Boxun Hu, Prabhakar Singh, "Cathode Poisoning and Mitigation in the Presence of Combined Cr and S Contaminants in SOFC" 2019 TMS, San Antonio, Texas.
- Ashish Aphale, Md Aman Uddin, Boxun Hu, Justin Webster, Su Jeong Heo, Junsung Hong and Prabhakar Singh, “Role of Select Minor Airborne Impurities on SOFC Cathode Degradation: Computational Simulation and Experimental Studies”, 42nd ICACC, Daytona, Fl Jan 2018 (Talk)
- Ashish Aphale, Md Aman Uddin, Boxun Hu, Justin Webster, Su Jeong Heo, Junsung Hong and Prabhakar Singh, “Cost Effective Cr Getters for Mitigation of Cathode Poisoning in SOFC Power Systems”, Fuel Cell Seminar, Long Beach, CA, Nov 2017 (Talk)
- A. N. Aphale, M. A. Uddin, B. Hu, C. Liang, J. Webster, Junsung Hong and P. Singh, “Electrochemical validation of “In-cell Cr Getter” for the mitigation of cathode poisoning in SOFC power systems. Presented at the 18th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting (DOE/NETL), Pittsburg, July 2017
- Chiying Liang, Boxun Hu, Ashish Aphale, Mahesh Venkataraman, Manoj Kumar Mahapatra and Prabhakar Singh, Mitigation of Chromium Assisted Degradation of LSM Cathode in SOFC, ECS Trans. 2017 75(28): 57-64.
- Chiying Liang, Boxun Hu, Ashish Aphale, Mahesh Venkataraman, Manoj Kumar Mahapatra and Prabhakar Singh, Mitigation of Chromium Assisted Degradation of LSM Cathode in SOFC, ECS. 2016

Conclusions

- Gas phase extrinsic and intrinsic impurities originate from incoming air, cell/stack and BOP components.
- Significant degradation of SOFC cathode has been observed in the presence of airborne impurities.
- Cathode degradation mechanisms have been identified and experimentally validated.
- Cr capture using "Getters" has been successfully demonstrated from In-cell and BOP sources.
- Getters have also confirmed combined capture of Cr and SO2 impurities present in air.
- Characterization of experimentally tested getters reveal high concentration of S and Cr near the inlet only.
- Novel getters are being tested for validation of multiple contaminant capture (Cr, S, Si and B) in air.

Application of "Getters" provide a cost-effective method of mitigating electrode poisoning and performance degradation in high-temperature electrochemical systems:

SOFC ↔ SOEC ↔ P-SOEC ↔ OTM

Acknowledgements

- Financial support from the US DOE (Office of Fossil Energy)
- Dr. Rin Burke for guidance
- UConn for providing laboratory support

NATIONAL ENERGY TECHNOLOGY LABORATORY

UCONN UNIVERSITY OF CONNECTICUT

Thank you

Supporting slides

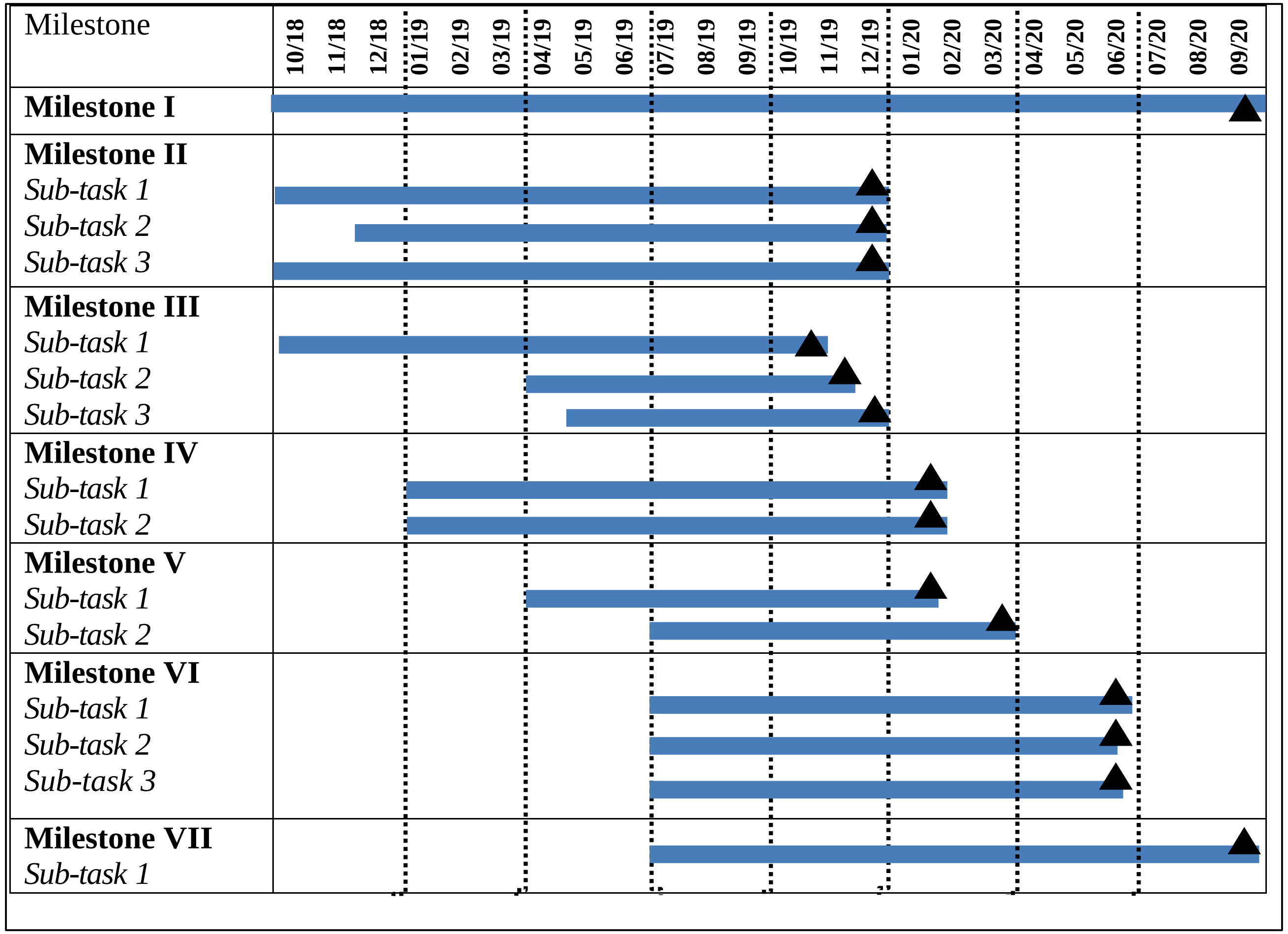
Milestones of Project 1

Task / Subtask Number	Deliverable Title	Anticipated Delivery Date
1.0	Project Management Plan	Update due 30 days after award. Revisions to the PMP shall be submitted as requested by the Project Officer.
2.0	Getter materials identification, selection and synthesis	30 days after completion of task 2
2.1	Rational section of candidate getter materials	
2.2	Getter materials synthesis	
2.3	Thermodynamic modeling to screen potential getter materials	
3.0	Synthesis of HSA nano-porous coating and optimized getter architecture	30 days after completion of task 3
3.1	High surface area (HSA) getter powder synthesis	
3.2	Characterization of synthesized getter materials	
3.3	Identification of materials properties and development of coating technique	
4.0	Getter validation for combined capture of gas phase impurities	30 days after completion of task 4 and three months after task 3
4.1	Electrochemical validation of getters	
4.2	Posttest getter parametric study	
5.0	Getter design optimization using computational flow analysis	30 days after completion of task 5
5.1	Getter optimization using computational modeling	
5.2	Development of optimal coating and getter design	
6.0	Scale-up and long-term testing under SOFC systems conditions	30 days after completion of task 6 and three months after task 5
6.1	Materials scale-up to meet large systems requirements	
6.2	Identification and development of quality control procedures	
6.3	Independent validation of getters by SOFC industrial partners	
7.0	Post-test characterization and mechanistic understanding	30 days after completion of task 7 and three months after task 6

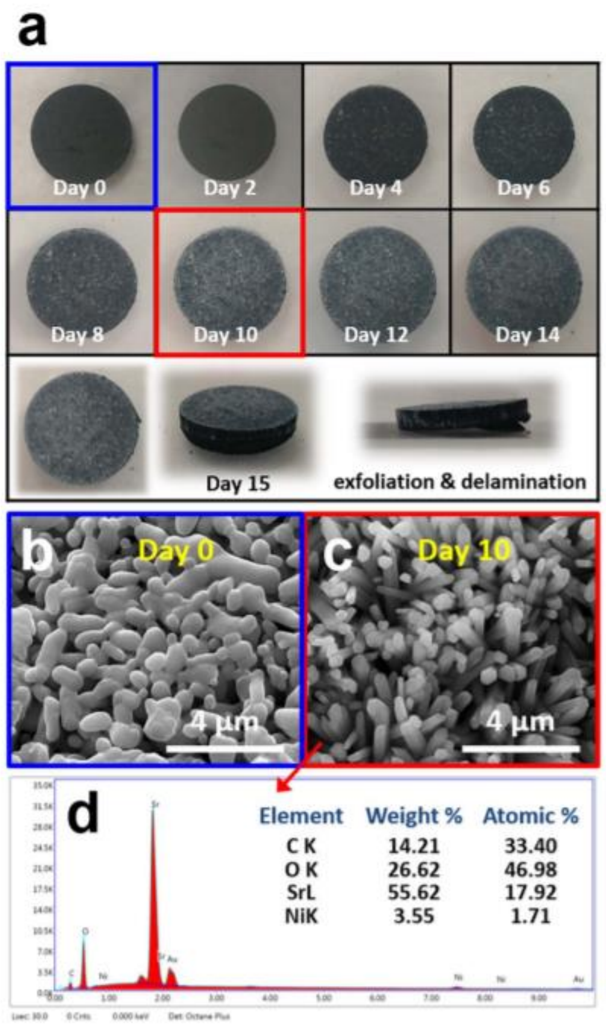
Milestones of Project 2

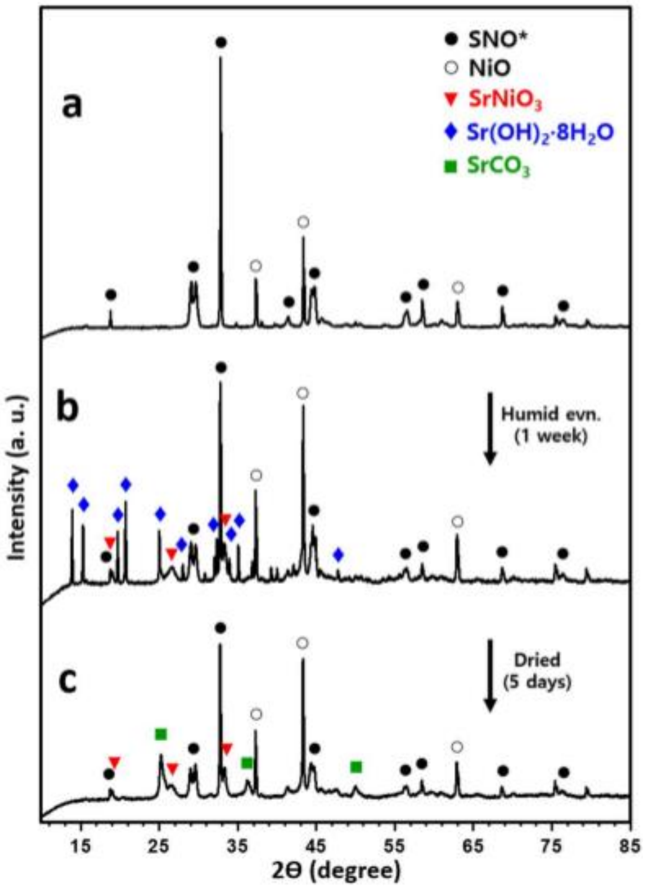
MILESTONE LOG			
Task/ Subtask #	Milestone Title/Description	Planned Completion Date	Actual date & Current Status
1.1	Establishment of program priorities with program manager	12/31/2107	12/31/2017 Milestone meet
2.1-2.3	Select target HEA anode materials	3/30/2019	In process, Close to target
3.1-3.2	Identification of carbon formation conditions	03/30/2019	In process
4.1-4.2	Obtain optimal activation energy.	2/28/2019	In process
5.1-5.3	Stable CH_4 reforming is achieved.	6/30/2019	In process
6.1-6.3	Achievement of large-scale synthesis.	0930/2019	25 gram batch is achieved.
7.1-7.2	Characterization of posttest materials and long-term degradation mechanisms	09/30/2019	In process
8.1-8.2	Documentation, Reporting, and Publication	9/30/2019	In process
9.1	Intellectual property and technology transfer	9/30/2019	In process

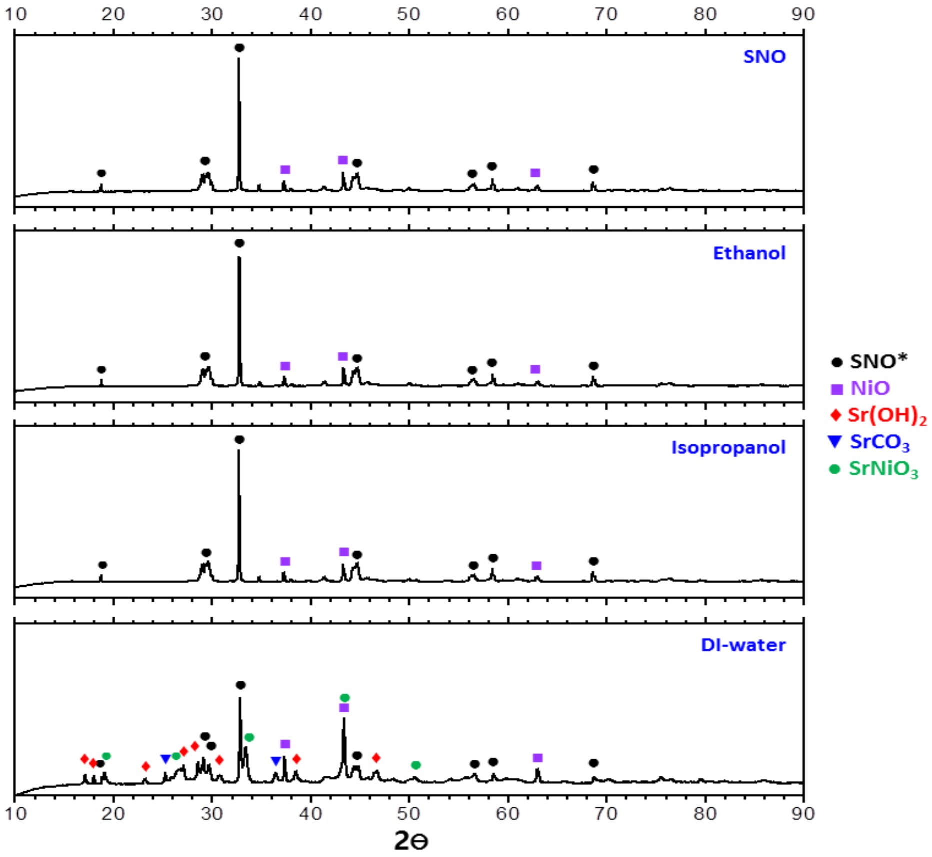
Project schedule (which format you want to use?)



Long-term stability of SrNiOx Getter in Ambient Air





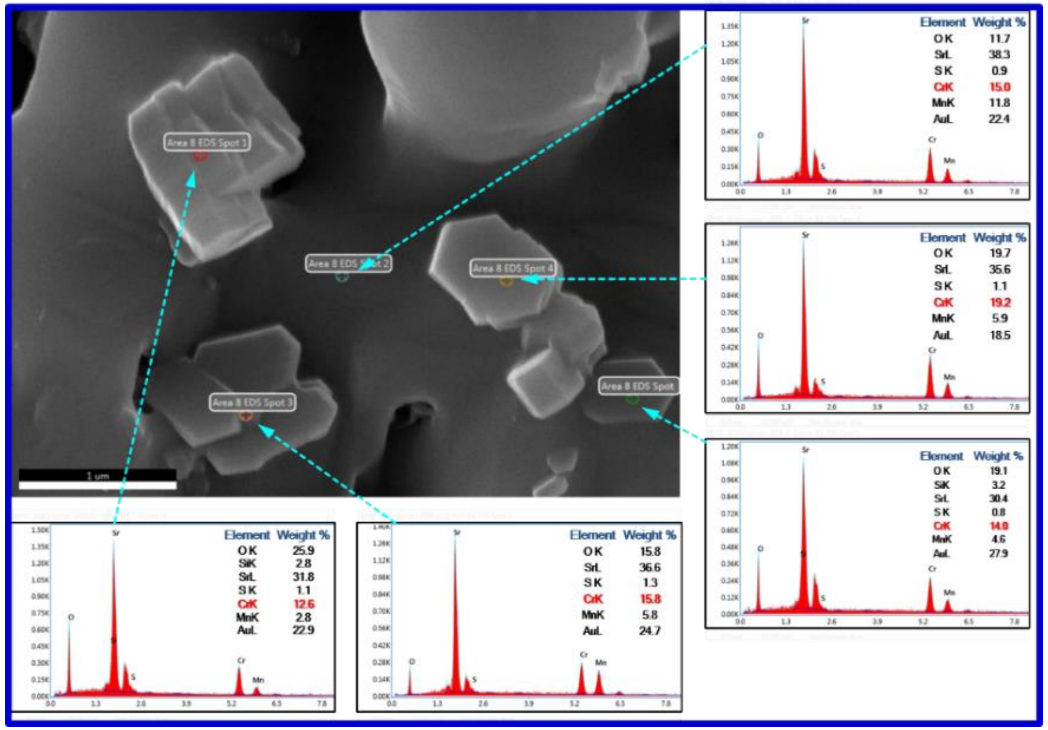


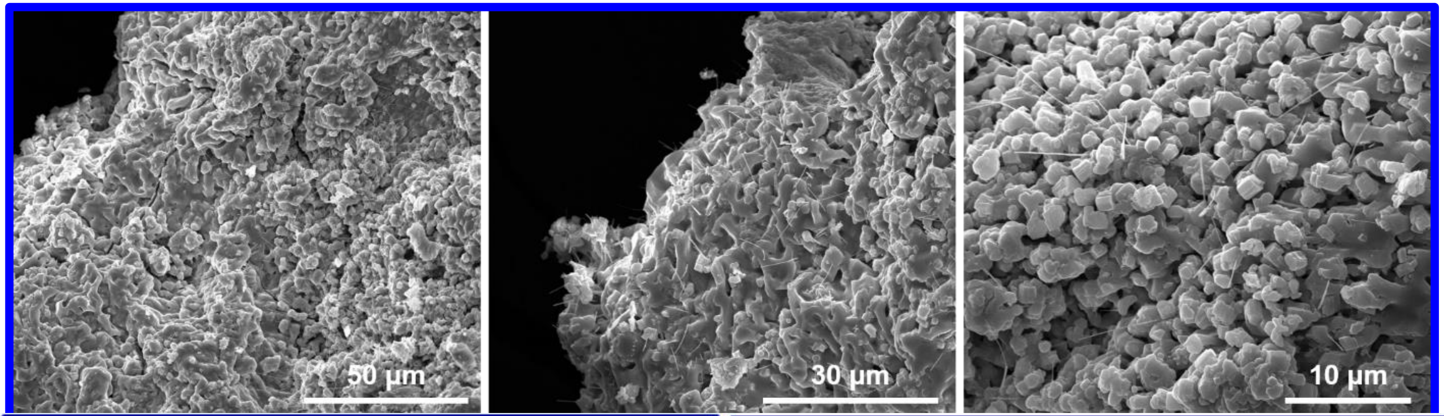
SNO phase has tendency for being hygroscopic accompanied by volume expansion

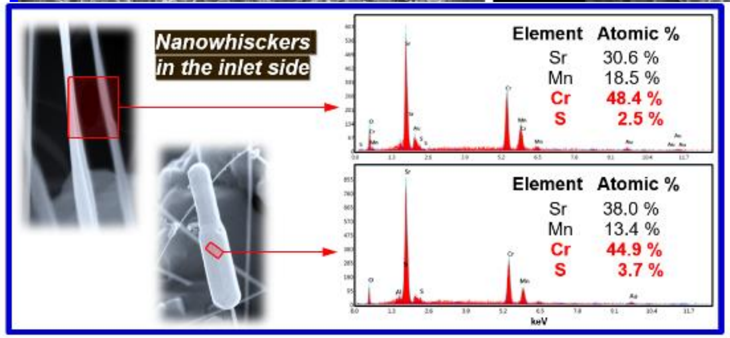
$Sr_9Ni_7O_{21} + xH_2O \rightarrow 2Sr(OH)_2.8H_2O + 7SrNiO_3$

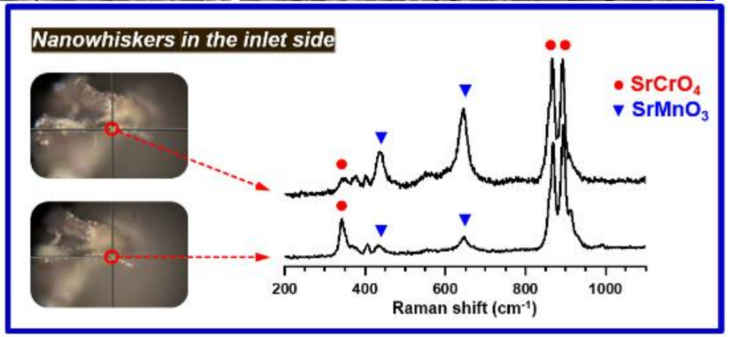
J. Hong et al, J Electrochem. Soc., 166(2), 2019

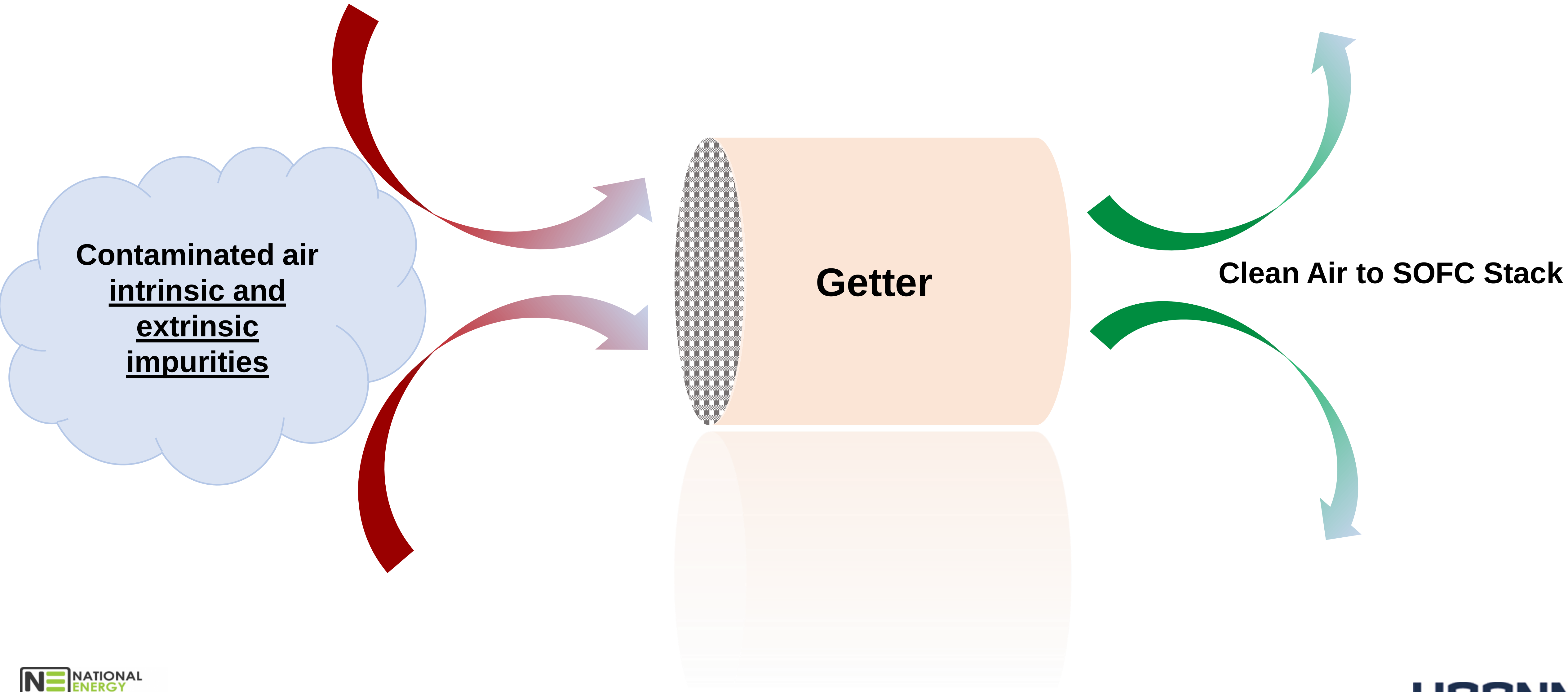
500 hrs Getter Transpiration Test





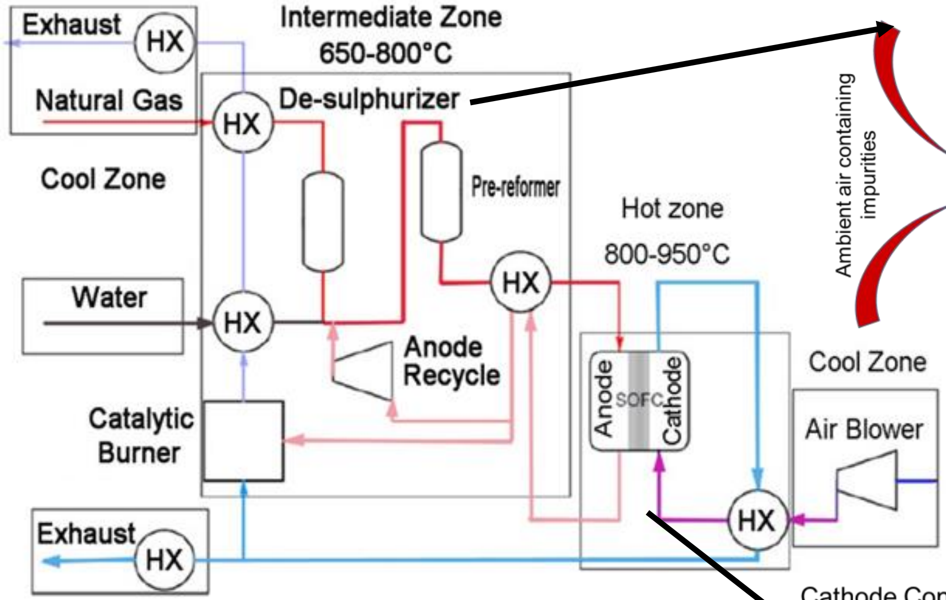





Contaminated air
intrinsic and
extrinsic
impurities
Getter
Clean Air to SOFC Stack

Getter Architecture

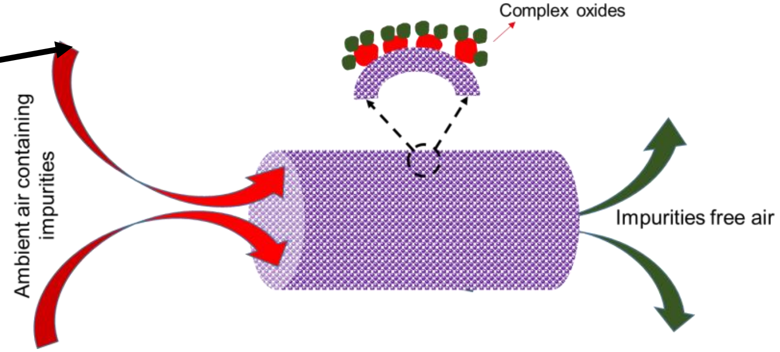
Use of Alkaline earth – Transition-metal elements for Getter



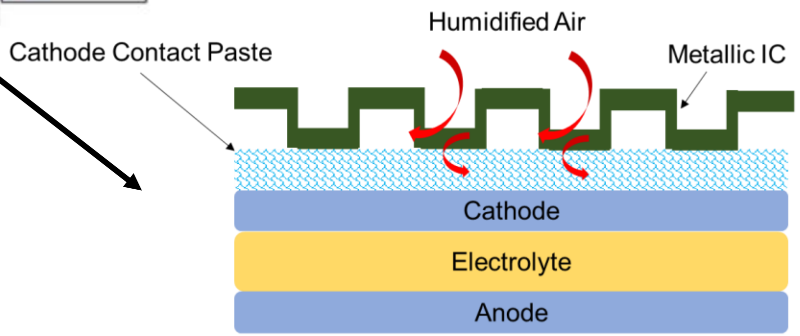
Stack

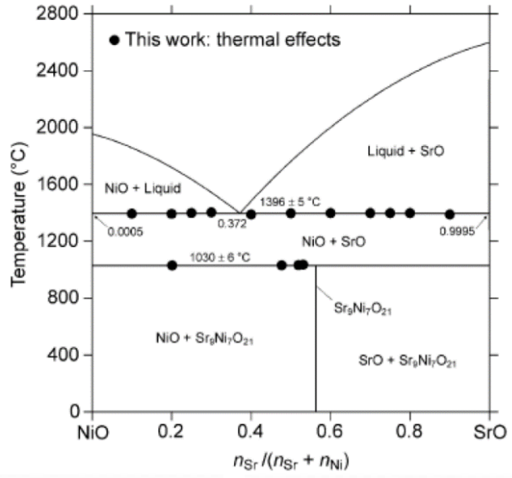
Balance of Plant (BOP)

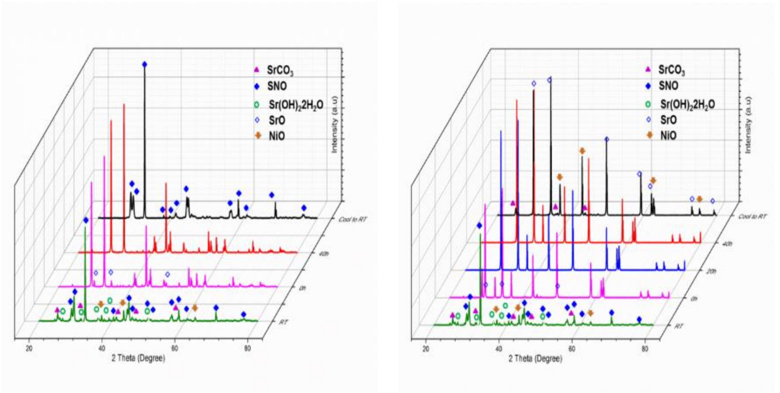
For BOP Application



For Application in Stack







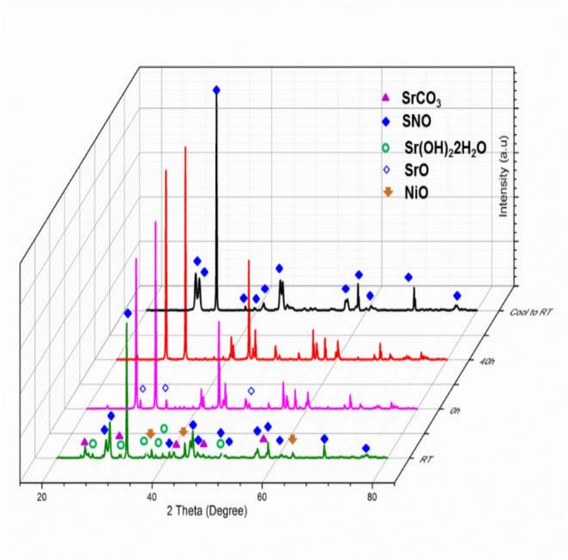
850˚C 1000˚C

Capture of intrinsic and extrinsic contaminants from both BOP and Stack has been demonstrated

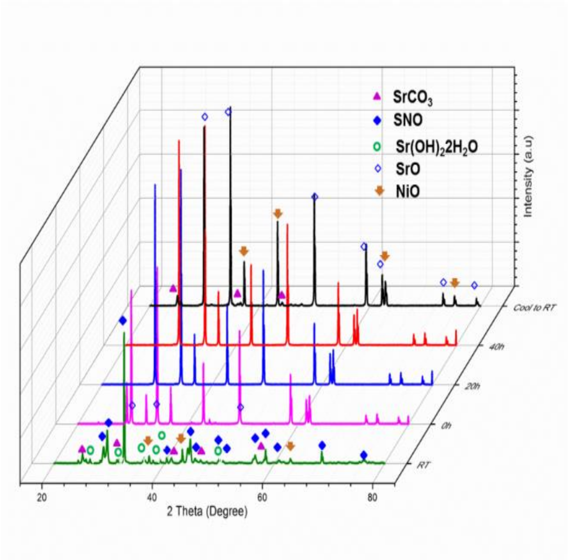
- *Ge, L., Verma, A., Goettler, R. et al. Metall and Mat Trans A (2013) 44(Suppl 1): 193.*
- *Ashish Aphale, Aman Uddin, Boxun Hu, Su Jeong Heo, Junsung Hong and Prabhakar Singh, ECS, 2018*

Thermal Stability of Cr getters

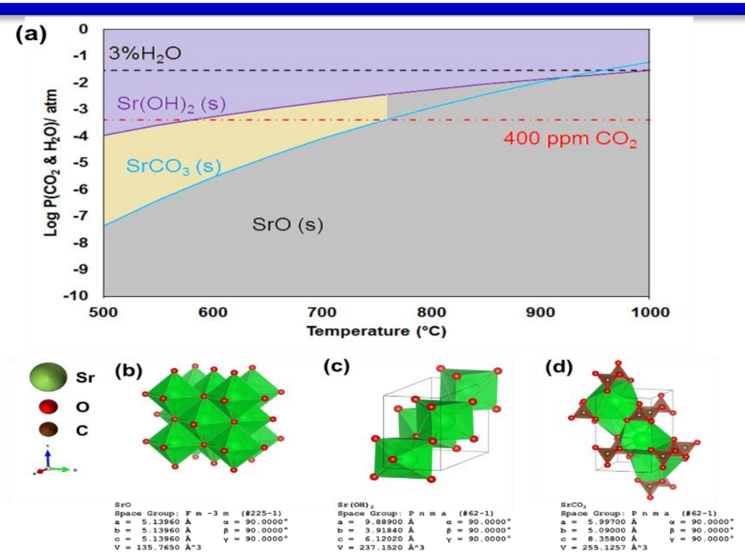
High temperature *in-situ* XRD performed on SrNiOx powder for 40h



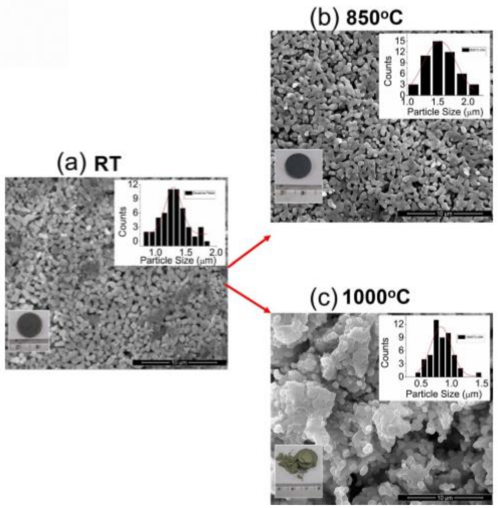
850˚C



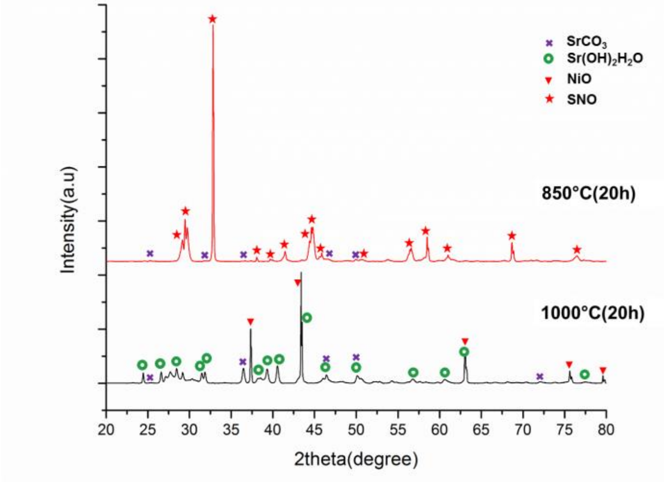
1000˚C



VESTA and COD utilized for crystallographic representation



XRD analysis after sintering



- **SrNiOx maintains phase stability below sintering temperature of 900ºC**
- **Sintering SrNiOx above 950ºC leads to dissociation into separate SrO and NiO phases**
- **Volume expansion and pulverization is observed above 950°C sintering temperature**

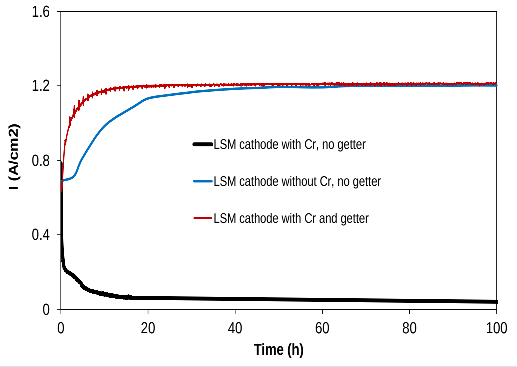
Ashish Aphale, Aman Uddin, Boxun Hu, Su Jeong Heo, Junsung Hong and Prabhakar Singh, Synthesis and Stability of SrxNiyOz Chromium Getter for Solid Oxide Fuel Cells", ECS, 2018

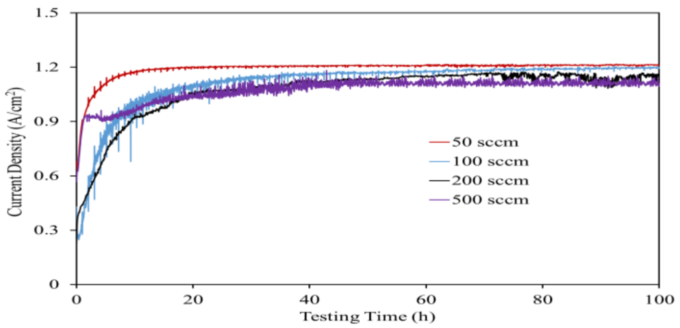
Chromium Capture Validations

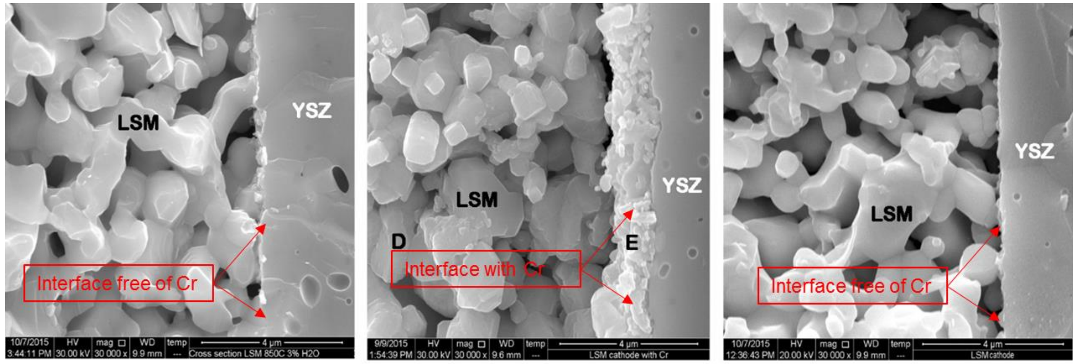
Transpiration Tests

Without getter

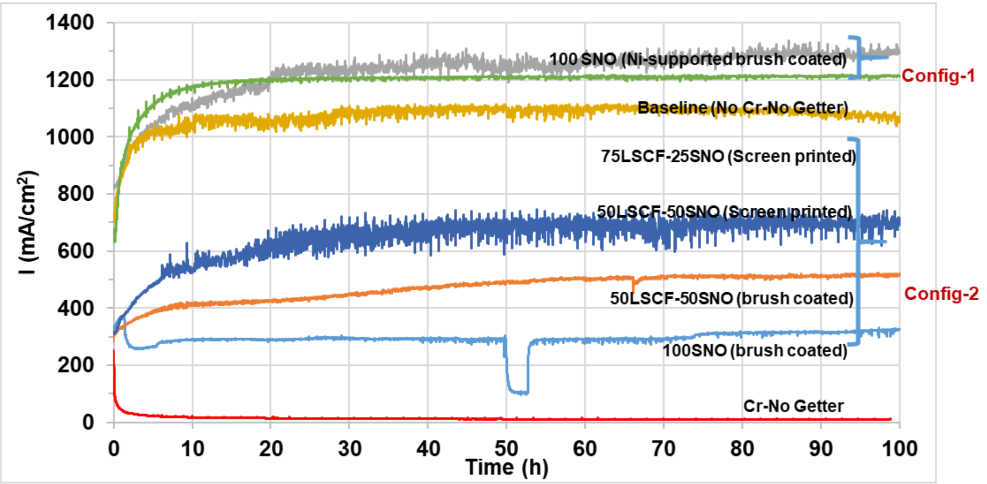
With getter

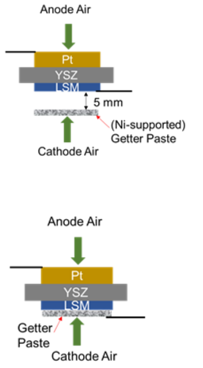






I-t data

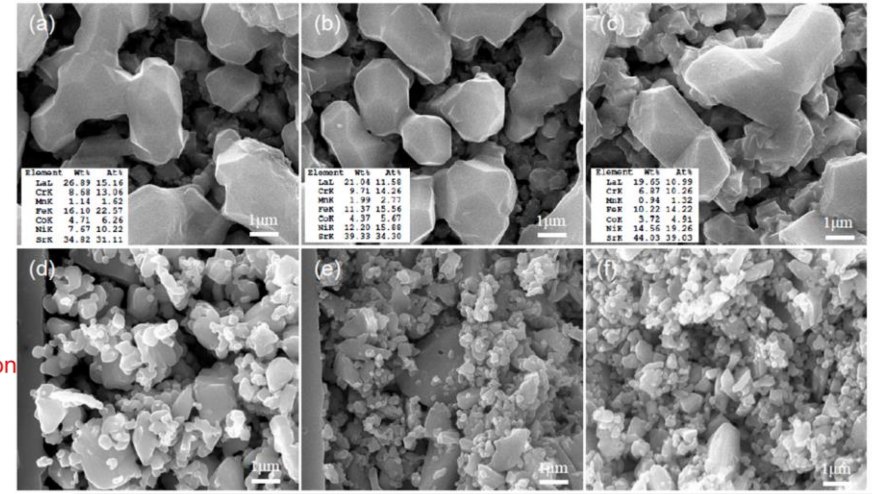




75LSCF-25SNO (screen printed) 50LSCF-50SNO (screen printed) 50LSCF-50SNO (brush coated)

Surface

Cross-section



Getter concept also validated independently by industries

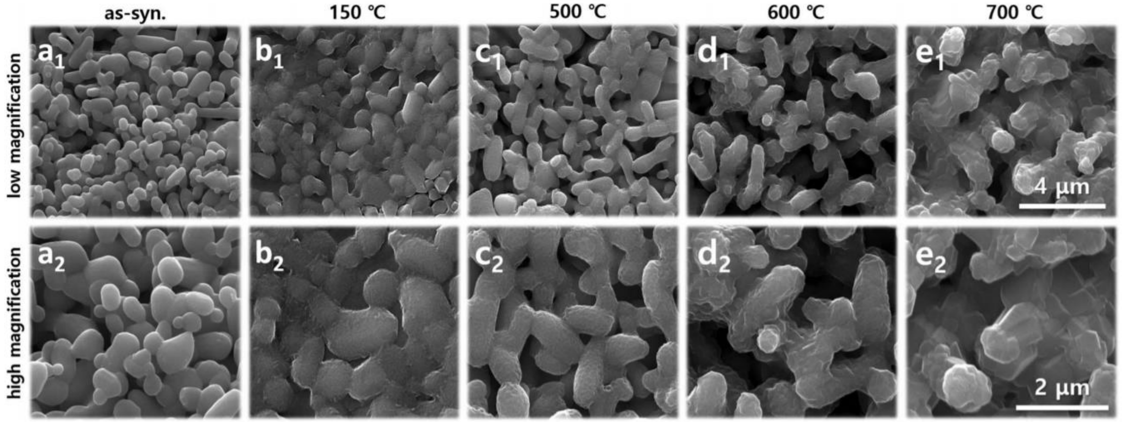
NATIONAL ENERGY TECHNOLOGY LABORATORY

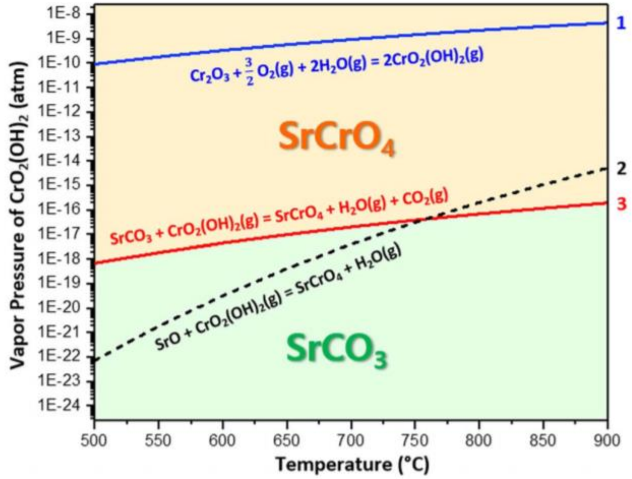
Md Aman Uddin, Ashish Aphale, Boxun, Hu, Su Jeong HeO, Ugur Pasaogullari and Prabhakar Singh, J. Electrochem. Soc. 2017

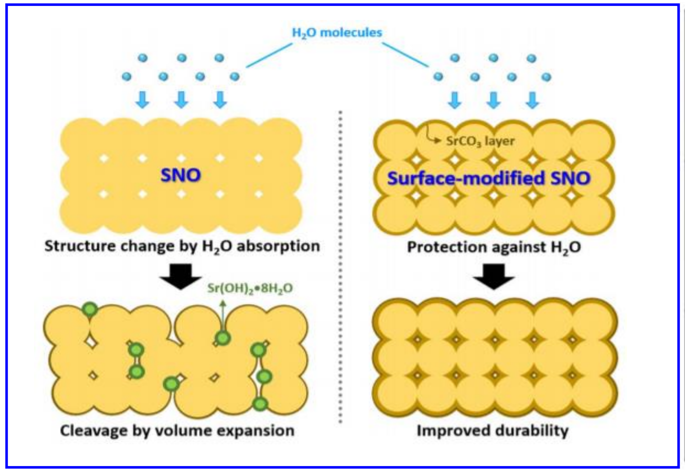
UCONN UNIVERSITY OF CONNECTICUT

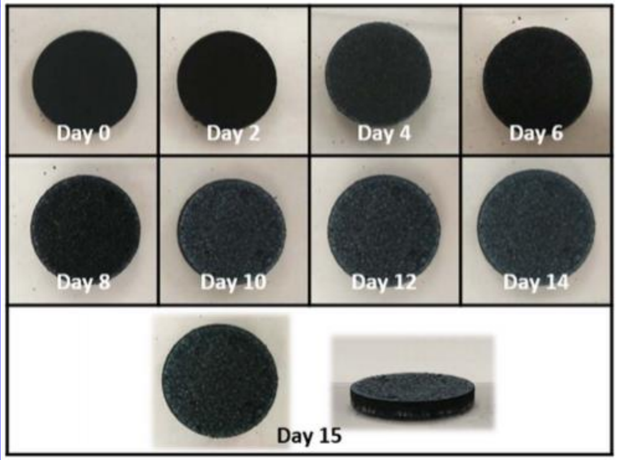
Advanced Getter: Stability and Performance

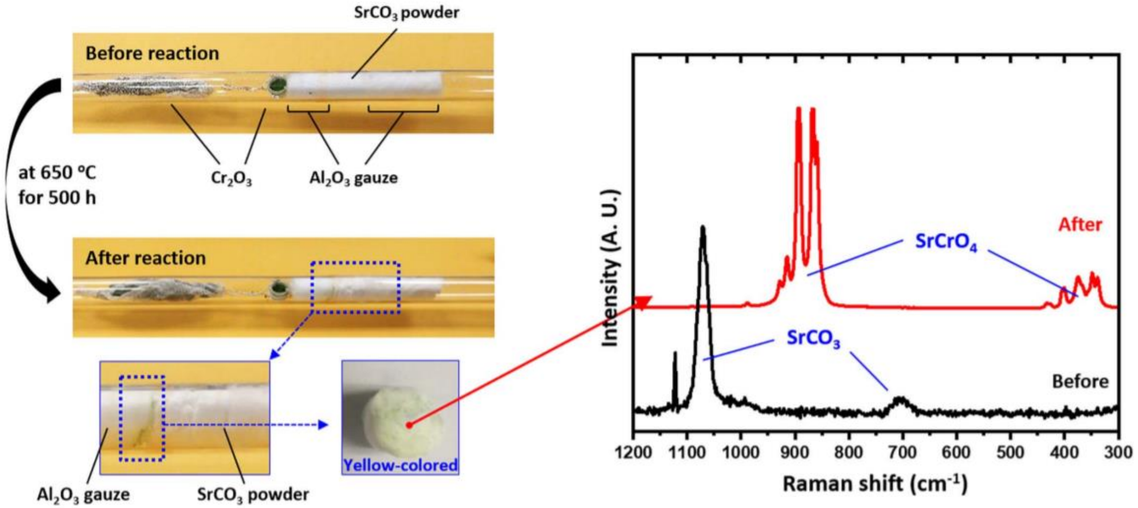
Getter heat-treatment in 30%CO_2-air atmosphere for 5hrs











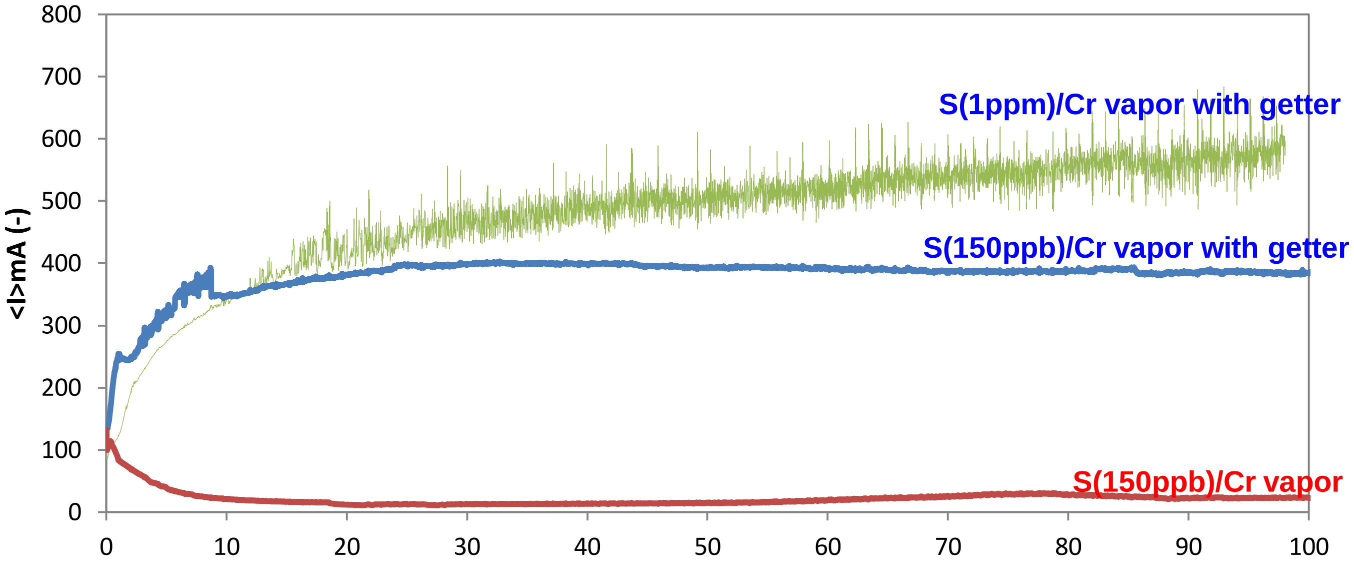
The stability of SNO is improved using $SrCO_3$ passivation layer while the ability to capture Cr vapor is maintained.

Junsung Hong, Su Jeong Heo, Ashish N Aphale, Boxun Hu, Prabhakar Singh, J Electrochem. Soc., 166(2), 2019

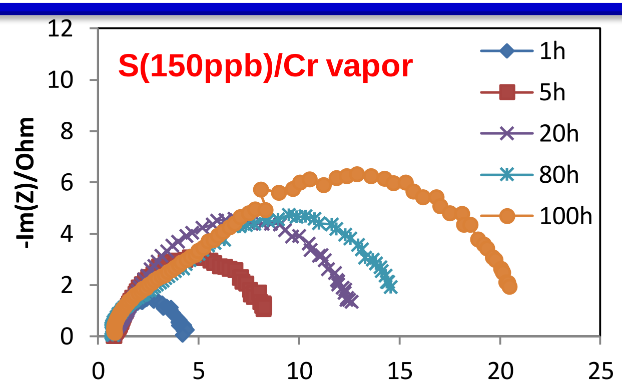
NATIONAL ENERGY TECHNOLOGY LABORATORY

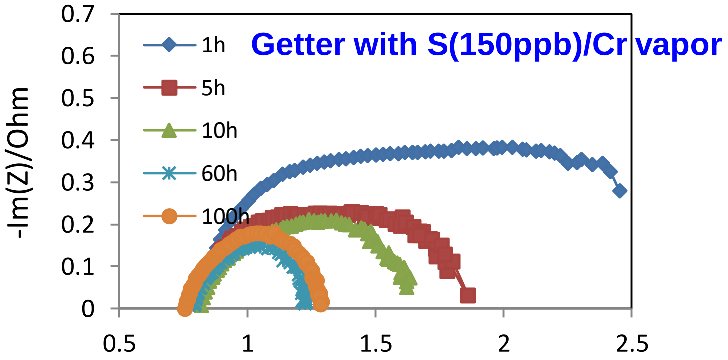
UCONN UNIVERSITY OF CONNECTICUT

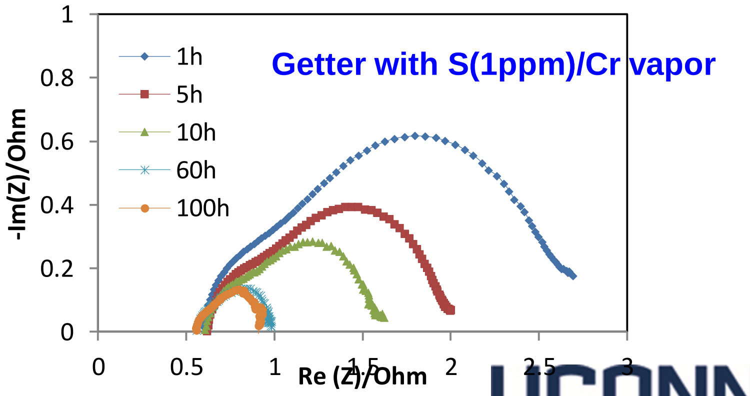
Co-Capture of Contaminants



Test #	With S & Cr	With S & Cr	With S & Cr
Materials	LSM/YSZ/Pt	LSM/YSZ/Pt	LSM/YSZ/Pt
Getter	No getter	SNO getter	SNO 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.