Multi-Constituent Airborne Contaminants Capture and Mitigation of Cathode Poisoning in Solid Oxide Fuel Cell

Kevin Lee, Pawan Dubey, Michael Reisert, Junsung Hong, Ashish Aphale, Seraphim Belko, Prabhakar Singh
University of Connecticut, Storrs, CT

US DOE Program: DE-FE-0031647

Program Manager: Dr. Patcharin Burke
Email: Patcharin.Burke@NETL.DOE.GOV

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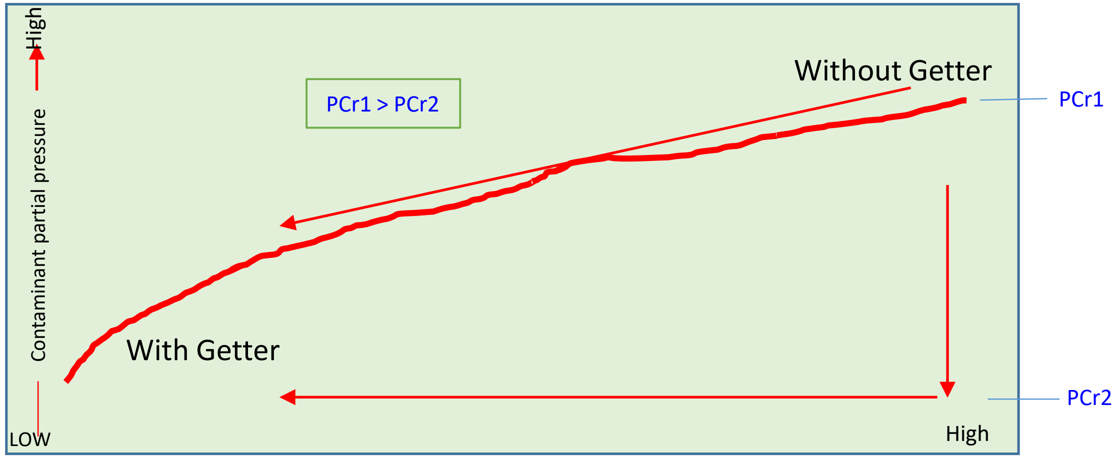
Pittsburgh Airport Marriott Hotel

Presentation Outline

- Program Objective
- Broader Impact
- Technical Accomplishments
- Approach, Results and Discussion
- Summary and Conclusions
- Acknowledgements

✓ Low cost
✓ Conventional materials and processes
✓ Wide range of applications



Identification → Validation → Mitigation → Implementation

Program Objectives

- Identify the origin, formation processes and the nature of gas phase airborne contaminants (intrinsic and extrinsic) present in the air stream entering elevated temperature electrochemical systems.

- Develop mechanistic understanding of contaminant interactions (chemical, electrochemical and structural) with conventional air electrode materials.

- Identify cost effective getter materials and processing techniques to capture trace contaminants. Synthesize and validate getter performance and efficacy.

- Design and fabricate getters for stack and BOP applications. Validate the above under system conditions. Transfer technology to industrial partners.

Accomplishments

- Intrinsic and extrinsic trace gaseous contaminants present in ambient air stream, entering the elevated temperature electrochemical systems, have been identified.
- Formation, transport and interactions of contaminants with the air electrode has been examined. Role of alloy surface scale chemistry, pre-treatment conditions, formation of point and 3D-defects in the scale and molecular transport have been studied.
- Pretreatment of alloys under controlled exposure conditions modify the scale chemistry and morphology influencing the formation and transport of trace extrinsic contaminants.
- Getters have been fabricated for the capture of trace S (intrinsic) and Cr, Si, B (extrinsic) gaseous contaminants.
- Getter materials can be provided for test validation with DOE permission.
- Technical approach offers pathway for the capture of trace gaseous contaminants present in high temperature fuel cells, electrolyzers and chemical reactor systems.

Large range of contaminants | large volume of reactants | longer operating times

Select publications: Cr evaporation and capture (my group)

1. Ashish Aphale[1], Junsung Hong[1], Boxun Hu[1,2], Prabhakar Singh “Development and Validation of Chromium Getters for Solid Oxide Fuel Cell Power Systems,” May 26, 2019 doi: 10.3791/59623
2. Junsung Hong, Su Jeong Heo, Prabhakar Singh “Combined Cr and S poisoning behaviors of $La_{1-x}Sr_xMnO_{3\pm\delta}$ and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ cathodes in solid oxide fuel cells” Applied Surface Science Volume 530, 15 November 2020, 147253
3. Junsung Hong, Su Jeong Heo, Ashish N. Aphale, Boxun Hu and Prabhakar Singh ” H_2O Absorption Assisted Sr-Segregation in Strontium Nickel Oxide Based Chromium Getter and Encapsulation with $SrCO_3$” Journal of The Electrochemical Society, Volume 166, Number 2 January 2019
4. Junsung Hong, Ashish N. Aphale, Su Jeong Heo, Boxun Hu, Michael Reisert, Seraphim Belko, and Prabhakar Singh “Strontium Manganese Oxide Getter for Capturing Airborne Cr and S Contaminants in High-Temperature Electrochemical Systems” *CS Appl. Mater. Interfaces* 2019, 11, 38,
5. Su Jeong Heo, Junsung Hong, Ashish Aphale,Boxun Hu, and Prabhakar 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 (2019)
6. Shadi Darvish, Boxun Hu, Prabhakar Singh & Yu Zhong “Thermodynamic and Experimental Evaluation of $La_{1-x}Sr_xMnO_{3\pm\delta}$ Cathode in Presence of Cr-Containing Humidified Air” *JOM* volume 71, pages3814–3824 (2019)
7. Boxun Hu, Sridevi Krishnan, Chiying Liang, Su Jeong Heo, Ashish N.Aphale, Rampi Ramprasad, Prabhakar Singh “Experimental and thermodynamic evaluation of $La_{1-x}Sr_xMnO_{3\pm\delta}$ and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ cathodes in Cr-containing humidified air” International Journal of Hydrogen Energy, Volume 42, Issue 15, 13 April 2017, Pages 10208-10216
8. Ashish Aphale, Md Aman Uddin, Boxun Hu, Su Jeong Heo, Junsung Hong and Prabhakar Singh, “ Synthesis and Stability of $Sr_xNi_yO_z$ Chromium Getter for Solid Oxide Fuel Cells” Journal of The Electrochemical Society, Volume 165, Number 9
9. Fengyu Shen, Michael Reisert, Ruofan Wang, Prabhakar Singh, and Michael C. Tucker “Assessment of Protective Coatings for Metal-Supported Solid Oxide Electrolysis Cells” https://doi.org/10.1021/acsaem.2c00655 2022
10. Michael Reisert, Ashish Aphale an dPrabhakar Singh “Solid Oxide Electrochemical Systems: Material Degradation Processes and Novel Mitigation Approaches” *Materials* 2018, *11*(11), 2169; https://doi.org/10.3390/ma11112169
11. Ashish Aphale, Chiying Liang, Boxun Hu, Prabhakar Singh “Cathode Degradation From Airborne Contaminants in Solid Oxide Fuel Cells: A Review” Solid Oxide Fuel Cell Lifetime and Reliability Critical Challenges in Fuel Cells 2017, Pages 101-119
12. Yeong-Shyung Chou, Jung Pyung Choi, Jeffry W Stevenson, Chiying Liang, Boxun Hu, Weyshla Rodriguez, Ashish N Aphale and Prabhakar Singh “Performance and Microstructure of a Novel Cr-Getter Material with LSCF-Based Cells in a Generic Stack Test Fixture” ECS Transactions, Volume 78, Number 1

Background: Contaminant Types, Transport and Interactions

- **Intrinsic and extrinsic**
  - **originating and included wholly within** — **SO_x, H_2S, HX, VOC**
  - **originating from or on the outside** — **CrO_x, $CrOH_x$, $SiOH_x$, HBO_x**

- **Types and levels** — **ppm/ppb**
  - **acidic** — **SO_x, NO_x, H_2S, HCl, HBO_3, P_2O_5, $SiOH_x$, $CrOH_x$**
  - **basic** — **Ammonia, Alkali hydroxides, Alkali halides**

- **Influence on SOFC systems life and performance**
  - **Enhanced corrosion**
  - **Surface deposition**
  - **Reaction products formation**
  - **Performance/ Life reduction**

Breadth and complexity of the topic pertaining to trace contaminant, interactions and removal has been examined. The influence of contaminants on the performance and life can be further examined based on operational flexibility.

Options: Long term degradation mitigation

- Reduce contaminant formation and its transport – new materials ?
- Use contaminant tolerant cell components - new materials ?
- Consume contaminants at the component surface – additional reactions!
- Capture contaminants on low-cost getters – clean surface/ interface ?

Background: Trace Contaminants

Presence of trace gaseous contaminants are part of oxidant and fuel streams entering high temperature electrochemical systems (Fuel cells, electrolyzer etc.). There remains a need for the reduction/elimination of contaminants from the gaseous streams during long term operation to minimize performance degradation due to its accumulation / continued reaction in the electrodes.

Conditions	***Impurities***	***Impact***	***Implication***
State of the art	Intrinsic Extrinsic	Electrode poisoning + Structural changes	Degradation
Materials modification	Intrinsic Reduced extrinsic	Reduced poisoning + Structural changes	Lower degradation
Impurity capture	Reduced Intrinsic Reduced extrinsic	Reduced poisoning + >> Extended life	Lower degradation

Large input of air volume entering the electrochemical systems over its lifetime (000's of hrs.) can lead to accumulation of appreciable amounts of contaminants (100's of grams to kilo grams) in the electrodes.

Criteria Pollutants – National Ambient Air Quality Standards

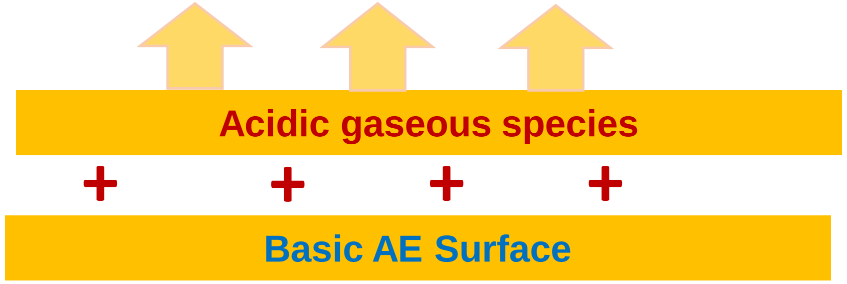
Pollutant [links to historical tables of NAAQS reviews]		Primary/ Secondary	Averaging Time	Level	Form
Carbon Monoxide (CO)		primary	8 hours	9 ppm	Not to be exceeded more than once per year
			1 hour	35 ppm	
Lead (Pb)		primary and secondary	Rolling 3 month average	0.15 μg/m³ (1)	Not to be exceeded
Nitrogen Dioxide (NO_2)		primary	1 hour	100 ppb	98th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		primary and secondary	1 year	53 ppb (2)	Annual Mean
Ozone (O_3)		primary and secondary	8 hours	0.070 ppm (3)	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years
Particle Pollution (PM)	$PM_{2.5}$	primary	1 year	12.0 μg/m³	annual mean, averaged over 3 years
		secondary	1 year	15.0 μg/m³	annual mean, averaged over 3 years
		primary and secondary	24 hours	35 μg/m³	98th percentile, averaged over 3 years
	PM_{10}	primary and secondary	24 hours	150 μg/m³	Not to be exceeded more than once per year on average over 3 years
Sulfur Dioxide (SO_2)		primary	1 hour	75 ppb (4)	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		secondary	3 hours	0.5 ppm	Not to be exceeded more than once per year

There is a need to understand the role of VOC, NH3, PM's, alkali, salt etc. on the long term accumulation in the porous electrodes.

Airborne Contaminants and Cathode Degradation in SOFC Systems

- Air electrode (predominantly basic, Lanthanide group) remain prone to degradation due to interactions with acidic contaminants.
- Degradation leads to dopant exsolution, compound formation, and surface/Interface morphology changes.

Electrocatalytic Deactivation
Compound Formation
Surface adsorption



Cathode Degradation

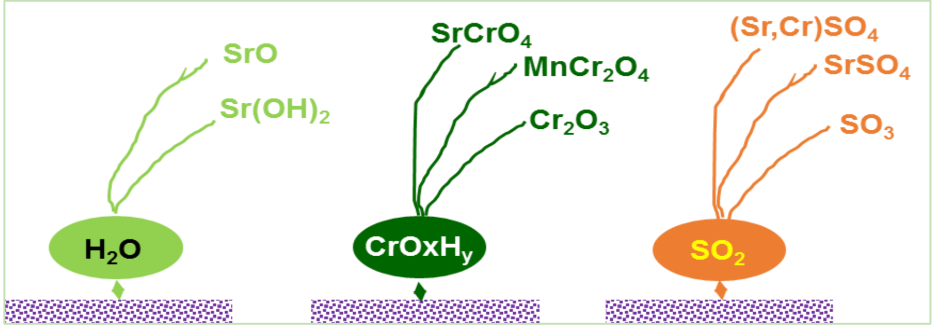
Solid-Gas

- Gaseous contaminants
- Airborne intrinsic impurities
- Evaporation of extrinsic impurities

Solid-Solid

- Solid state reaction and interdiffusion
- Cathode/electrolyte
- Cathode/interconnect

Ohmic losses, Non-ohmic losses, Mechanical changes



Trace contaminants accumulate with time in the electrode. Valance change, dopant exsolution, compound formation and electrode decomposition can occur during long term exposure to air.

Extrinsic contaminants formation in SOFC system

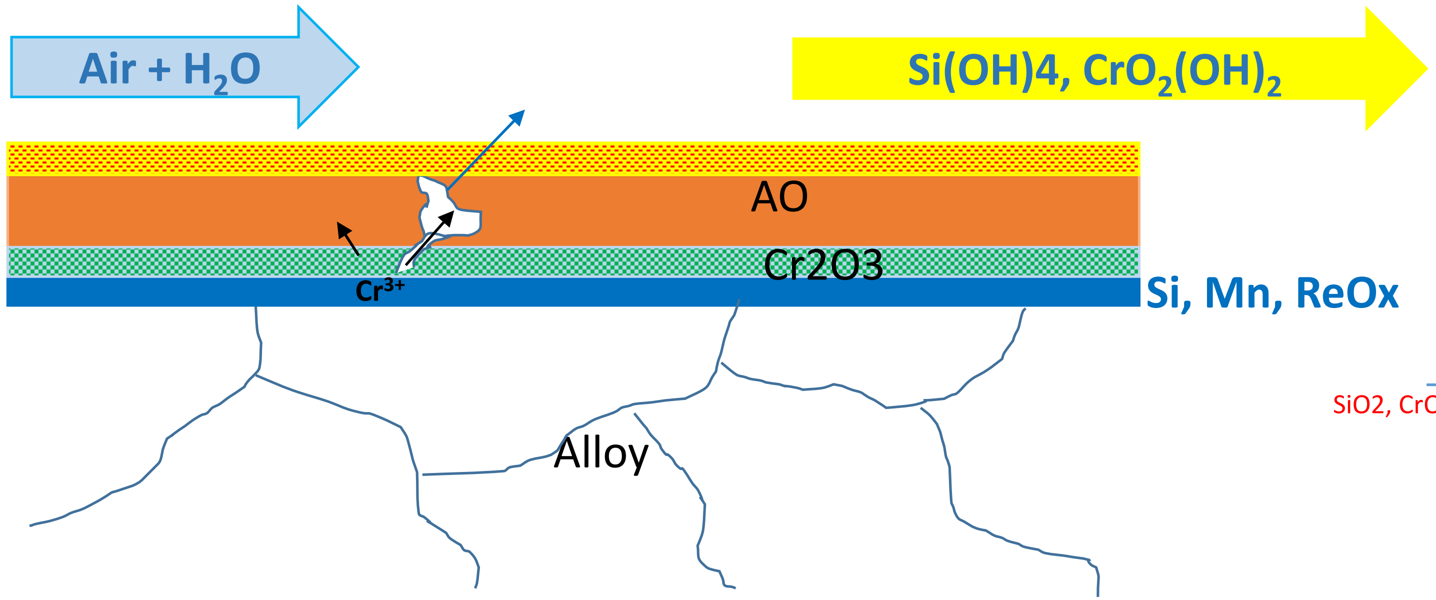
- **Surface reaction – Exposed surfaces on cell and BOP components**
- **Defects and second phases present in the surface oxides**
- **Spallation of oxides and exposure of internal reactive oxides**
- **Steam induced corrosion and transport of contaminants**

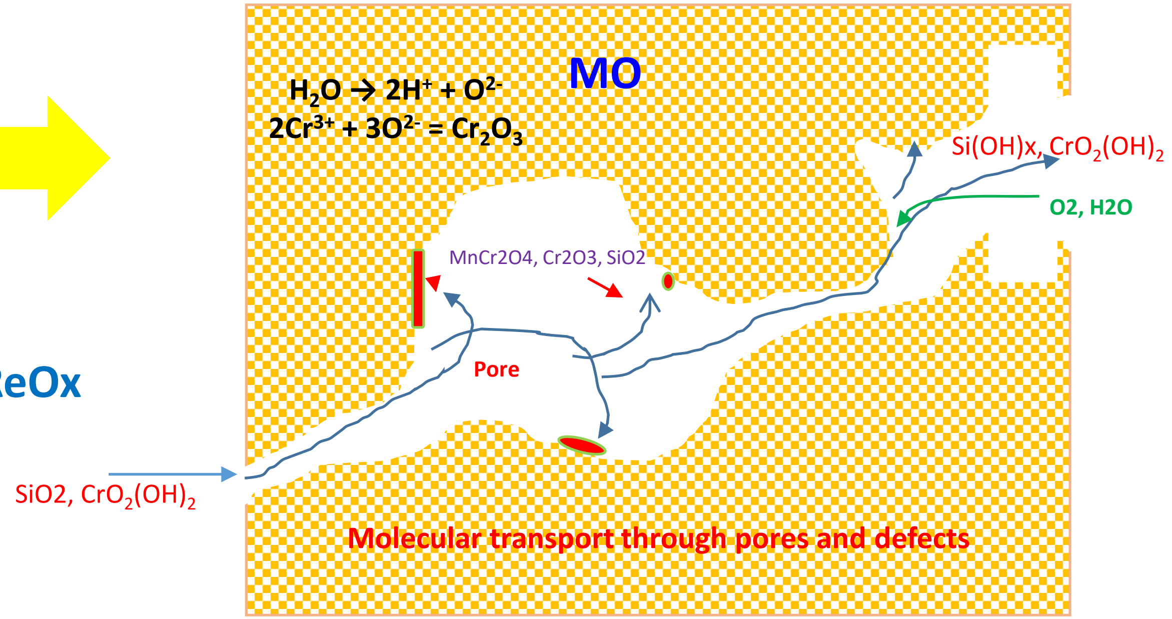
- **Formation of gaseous oxides are considered to be due to interactions between the gas phase (H2O) and surface oxides. Cr, Si, B, Bi present in the surface oxide can form their respective hydrated oxides.**
- **Transport of gaseous Si, Cr, B, Bi etc. in the form of oxides (Mog) is ruled out since their formation would not depend on the availability of water.**
- **Pretreatment of the surface to modify oxide chemistry benign to gaseous oxide formation**
- **Large cracks and open porosity in the scale can promote gaseous oxide formation from sub surface oxides.**

"Exploring the Effect of Silicon on the High Temperature Corrosion of Lean FeCrAl Alloys in Humid Air" T. Sand · A. Edgren · C. Geers · V. Asokan · J. Eklund · T. Helander · J. E. Svensson · L. G. Johansson; Oxidation of Metals (2021) 95:221–238

Evaporation and gas phase transport

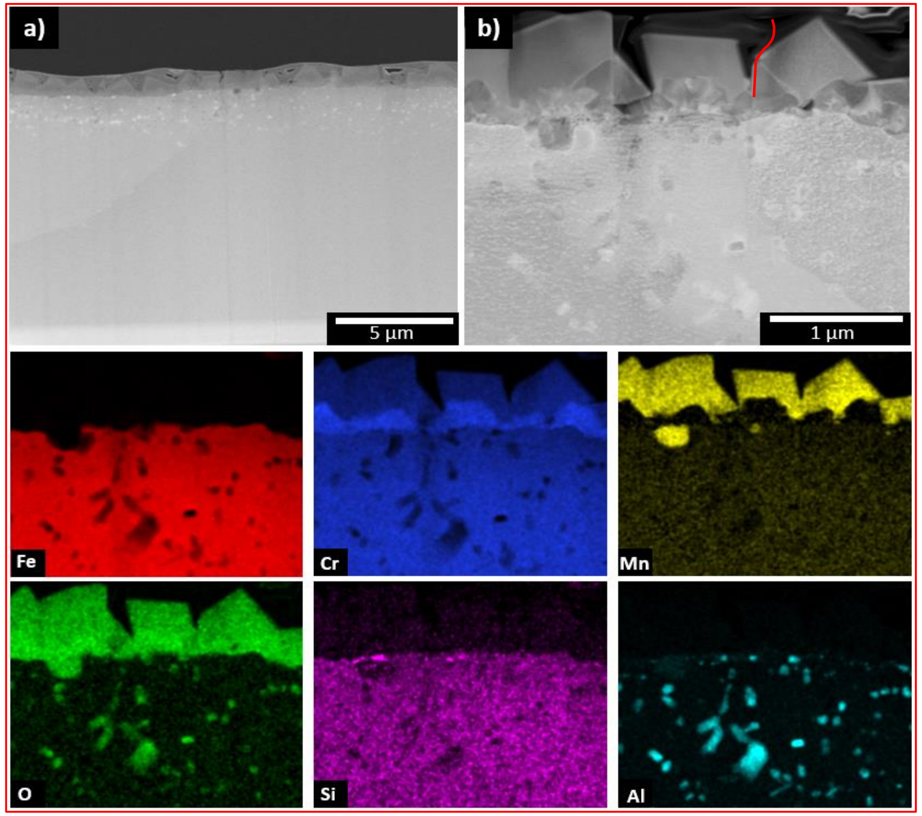
- Defects present in the surface oxides can lead to evaporation faster than through dense oxide / coatings (gaseous transport/redox).
- Reaction layers at underlying oxide interfaces can accelerate Cr, Si, B evaporation.
- Pretreatment of surface to modify oxide chemistry can reduce gaseous product formation.
- Formation of micro cracks with exposure time can promote evaporation.



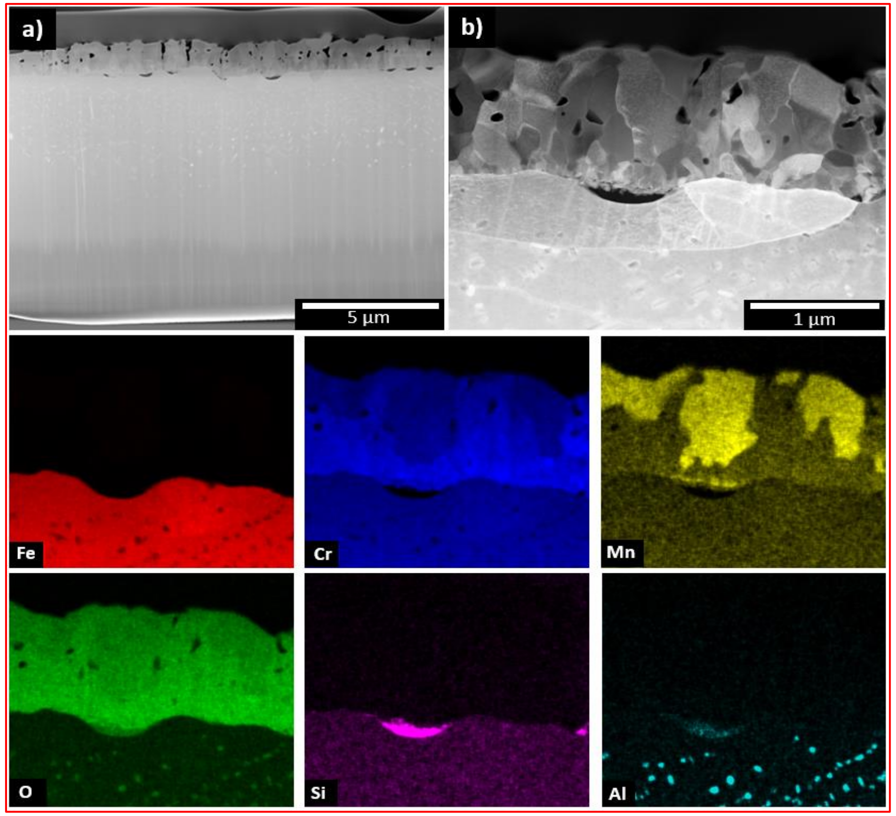


Examine molecular transport of reactants and products through defective surface oxides

Surface treatment and oxide scale chemistry



FIB cross-section (a) and high-resolution TEM image (b) of ZMG232G10® after 10 h pre-treatment in air at 900 °C. Elemental analysis is included for Figure (b).



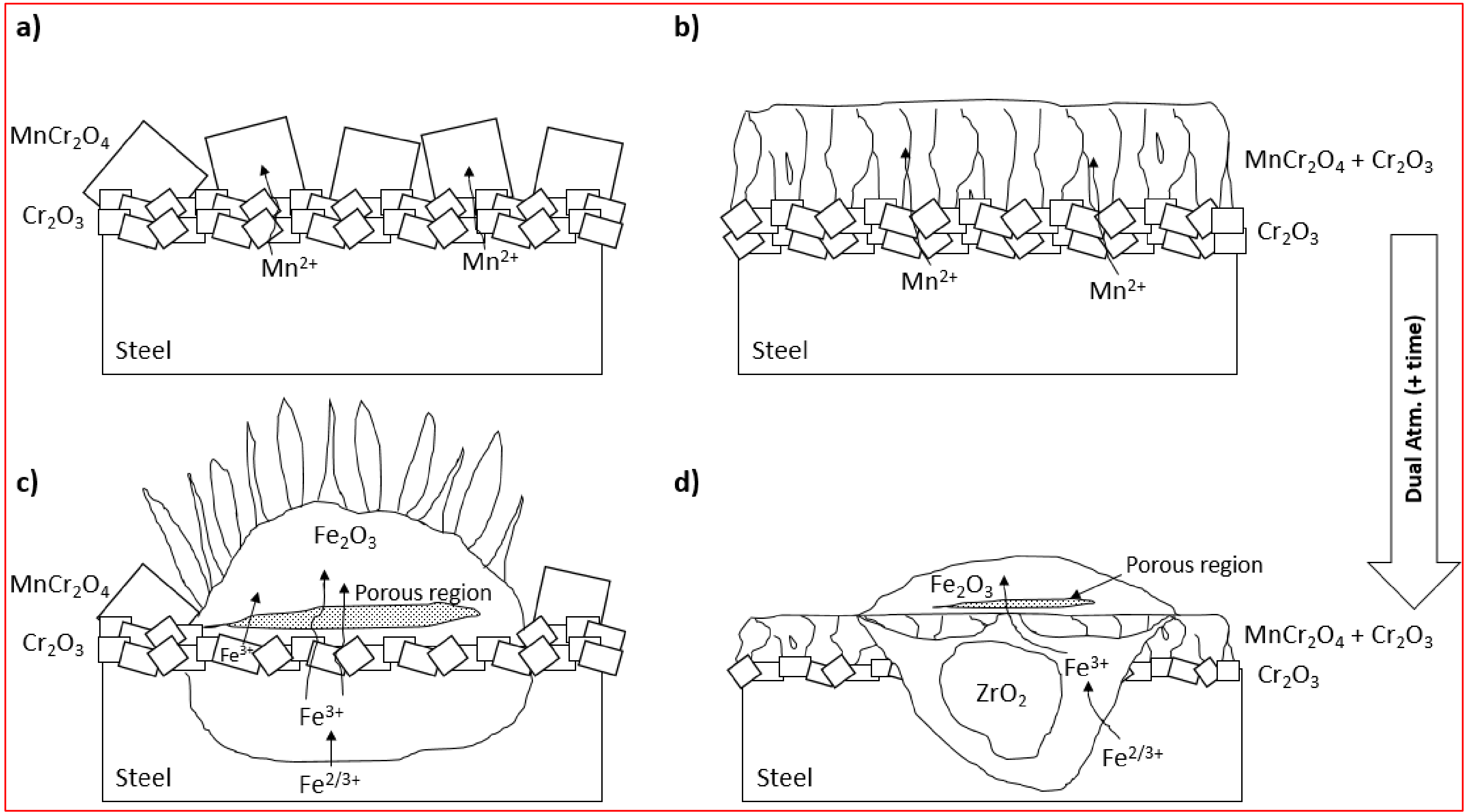
FIB cross-section (a) and high-resolution TEM image (b) of ZMG232G10® after 10 h pre-treatment in H_2-3%H_2O atmosphere at 900 °C. Elemental analysis is shown for Figure (b).

- Exposed metal surfaces lead to alloying additive oxide nuclei formation and growth at the surface.
- In air, all reactive constituents form oxide nuclei.
- In controlled atmosphere, only select alloying additive oxidize to form oxide nuclei.
- A modified surface oxide with Cr or other additives can be formed by controlling exposure atmosphere PO2

Composition (wt. %)									
Cr	Mn	Si	C	Zr	La	W	Al	Cu	Fe
24.0	0.3	0.10	0.02	0.25	.06	2.0	0.1	1.0	bal.

Reisert etal, "Controlled thermal pre-treatment of ZMG232G10® for corrosion mitigation under simulated SOFC interconnect exposure conditions" Accepted for publication, IJHE 2022

Surface treatment and oxide scale chemistry

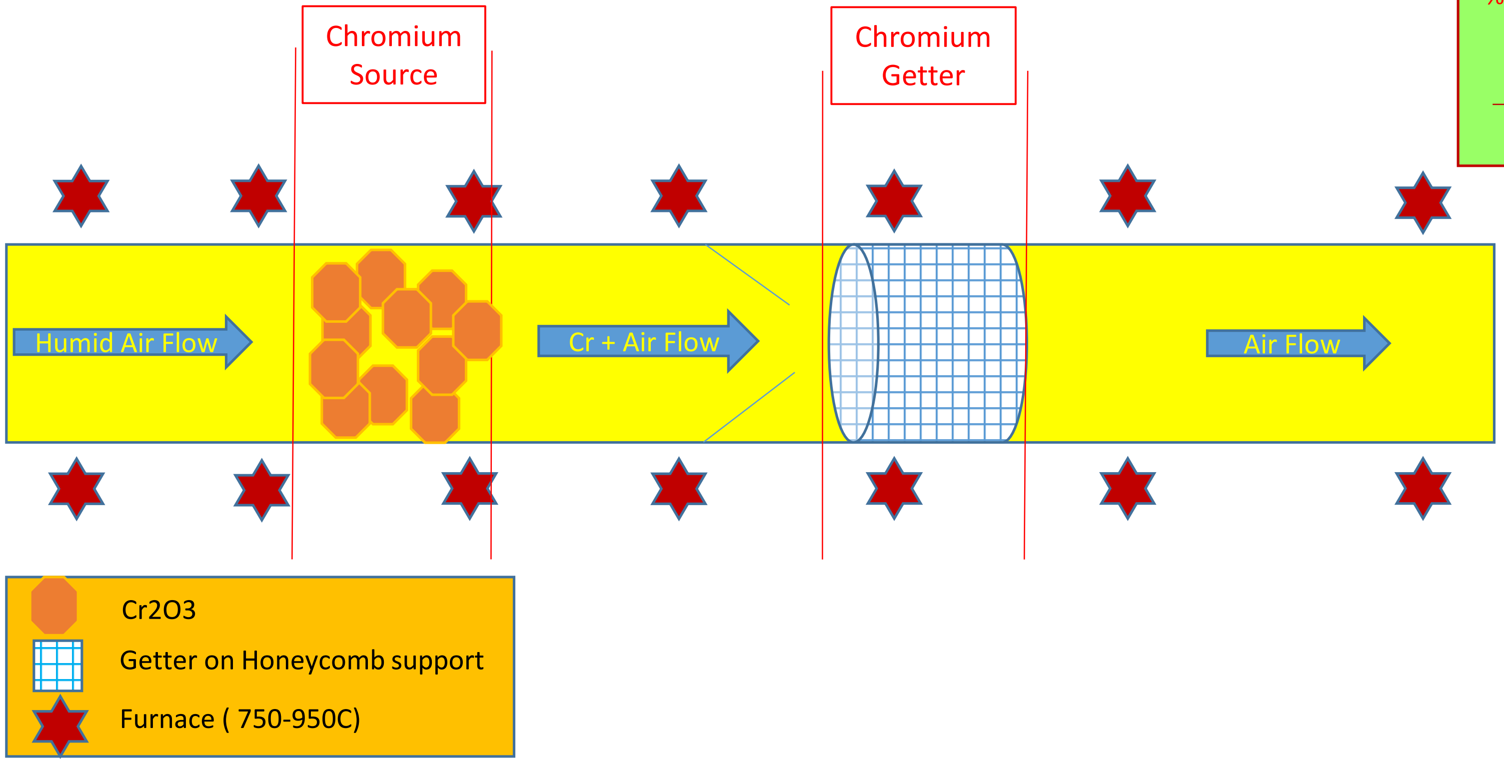


- Changes in the surface oxide chemistry and morphology is observed with changes in PO2.
- Formation of protective Mn-Cr oxide scale under controlled conditions lowers Cr evaporation rate due to lower Cr2O3 activity and blockage of underlying scale.
- Lower PO2 exposure minimizes Fe contamination in the outer scale leading to the prevention of iron oxide rich nodules.

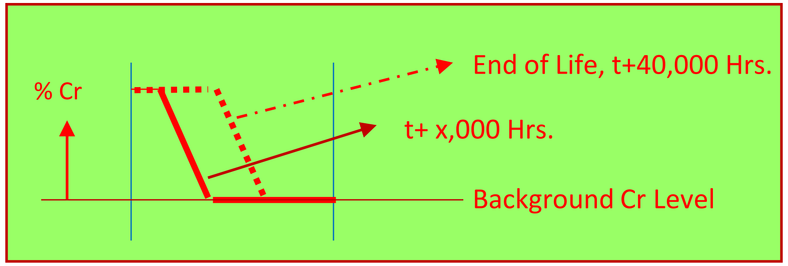
Schematic of scale formation and Mn^{2+} diffusion during (a) air and (b) H_2-3%H_2O pre-treatment. Fe^{3+} diffusion pathways and iron oxide rich scale formation during pretreatments in (c) air and (d) H_2-3%H_2O.

Reisert etal, “Controlled thermal pre-treatment of ZMG232G10® for corrosion mitigation under simulated SOFC interconnect exposure conditions” Accepted for publication, IJHE 2022

Experimental Arrangement



Design Philosophy



Design Parameters:

Input:

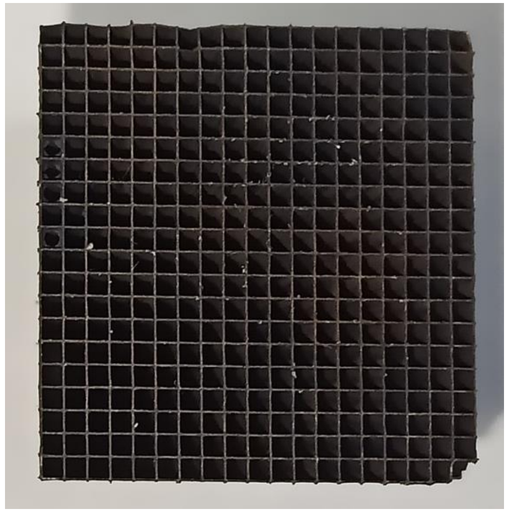
- **Residence time, Space velocity**
- **Cr_2O_3 activity (Scale)**
- **Humidity level, temperature**
- **Coating SA, uniformity**

Response:

- **Product stability, ΔG_R**
- **Getter utilization, PB ratio**
- **Thermal cyclability and adherence**

Getter Processing



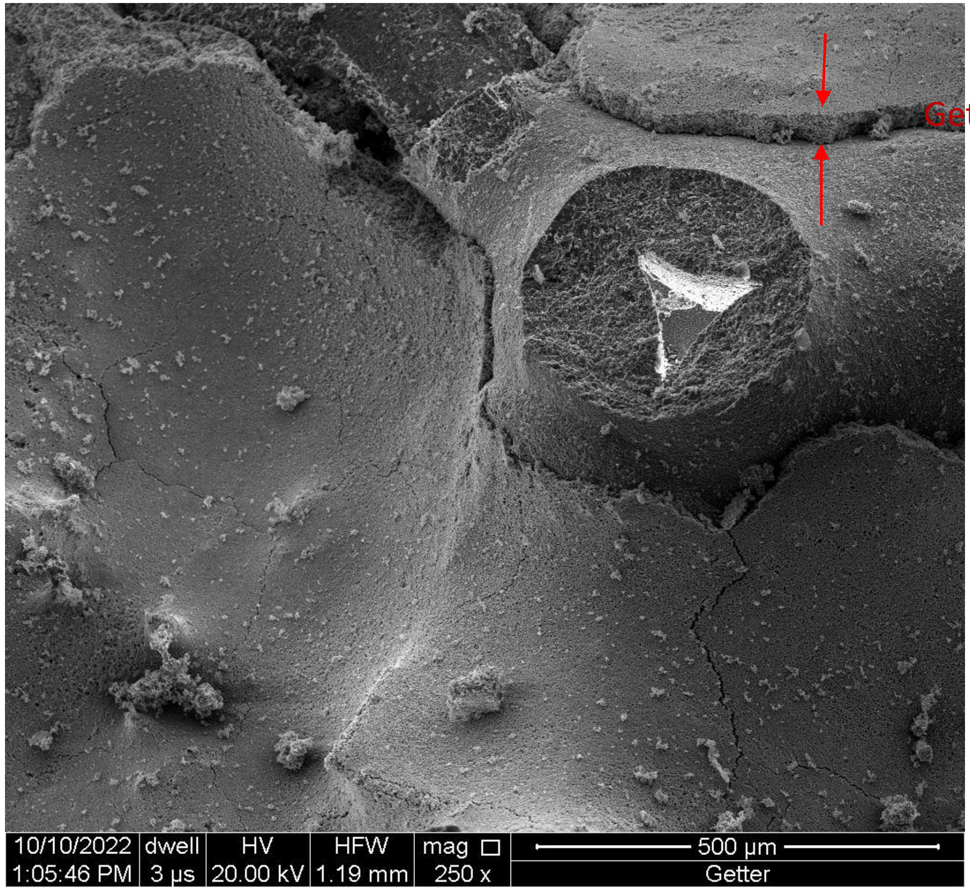


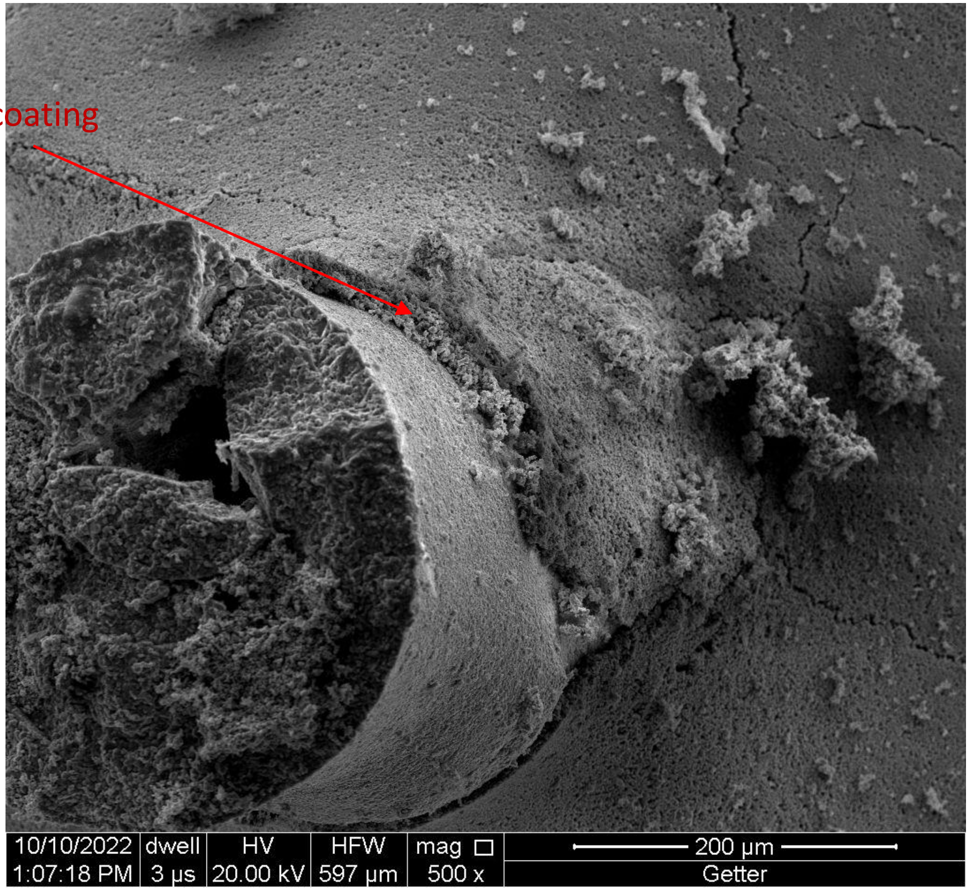
Cordierite honey comb
Alumina foam
Getter – SMO (sol-gel)
Heat treated in air



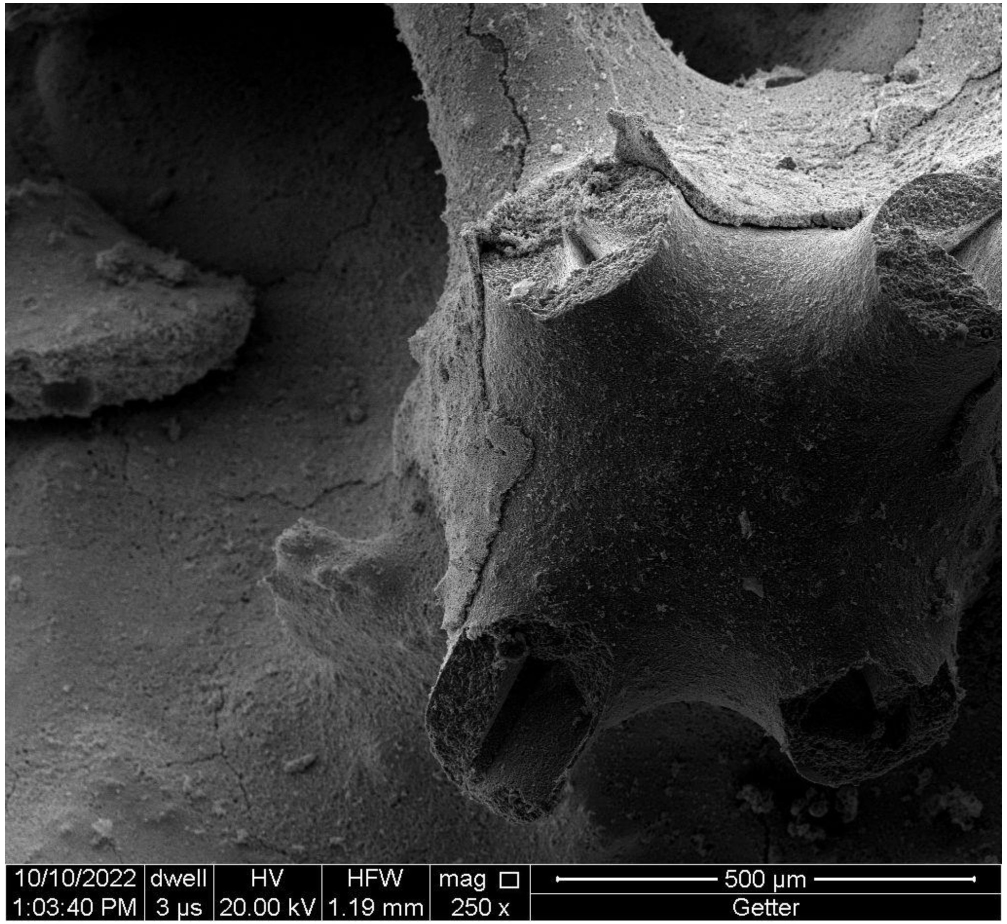
Collaboration with Professor Scott Misture, Alfred U.

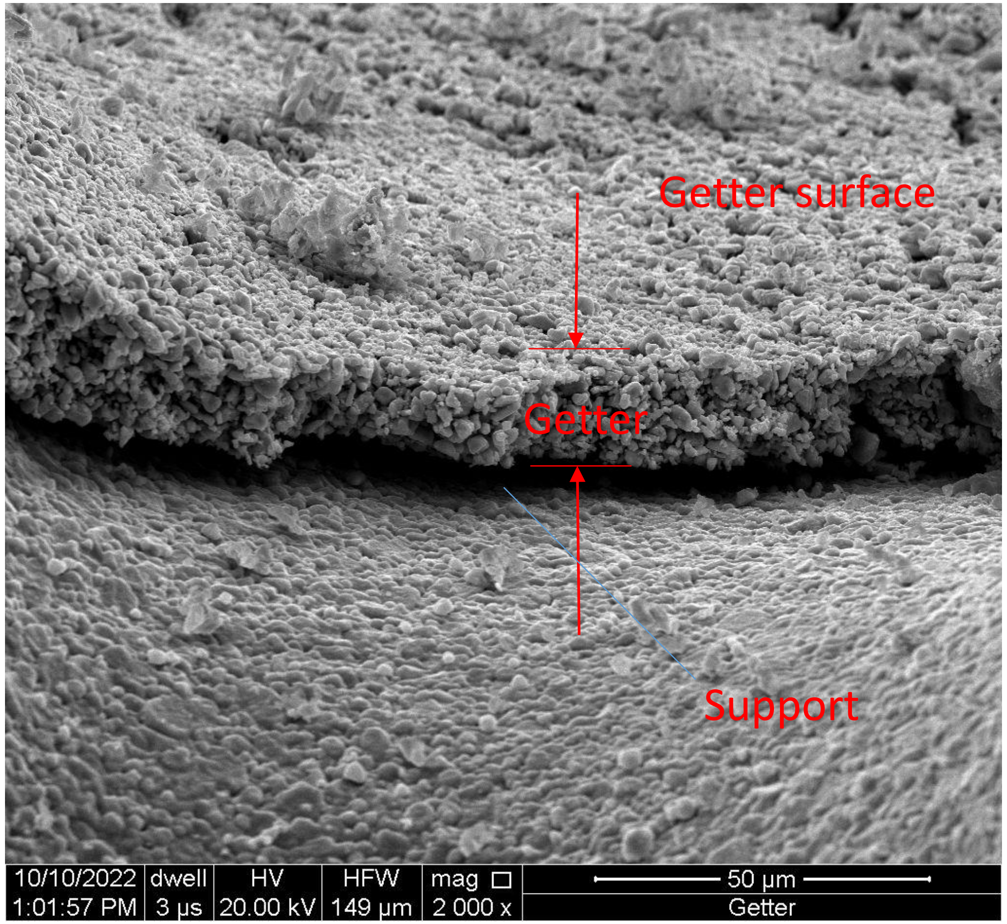
Getter Processing: Fracture surface



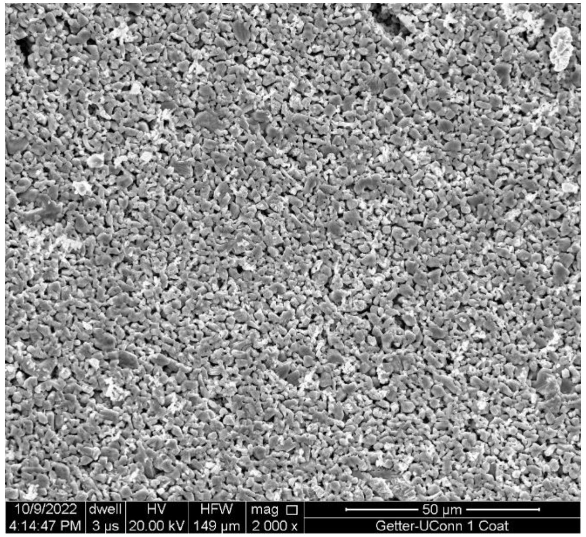


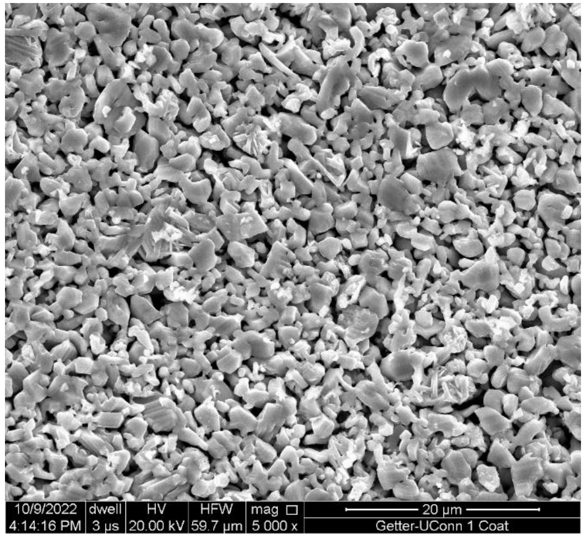
Getter Processing: Fracture surface

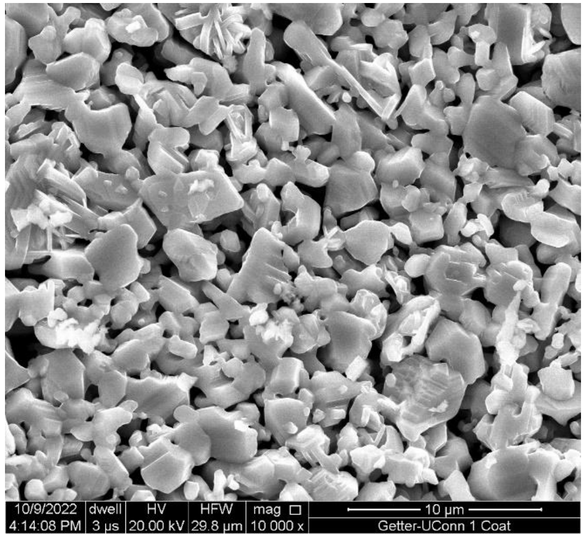


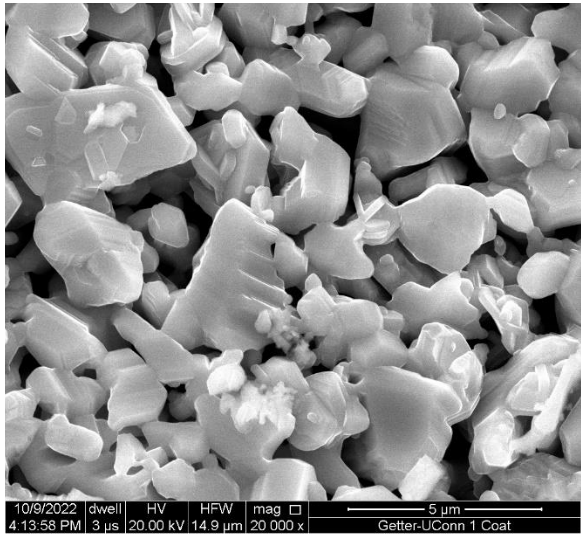


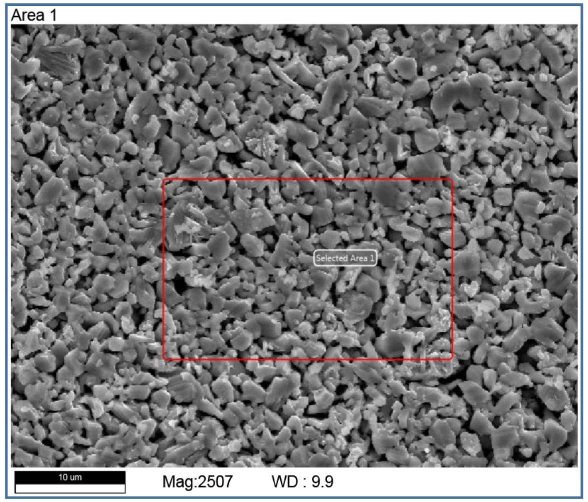
Getter Processing: Surface morphology

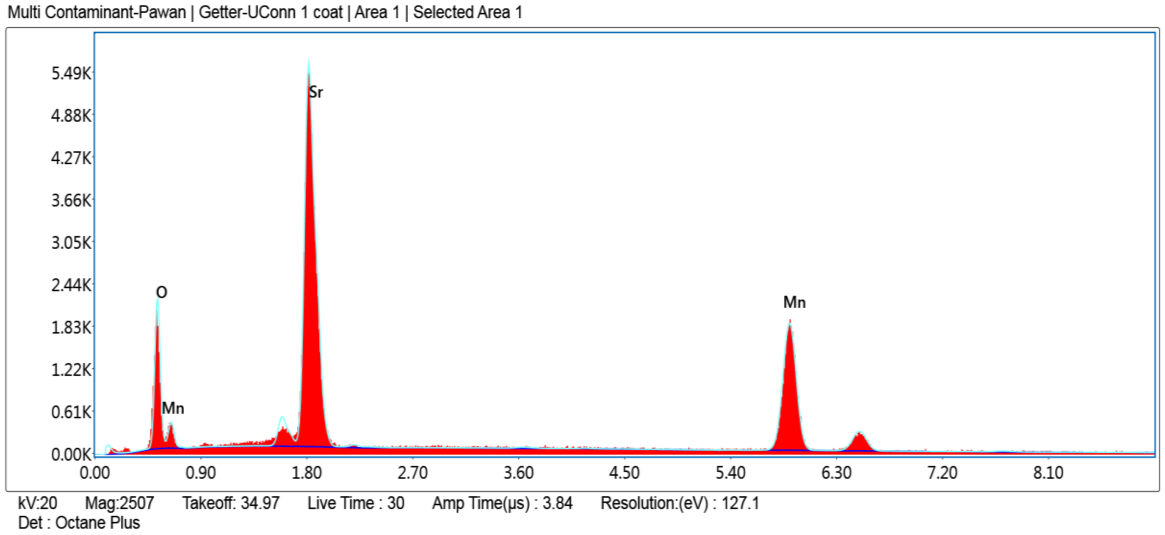






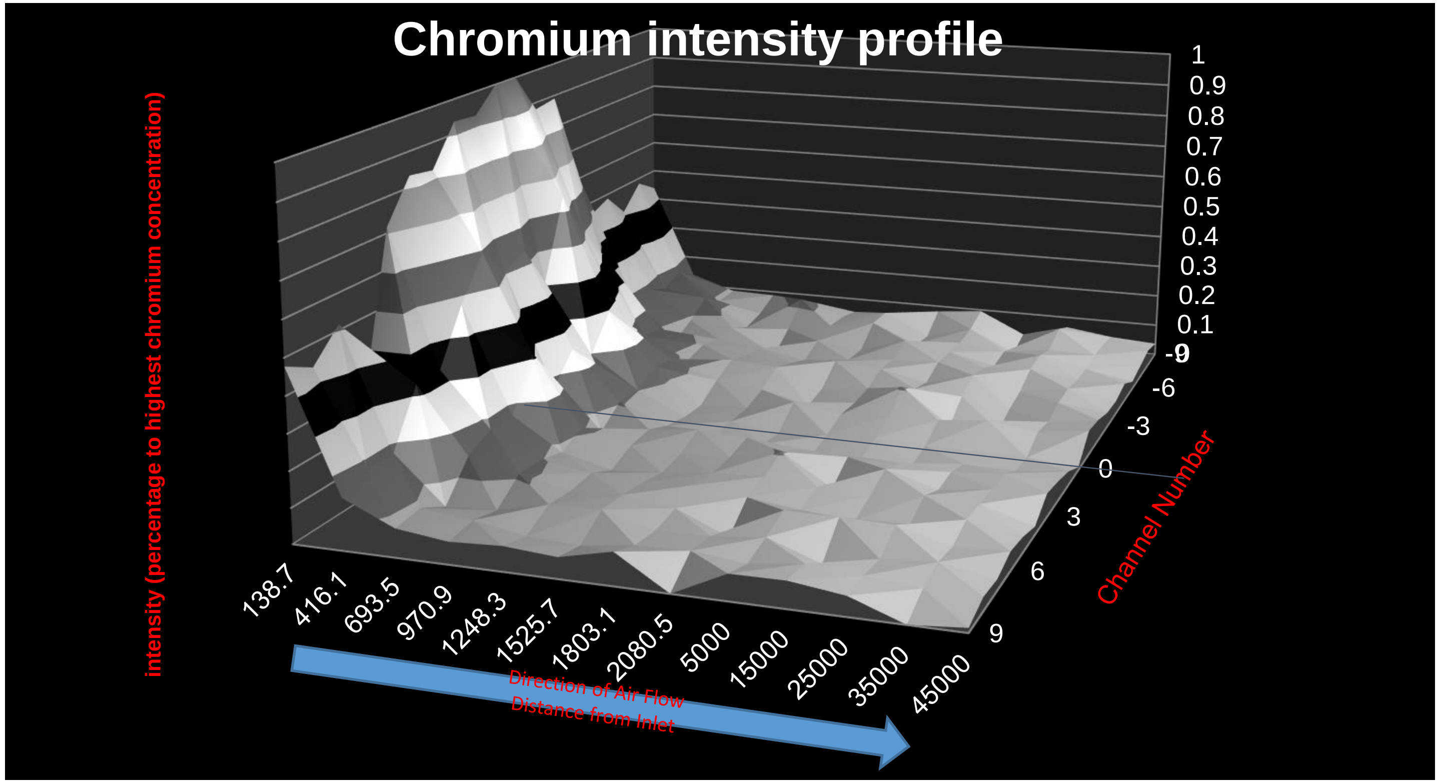






Element	Weight %	Atomic %
O K	26.50	61.20
Sr L	42.40	17.90
Mn K	31.10	20.90

Cr Intensity Profile – Entire length



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.

Gaseous Silica Contaminant formation and cell component interaction

Gas phase silica transport in both oxidizing and reducing atmospheres of electrochemical cells can take place during operation. Humidity in air or its increased concentration with the addition of steam can lead to increased evaporation and degradation of air and fuel electrodes

Ambient air → Oxygen ion conducting electrolyte → SiOHx transport and interactions with perovskite

Ambient air + water (Increased humidity) → Proton conducting electrolyte → SiOHx transport and interactions with perovskite

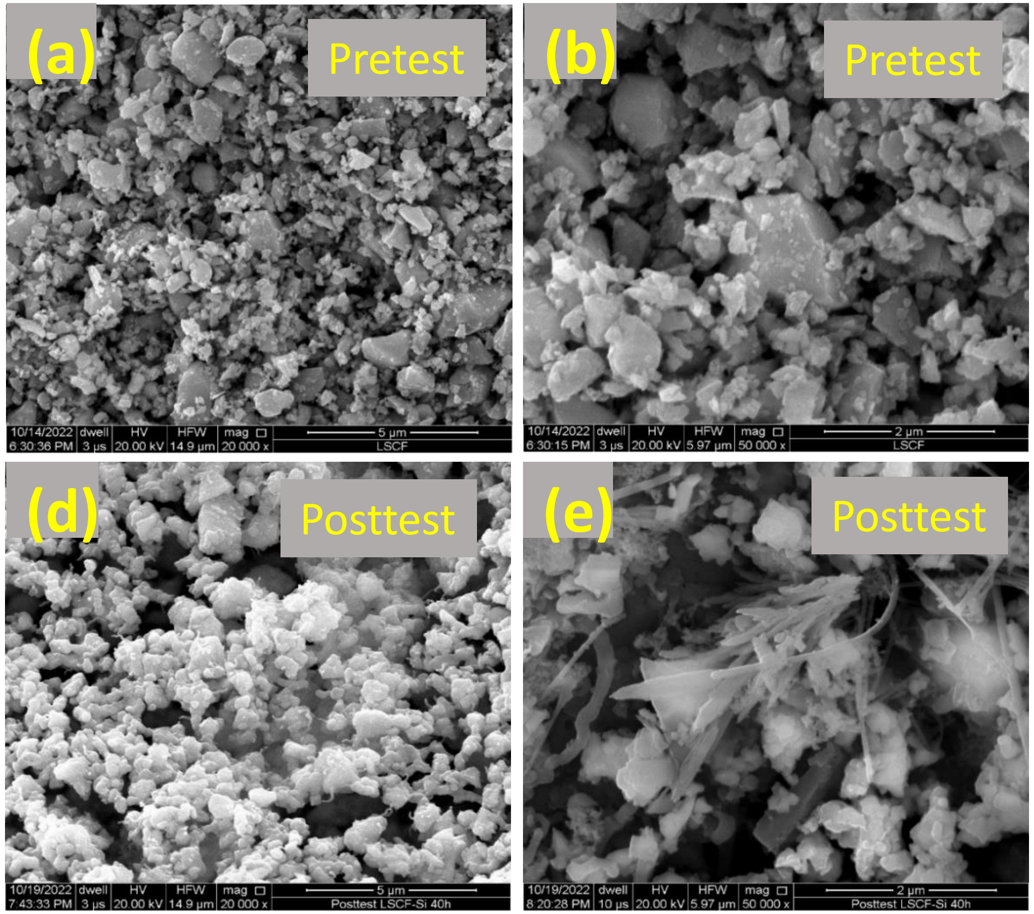
Hydrocarbon fuels + water (Reforming) → Catalytic poisoning of anode → SiOHx transport, deposition on anode, carbon formation

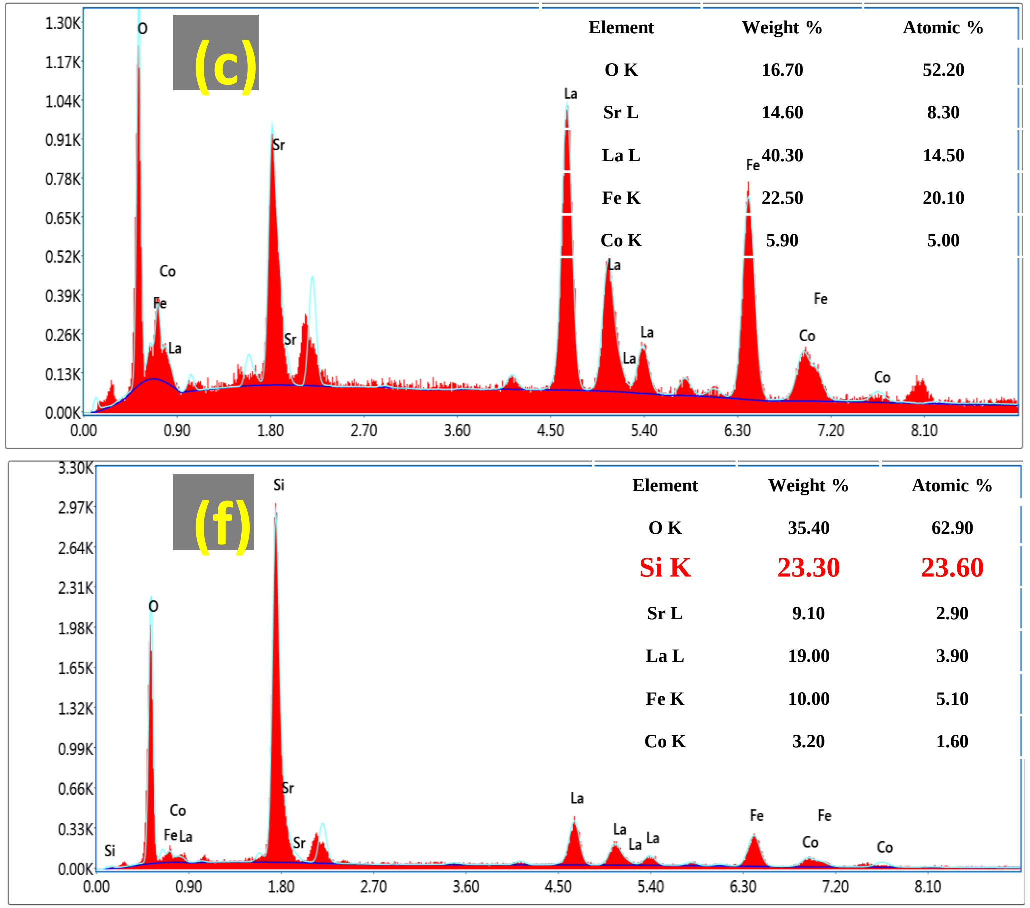
Sources of Si contaminant – Raw materials, Corrosion products, cell/ system component materials, PM, Water

Surface morphology of LSCF: Exposure to Air-H2O-SiO2

SOFC Program Review
DE- FE-0031647

LSCF exposed to humidified air (over SiO_2 source) at 800C for 50 hrs.



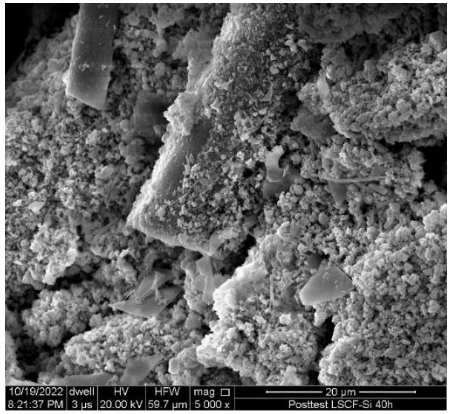


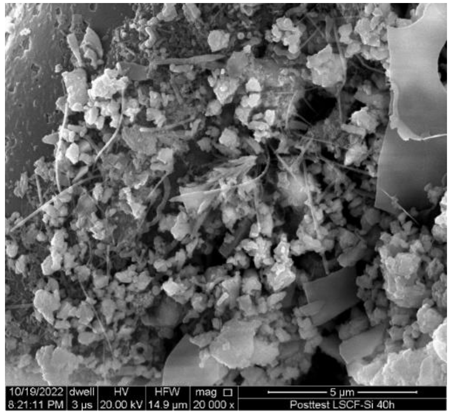
Element	Weight %	Atomic %
O K	16.70	52.20
Sr L	14.60	8.30
La L	40.30	14.50
Fe K	22.50	20.10
Co K	5.90	5.00

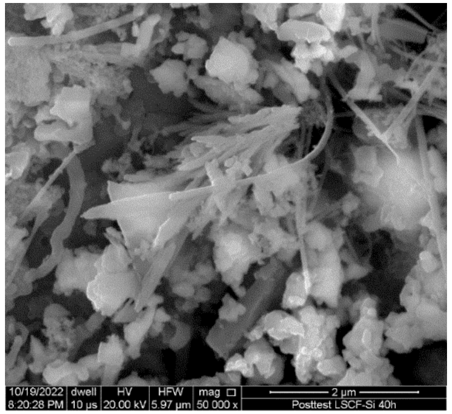
Element	Weight %	Atomic %
O K	35.40	62.90
Si K	23.30	23.60
Sr L	9.10	2.90
La L	19.00	3.90
Fe K	10.00	5.10
Co K	3.20	1.60

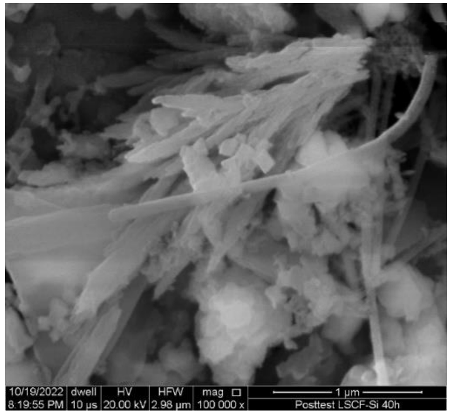
Glassy surface deposit observed

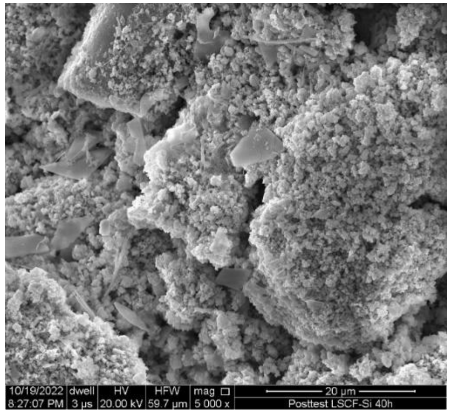
Surface Deposit Morphology: LSCF Substrate

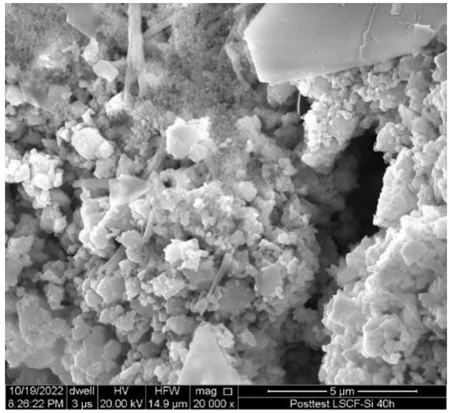


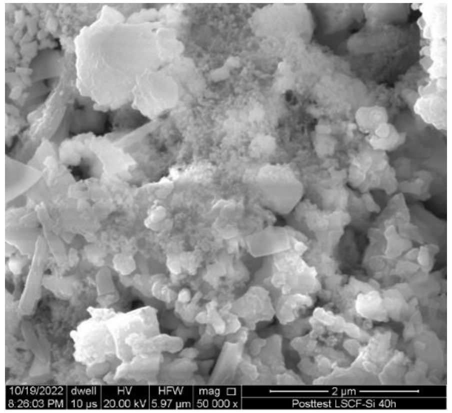


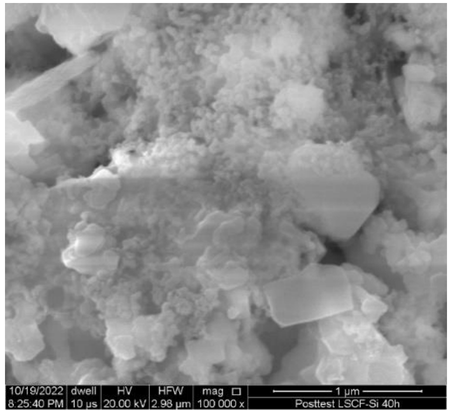












Conclusions

- Intrinsic and extrinsic trace gaseous contaminants, present in ambient air stream entering the elevated temperature electrochemical systems, have been identified.
- Formation, transport and interactions of contaminants with perovskite air electrode has been examined.
- Role of surface scale chemistry, pre-treatment conditions, formation of defects in the scale and molecular transport have been studied.
- Pretreatment of alloys under controlled exposure conditions modify the scale chemistry and morphology influencing the formation and transport of trace extrinsic contaminants.
- Getters have been fabricated for the capture of trace S (intrinsic) and Cr, Si, B (extrinsic) gaseous contaminants.
- Technical approach offers pathway for the capture of trace gaseous contaminants present in high temperature fuel cells, electrolyzers and chemical reactor systems.

➢ Cell to cell interconnect shows accelerated corrosion and spallation of scale. Cr evaporation under accelerated corrosion condition will be experimentally evaluated.

➢ Approaches for the mitigation of scale spallation and Cr evaporation have been examined.

Acknowledgements

- Dr. Rin Burke for technical and programmatic discussion
- Drs. Nilesh Dale, AbdulJabbar Hussain, Takeshi Shiomi (Nissan Motors) for technical discussion
- Dr. Toshio Suzuki (PCI) for technical discussion
- Professor Scott Misture for collaboration and getter coating
- UConn for providing test facility

Thank you