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

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22nd ANNUAL SOLID OXIDE FUEL CELL (SOFC) PROJECT REVIEW MEETING

Outline

- Program Objective-Vision and Strategy
- Technical and Broader Impact
- Accomplishments
- Technical approach
- Results and Discussion
- Summary and Conclusions
- Acknowledgements

✓ Novel approach for the capture of trace impurities present in air stream
✓ Concept applicable to IT-HT SOFC, SOEC, and OTM systems

Airborne contaminants → Electrode poisoning → Contaminant Getter → Test validation

Program Objectives

- Develop a comprehensive understanding of the origin, formation processes and the nature of gas phase airborne contaminants present in the air stream entering elevated temperature electrochemical systems.

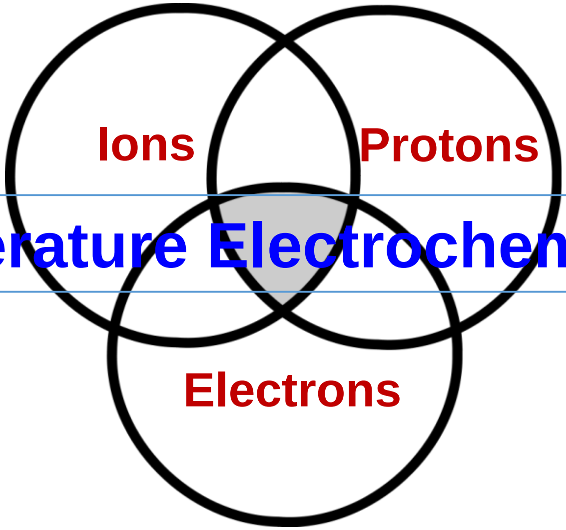
- Identify trace airborne gas phase contaminants (intrinsic and extrinsic) and develop mechanistic understanding of interactions (chemical, electrochemical and structural) with conventional air electrode materials.

- 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 at stack/ system level. Transfer technology to industrial partners.

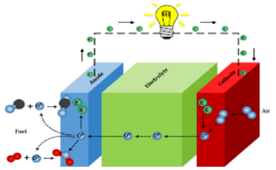
Broader Impact: High Temperature Electrochemistry

Airborne contaminants | Surface-interface processes | Electrode poisoning

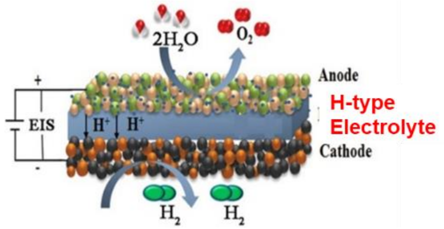


High Temperature Electrochemical Systems

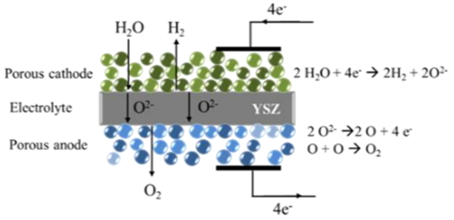
Power Generation



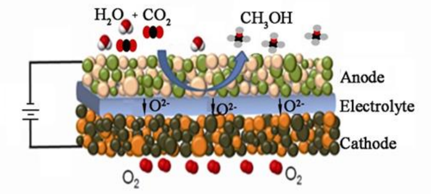
Energy Storage



Gas Separation



Fuel Production



Trace contaminants and accumulation in electrodes

→ **Thermally assisted chemo/electro/mechano degradation**

Broader Impact

- **Graduate / Undergraduate students being trained - 7**
- **Post-doctoral fellows: 3**
- **Outreach: Middle and High School, Davinci Program, STEM**
- **Undergraduate Internship: 4**

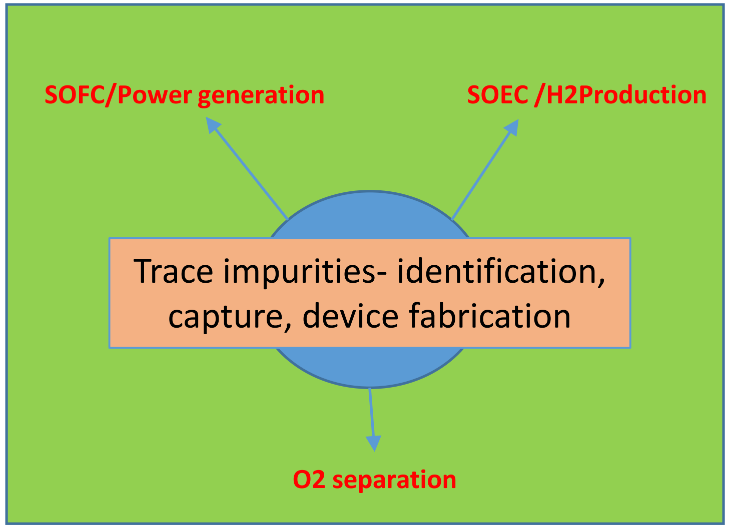
Application

Terrestrial	**Space**
Civilian	**Defense**

Training and Placement

Mr. Michael Reisert	Bloom Energy
Dr. Ashish Aphale	Asst. Professor, Kennesaw University
Mr. Justin Webster	Collins Aerospace (Pratt & Whitney)
Dr. Su Jeong Heo	Post-doctoral Fellow, NREL
Dr. Boxun Hu	Scientist, LBNL
Dr. Junsung Hong	Post-doctoral Fellow, Northwestern University
Dr. Sapna Gupta	Intel Corporation
Dr. Amman Uddin	Assistant Professor, BUET, Bangladesh

Advanced IT/HT Electrochemical Systems



This project develops basic scientific and engineering understanding of electrode degradation processes arising due to the presence of intrinsic and extrinsic gaseous impurities present in air stream. Research efforts also provide pathways for the mitigation of the cathode degradation. Low cost getters, identified and fabricated, will be used in the stack and system to offer long term resistance to electrode poisoning.

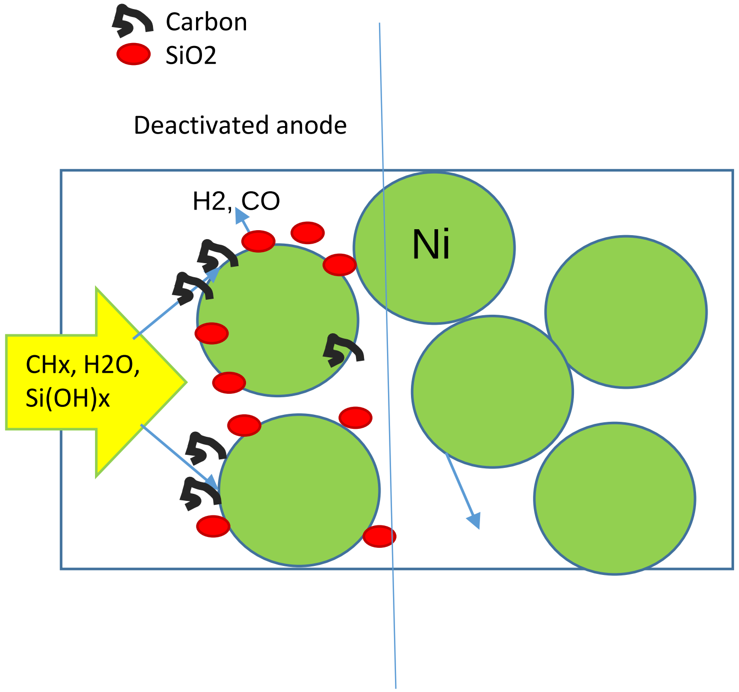
Broader Impact: Electrode poisoning in IT/HT Electrochemical Systems

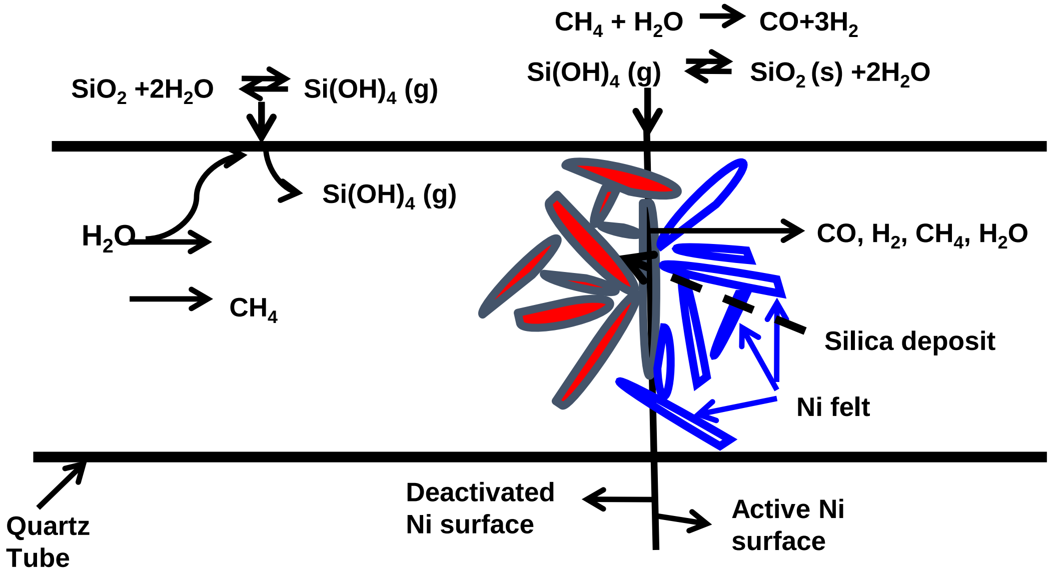
- **Intrinsic and extrinsic trace gas phase contaminants**
  - **Originating from BOP, Stack and cell components**
  - **Ingested through water**

- **Vapors of Cr, B, Bi etc. from alloys/ seals**
- **Vapor of Si from water**

Broader Impact: Electrode Poisoning and SiO_2 Deposition

Water containing SiOHx have tendency to deposit on catalytically active Ni surface. Surface coverage by SiO2 can promote carbon deposition, pulverization and electrode poisoning.

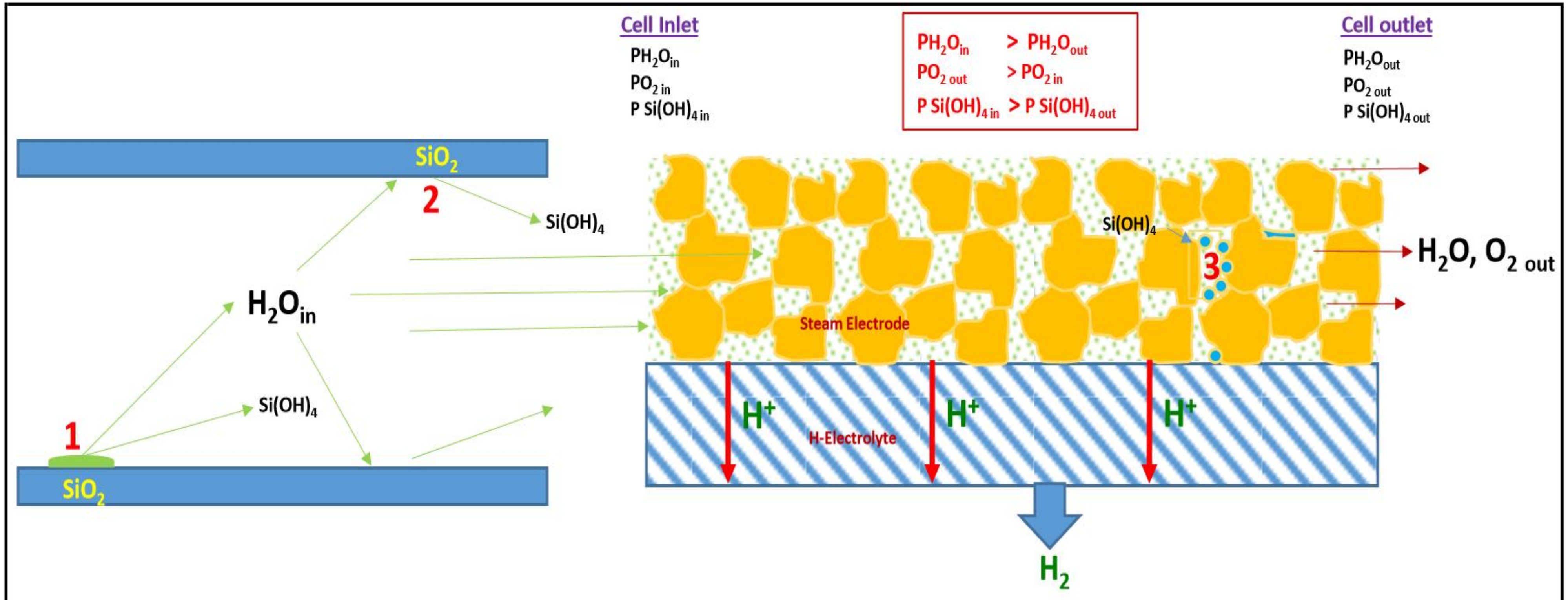




- Reduction in P_{H2O} leads to silica deposit formation
- Silica deposition in the anode is dictated by H_2O concentration profile
- Electrolysis mode may be more prone to SiO_2 deposition at FE-Elec interface

P. Singh and S.D. Vora " Vapor Phase Silica Transport" Advances in Solid Oxide Fuel Cells: Ceramic Engineering and Science Proceedings, Volume 26, Number 4, 2008

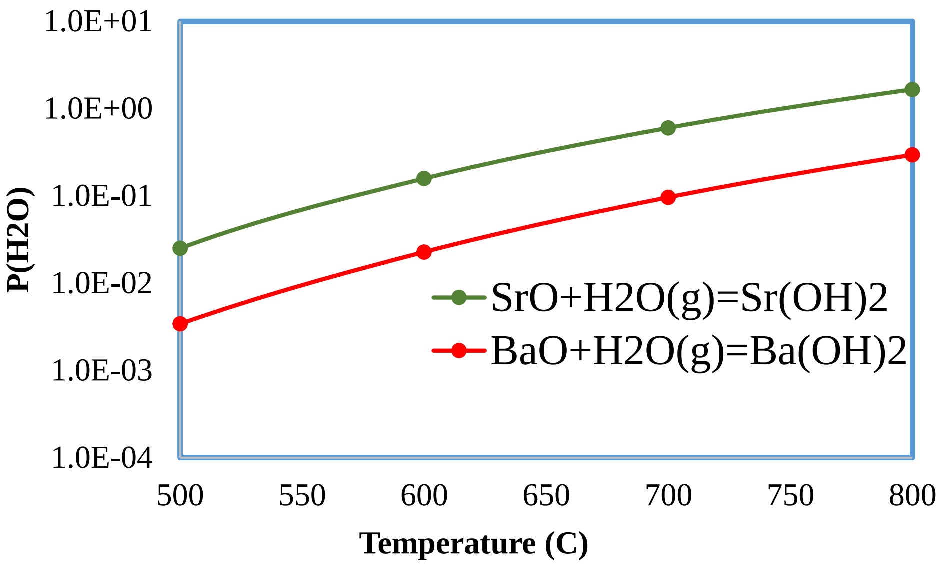
Electrode poisoning : Role of water and air borne contaminants



Silica dissolution at site 1:	(solid-Liquid)	$[SiO_2] + (H_2O)_l = \{Si(OH)_4\}_l$	(1)
Silica evaporation at site 2:	(Solid-Gas)	$[SiO_2] + (H_2O)_g = \{Si(OH)_4\}_g$	(2)
Silica deposition at site 3:	(Gas-solid)	$\{Si(OH)_4\}_g = [SiO_2] + (H_2O)_g$	(3)

Water chemistry monitoring and control remains important for long term stable operation of electrolyzers. Electrode can poison leading to increased polarization during long term.

SrO and BaO interactions with Si vapor



Thermocalc shows chemical interaction between cations and Si(OH)4

BaO (s) + Si(OH)4 (g) = BaSiO3 (s) + 2H2O(g); ΔG = -489.486 kJ/mole

SrO(s) + Si(OH)4 (G) = SrSiO3 (s) + 2H2O(g) ; ΔG = -458.953 kJ/mole

Sample calculation for $BaSiO_3$ (FactSage):

$$\Delta G = G_{product} - G_{reactant}$$
$$= (G_{BaSiO3} + 2G_{H2O}) - (G_{BaO} + G_{Si(OH)4})$$
$$= (-1788366-2*448571) - (-646130-1549892)$$
$$= -489.486 \text{ kJ/mole}$$

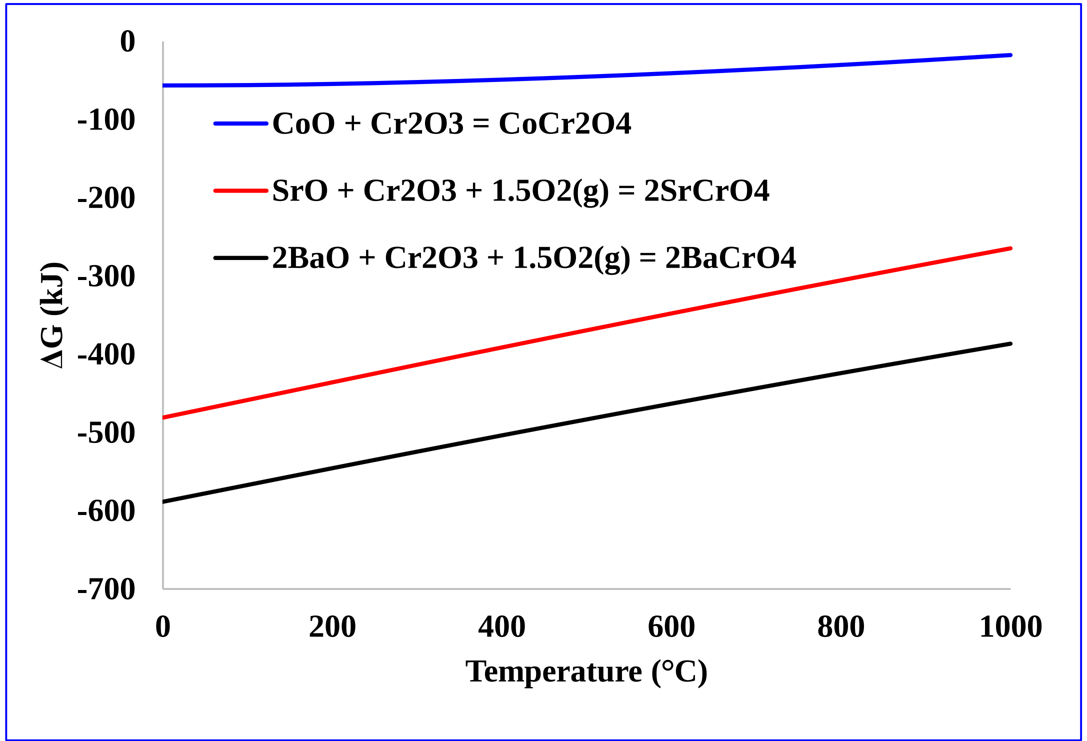
TABLE 4 Recommended thermodynamic properties of $Si(OH)_4$(g) at 298.15-2000 K

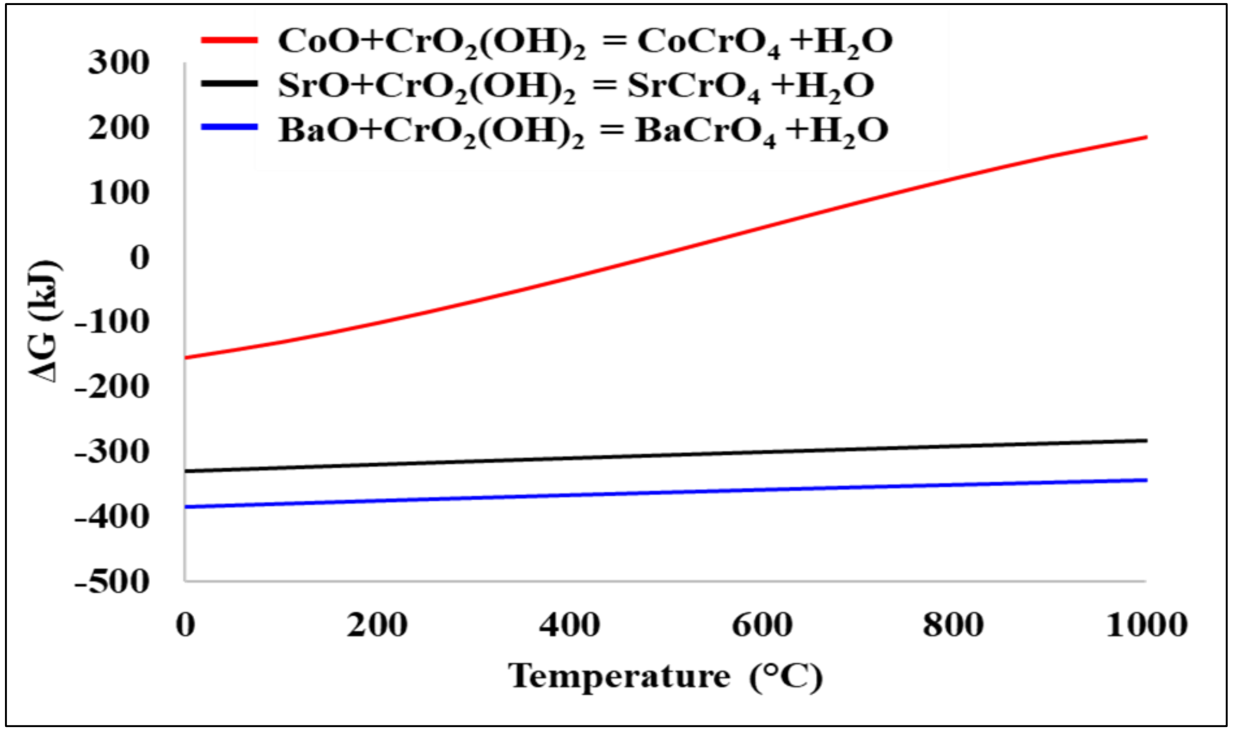
T, K	C_p, J K^{-1} mol^{-1}	S^o, J K^{-1} mol^{-1}	$H^o_T - H^o_{T_r}$, kJ/mol	$(G^o_T - H^o_{T_r})/T$, J K^{-1} mol^{-1}	G^o, kJ/mol	$\Delta_f H^o(T_r) + (H^o_T - H^o_{T_r})$
298.15	115.28	338.550	0.000	338.550	−1241.370	−1346.300
Uncertainty		±1.32		±1.32	±2.34	±2.37
500	144.83	406.252	26.687	352.878	−1316.870	−1319.613
1000	170.32	516.118	106.657	409.461	−1549.892	−1239.643
1500	182.95	587.723	195.169	457.610	−1826.846	−1151.131
2000	191.24	641.607	288.922	497.146	−2134.723	−1057.378

C_p/R (298.15-2100 K) = $27.4945 - 6.22157 \times 10^{-3}T + 4.34739 \times 10^{-6}T^2 - 9.07719 \times 10^{-10}T^3 - 4.48699 \times 10^{3}T^{-1} + 2.58937 \times 10^{5}T^{-2}$

Plyasunov, A. V., Zyubin, A. S., & Zyubina, T. S. (2018). Thermodynamic properties of Si (OH) 4 (g) based on combined experimental and quantum chemistry data. Journal of the American Ceramic Society, 101(11), 4921-492

SrO and BaO interactions with Cr vapor

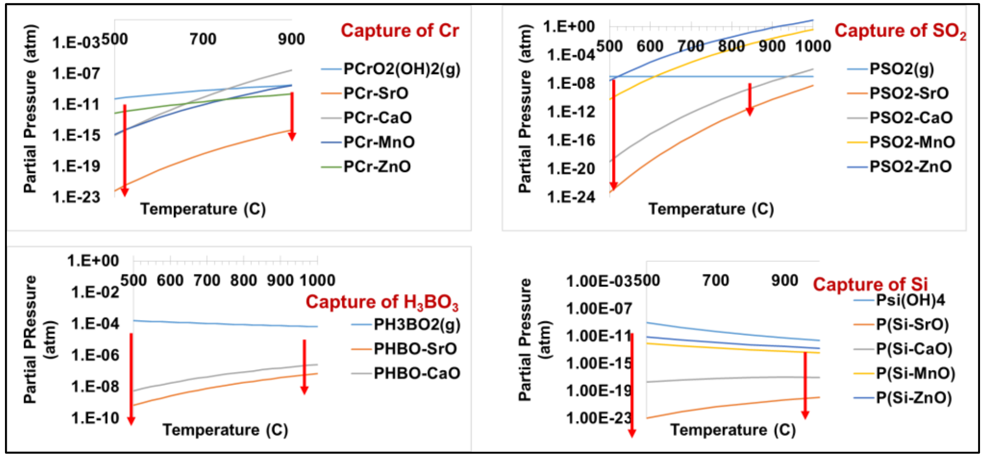


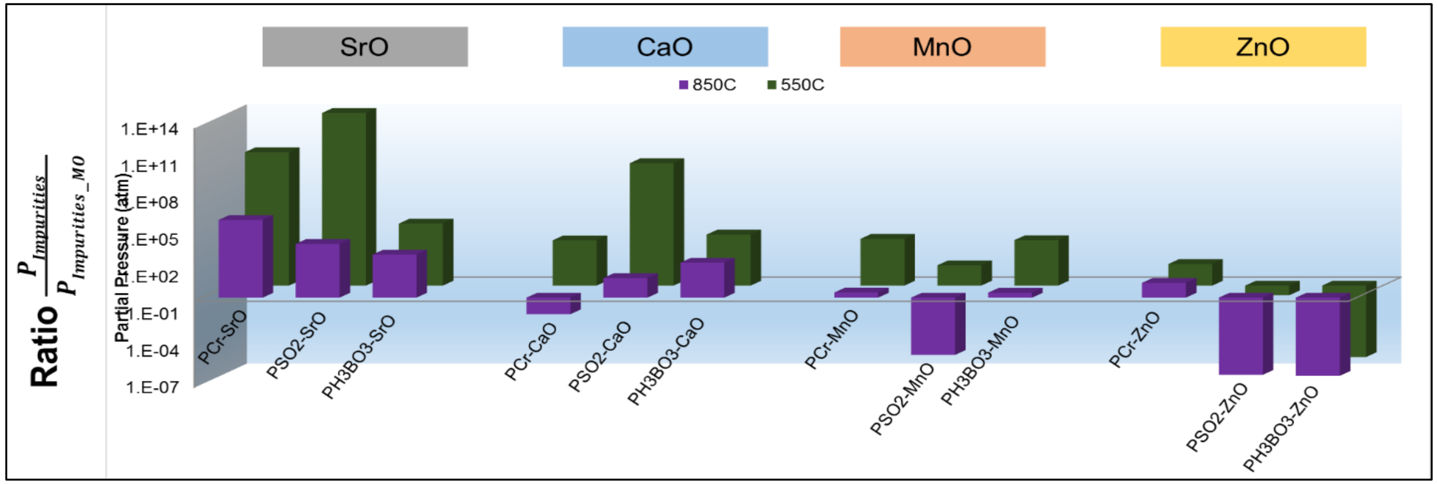


The calculations confirm the thermodynamic feasibility of stable $CoCr_2O_4$, $BaCrO_4$ and $SrCrO_4$ formation in the presence of Cr_2O_3 or Cr vapor exposure

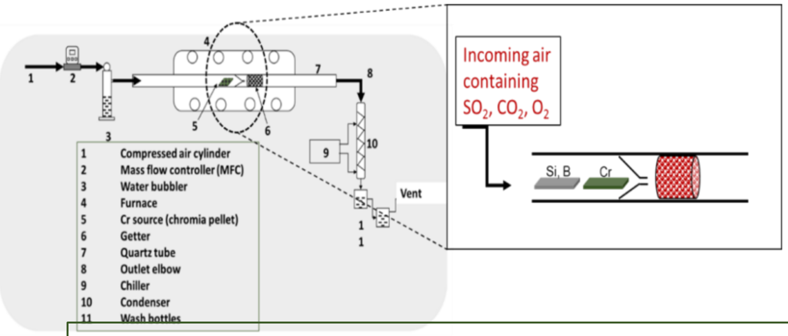
Getter selection for multi-contaminant systems

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

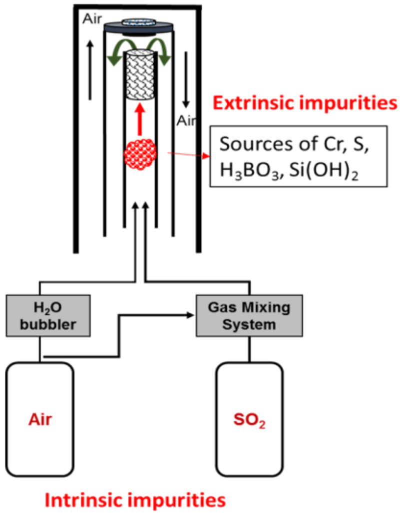




Transpiration tests



Electrochemical tests



Response parameters:

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

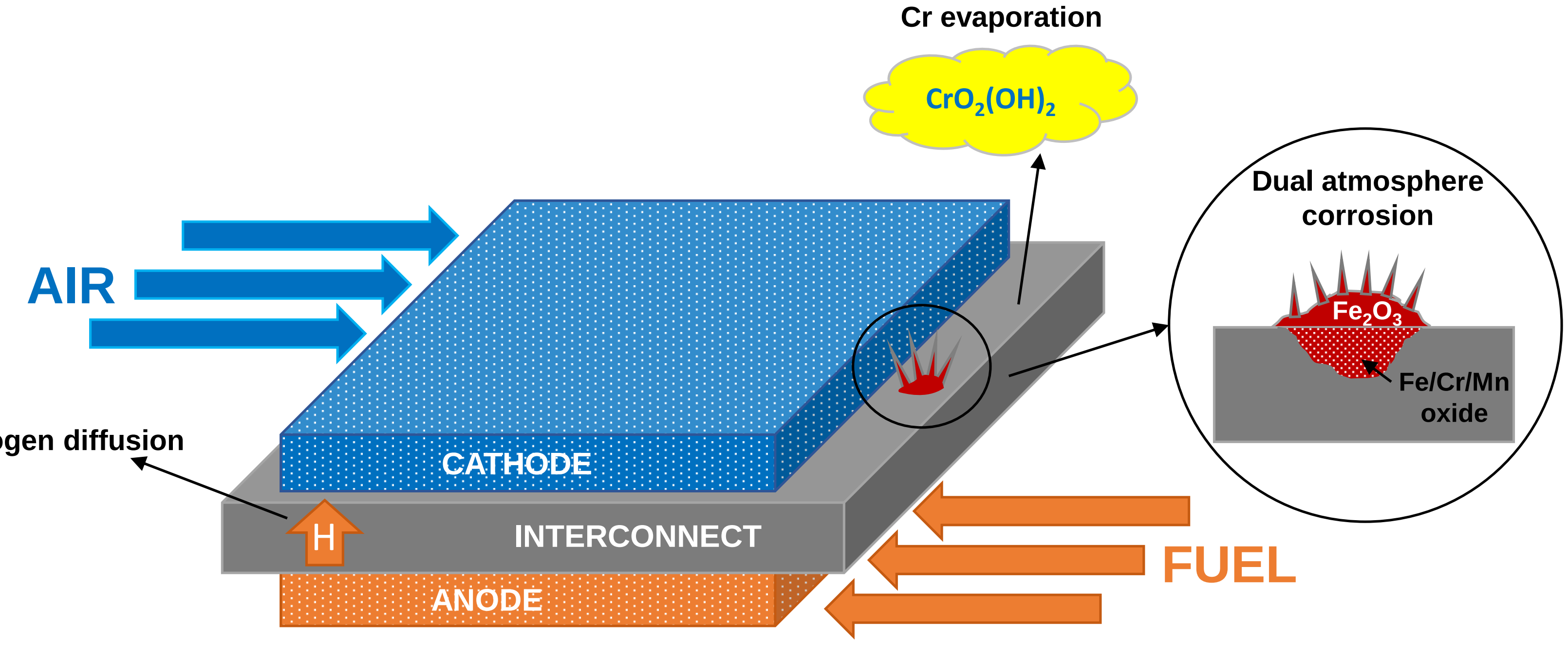
- Calculated ratio of partial pressures of various gas phase impurities over their partial pressure in presence of getters at 850 and 550°C.
- SrO getter can lower the partial pressure of all gas phase impurities in 550-950C.
- Intrinsic impurities can be captured before entering stacks
- Large amount (~200g) of getter powders have been provided to Alfred Univ. for developing optimized coating processes.

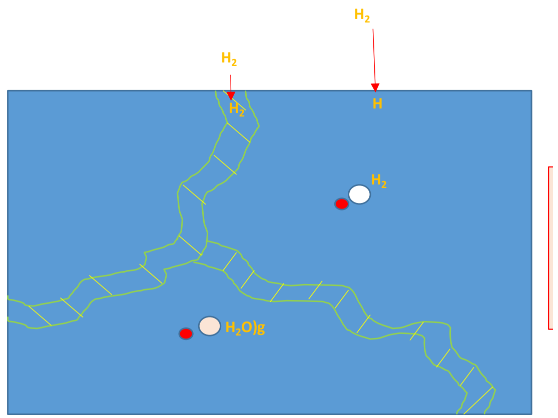
Combined Degradation

Localized metal loss, Scale spallation, High resistance

Continued Cr evaporation due to spallation, higher Cr loss

Metal-Hydrogen Interaction Pathways

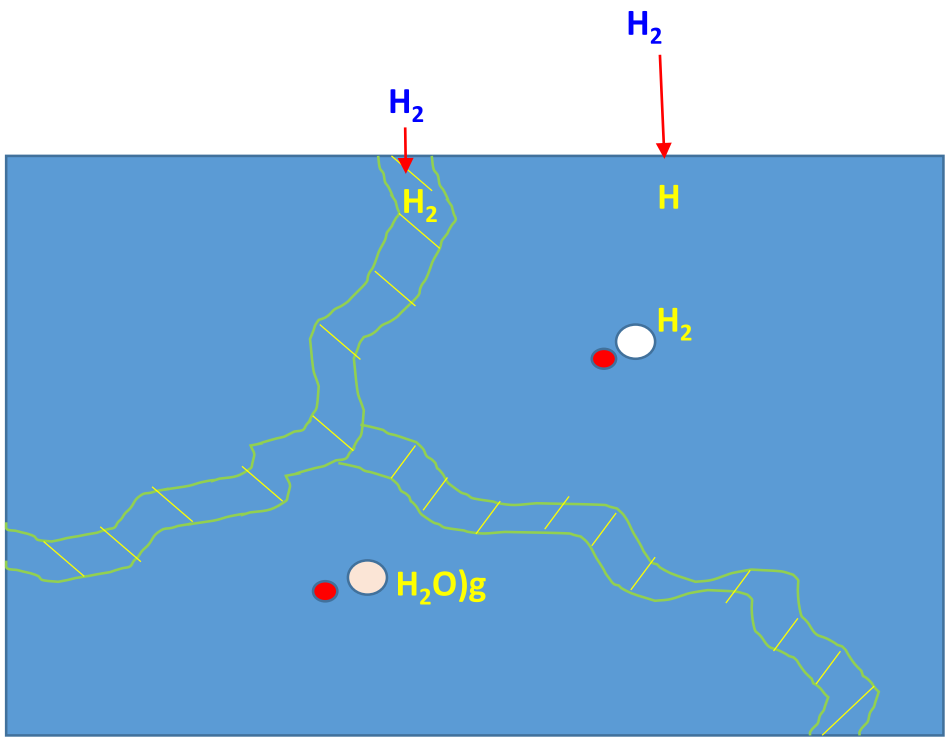




$H_2(g)^{Atm} = H_2(g)^{GB}$	(Grain boundary Transport)
$H_2(g) = 2(H)_{Metal}$	(Sievert's Law)
$(H)_M A = (H)^M B$	(Bulk transport)
$(H)^A = (H_2)g^A$	(Heterogeneous Nucleation)
$(H)_M + (O)_M = (H_2O)g$	(Dissolved species interaction)
$(H)_M + MO = (M) + (H_2O)g$	(Metal oxide Reduction)

T ~ 600-800 °C

Metal-Hydrogen Interaction Pathways



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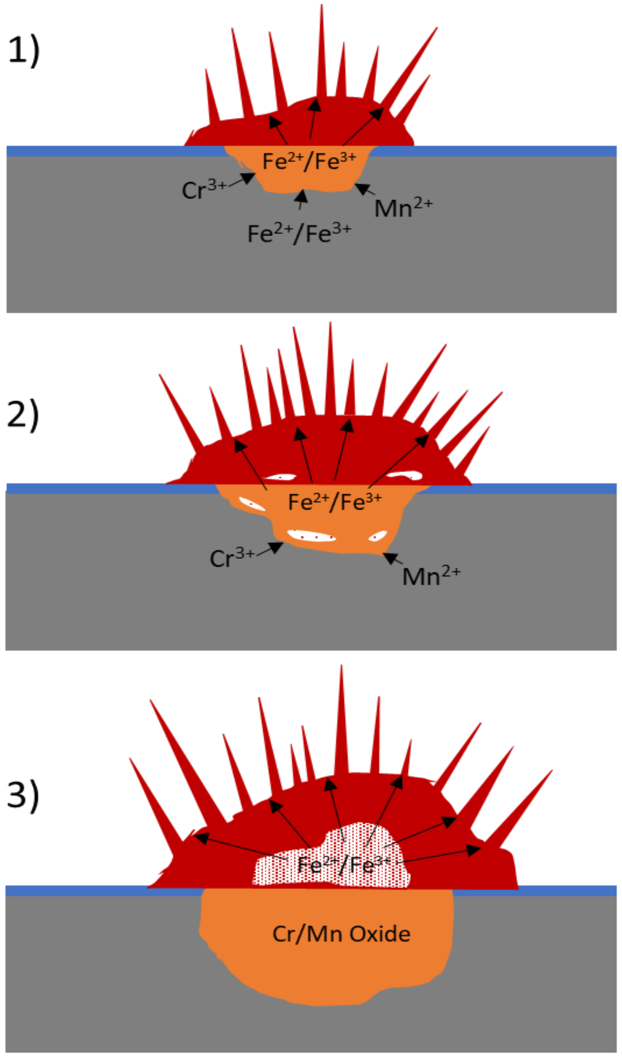
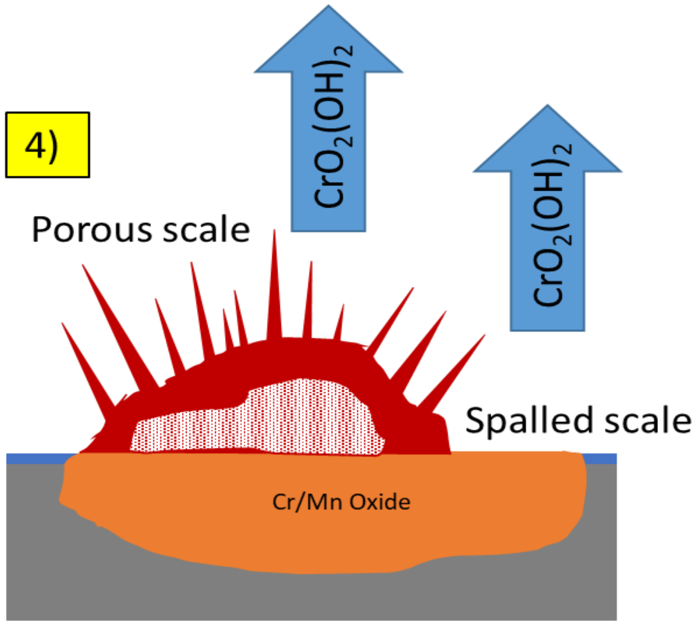
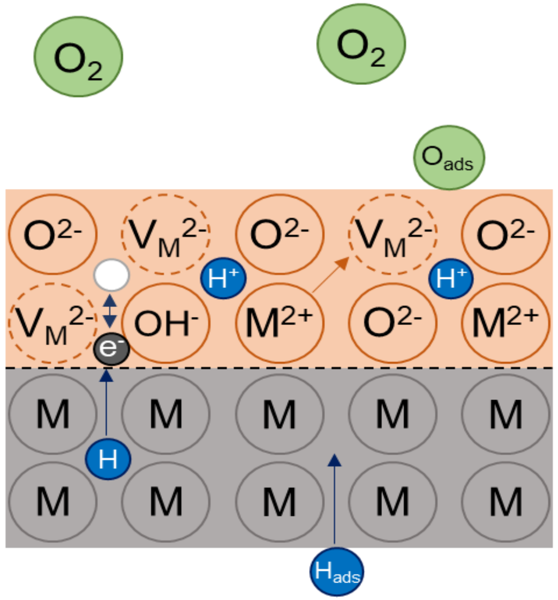
Corrosion behavior of FSS in dual atmosphere

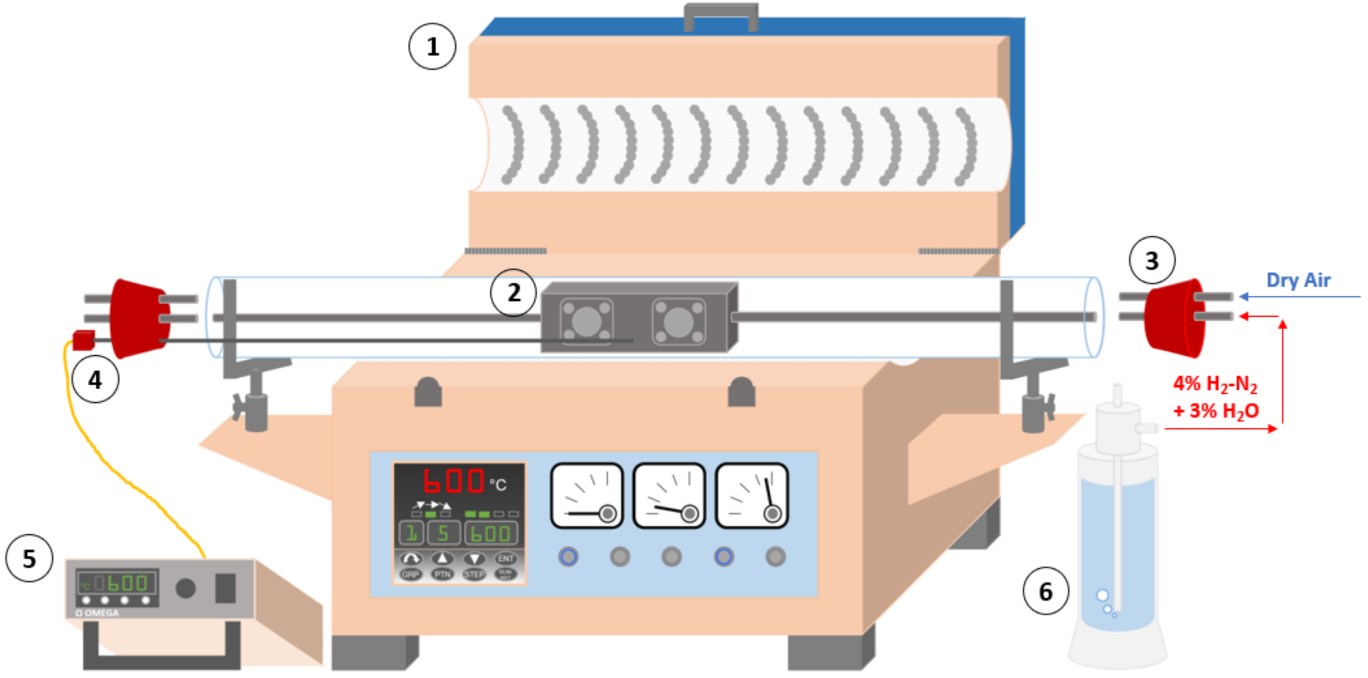




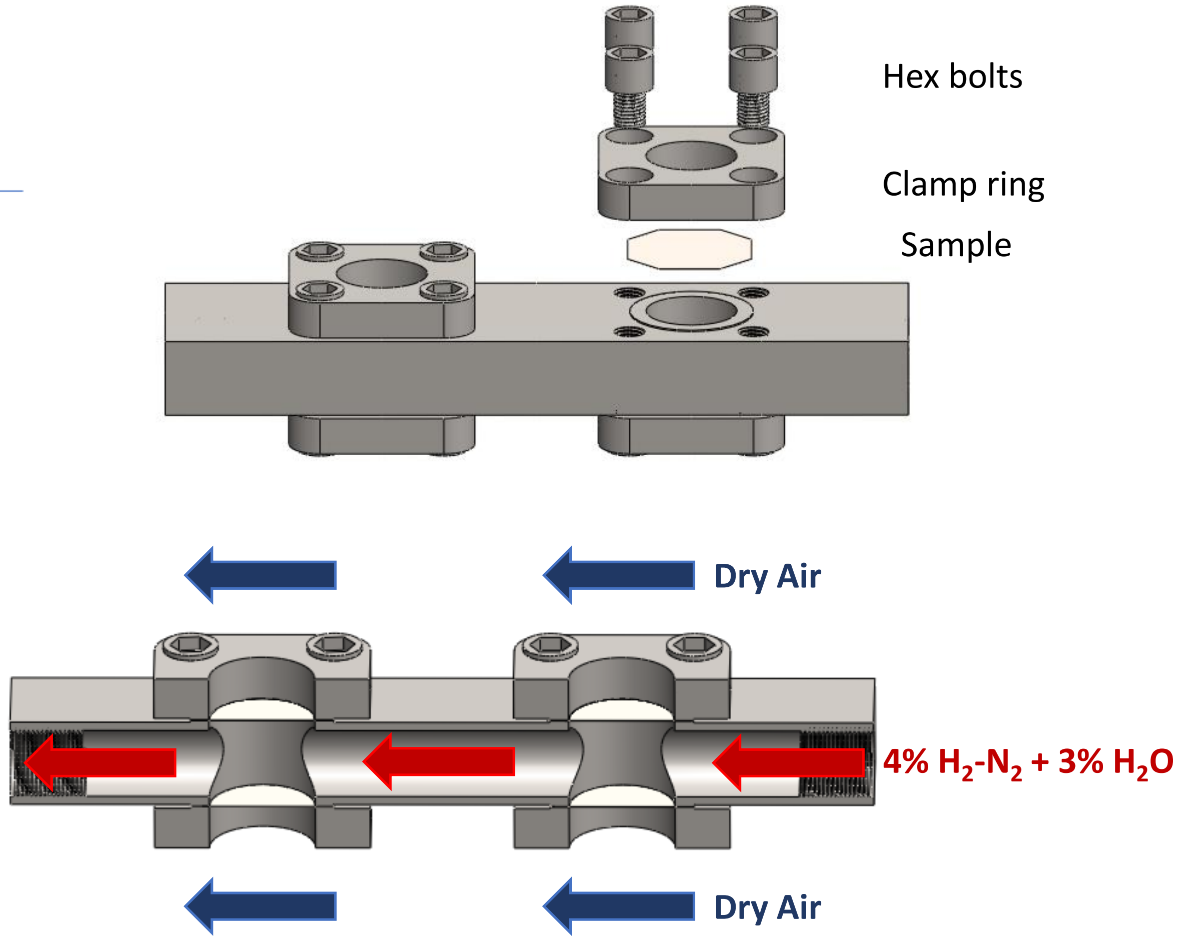


- Oxidation occurs via O_2 dissociation and H_2O dissociation at surface
- Monatomic hydrogen may diffuse into MO scale and become interstitial proton
- Charge imbalance from proton would induce more negative charge (metal ion vacancies)
- Leads to outward FeOx growth, porous scale, thicker CrOx below which is exposed upon scale spalling

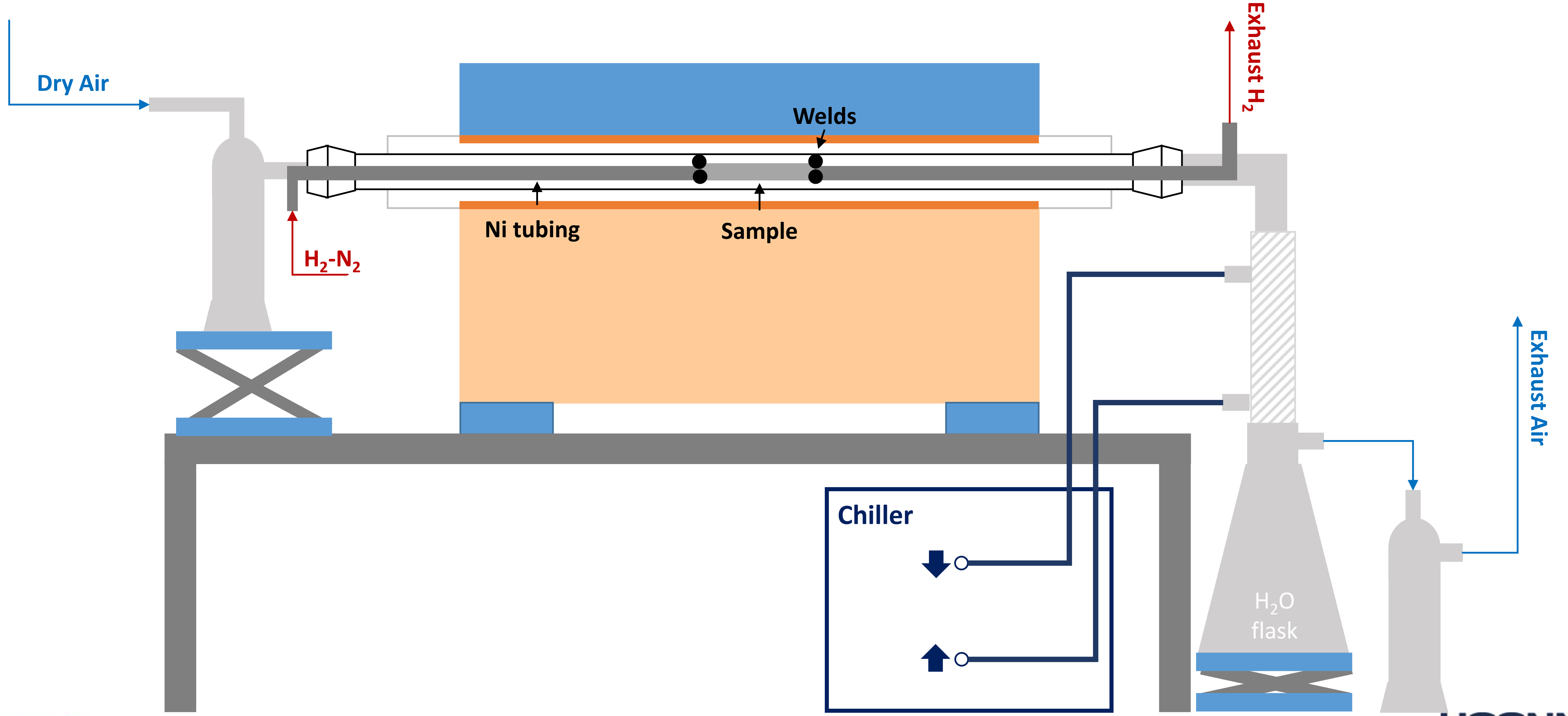
Dual Atmosphere Exposure: Test Validation



1. STF1200 furnace
2. Dual atmosphere reaction chamber
3. Si stopper
4. Thermocouple probe
5. Temperature feedback
6. 6. H_2O bubbler.

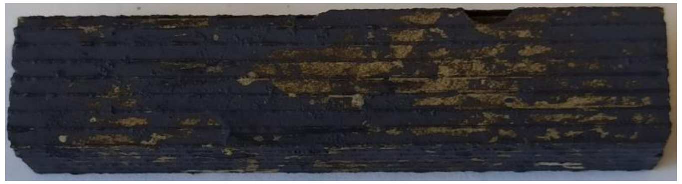


Cr Transpiration and Dual Atmosphere Test

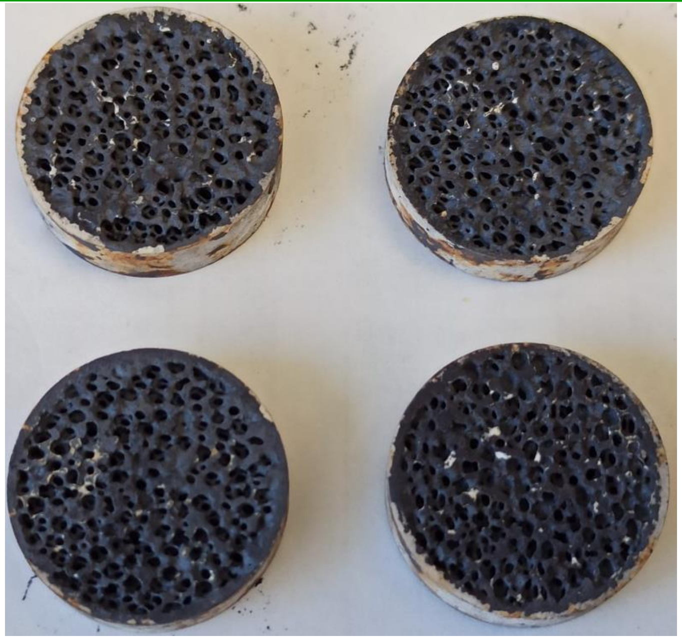


Getter Fabrication

Length=5.0 cm
Breadth= 2.5 cm
Height=2.5cm



Length=5.0 cm
Breadth= 1.0 cm
Height=2.5cm



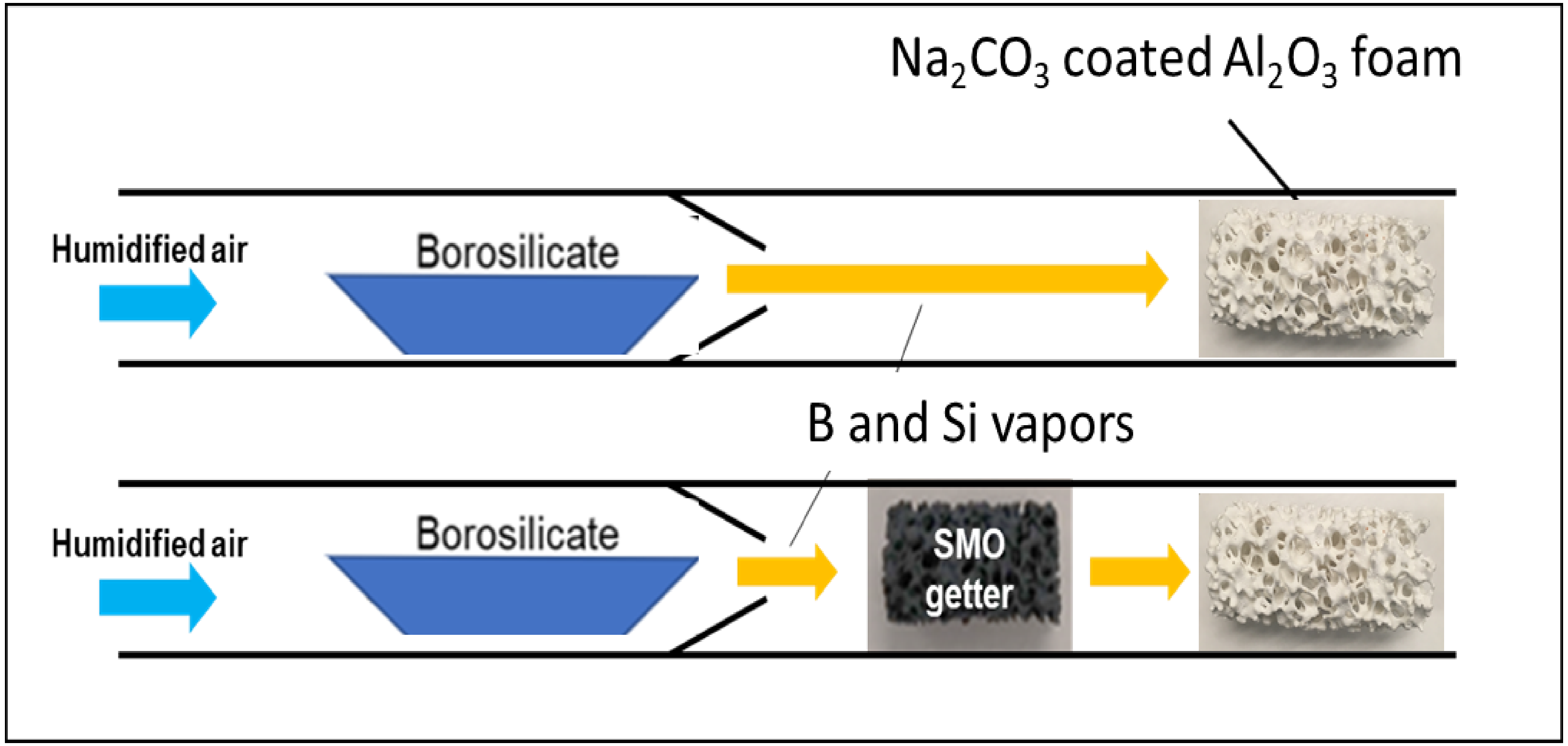
Diameter=2.5 cm
Height=0.5cm

Diameter=2.5 cm
Height=0.5cm

Optical Images and Dimensions of samples

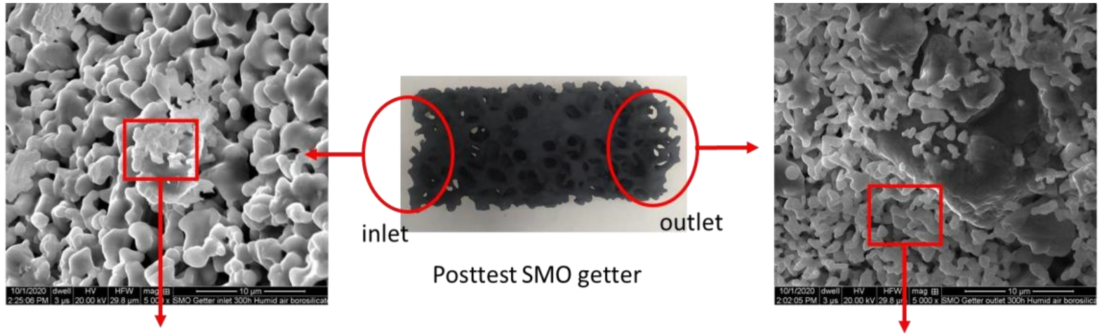
Work performed by prof. Scott Misture, Alfred University

Evaporation Studies: B and Si evaporation form glasses



Schematic of SMO getter performance test.

Evaporation Studies: B and Si evaporation form glasses



Element	Weight %	Atomic %
Al K	1.50	3.70
Si K	1.10	2.70
Sr L	50.80	38.00
Mn K	46.50	55.60

Element	Weight %	Atomic %
Al K	2.60	5.90
Si K	1.10	2.30
Sr L	33.00	22.60
Mn K	63.20	69.10

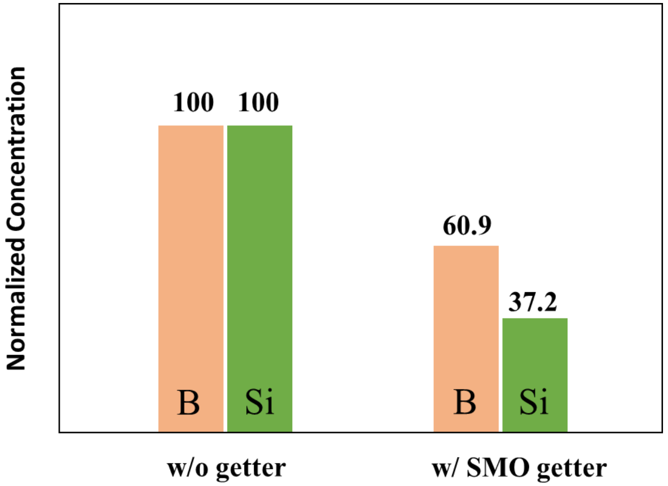
SEM morphology and EDS analysis of posttest SMO getter at inlet and outlet after test in humidified air for 300h at 700C

Sample Details	Boron concentration	Silicon concentration
A (Na_2CO_3 aqueous solution): without SMO getter	10680 μg/L	21570 μg/L
B (Na_2CO_3 aqueous solution) : With SMO getter	6500 μg/L	8027 μg/L
(Concentration in A / Concentration in B) X 100	60.9 %	37.2 %

B and Si concentrations in Na_2CO_3 (determined by inductively coupled plasma (ICP)

Si and B gas phase contaminants are captured by alkali carbonates.

Comparison of the amount of boron and silicon concentration in the presence and in the absence of SMO getter



Conclusions

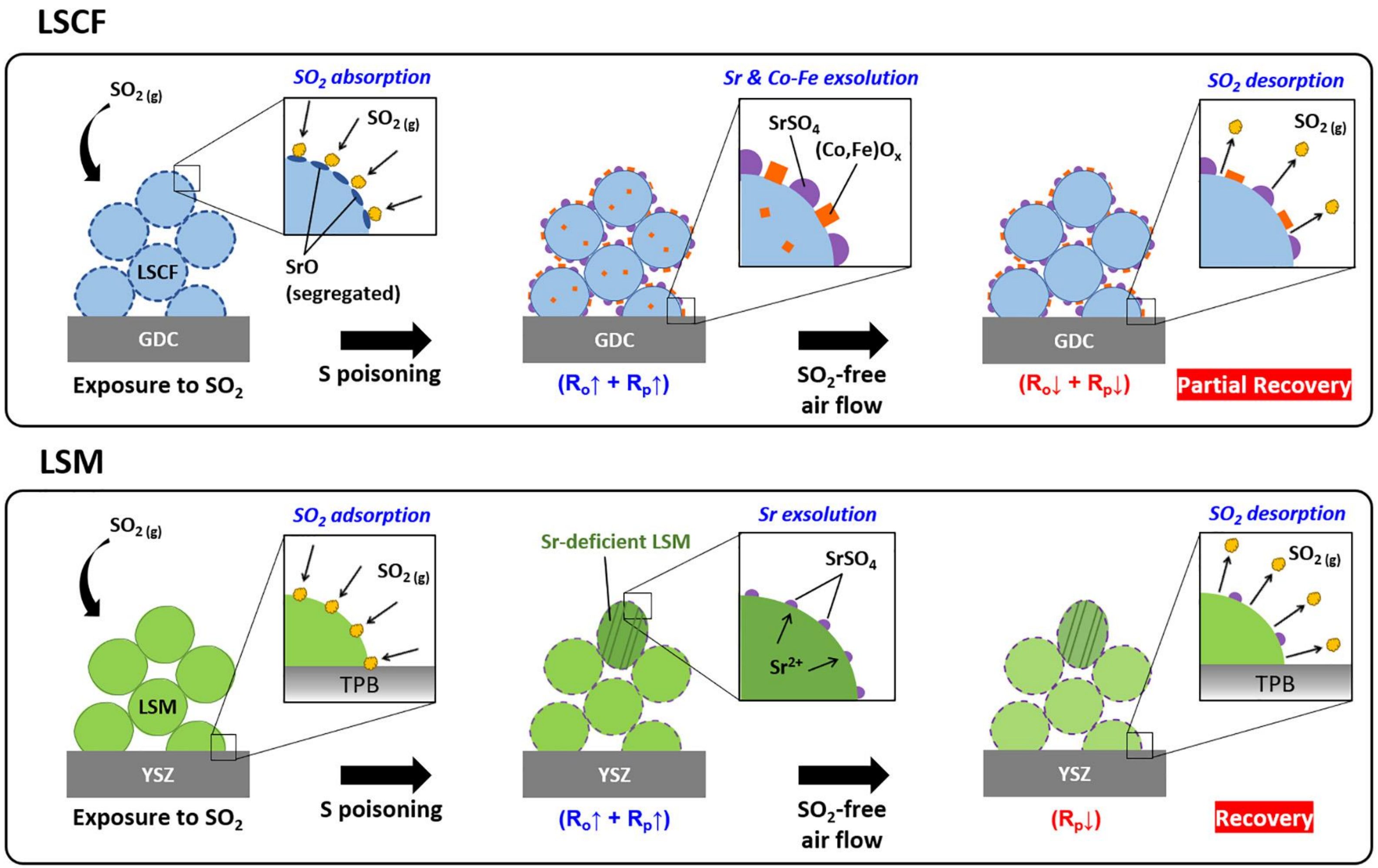
- Sources of airborne impurities have been identified. Trace (ppm to ppb) levels of impurities can exist in the gas phase.
- Gas phase impurities remain predominantly acidic in nature and have affinity to react with basic constituents of the air electrode resulting in the formation of thermodynamically stable and electrochemically inactive reaction products.
- Cell to cell interconnect shows accelerated corrosion and spallation of scale. Cr evaporation under accelerated corrosion condition will be experimentally evaluated.
- Approaches for mitigation of scale spallation and Cr evaporation will be examined based on thermochemical models.

Acknowledgements

- **Dr. Rin Burke for technical and programmatic discussion**
- **Dr. Nilesh Dale for technical discussion**
- **Professor Scott Misture for getter fabrication**
- **UConn for providing test facility**

Thank you

Electrode Poisoning



Schematic diagram of the sulfur poisoning and recovery process of the LSCF and LSM electrodes under the presence and absence of SO2.g/ : (A) SO2 absorption at SrO present on the LSCF particle surface, (B) SrSO4 formation and Co-Fe exsolution over LSCF, (C) SO2 desorption and partial dissolution of SrSO4 and (Co,Fe)Ox onto LSCF under SO2-free air flow, (D) SO2 absorption on the Sr-terminated LSM particle surface, (E) SrSO4 island formation on the LSM surface leaving a Sr-deficient LSM, and (F) SO2 desorption and partial dissolution of SrSO4 onto LSM under SO2-free air flow.