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

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U.S. DEPARTMENT OF ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY

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Presentation Outline

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

➢ Airborne trace contaminants present in both high and low temperature electrochemical and conventional combustion systems
➢ Long term performance degradation due to the accumulation and interaction of contaminants
➢ Getters effectively capture the airborne contaminants and prevent long term degradation
➢ Getters can be effectively used in SOFC's, R-SOFC's , SOEC's, chemical reactors and gas separation systems.

✓ 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.

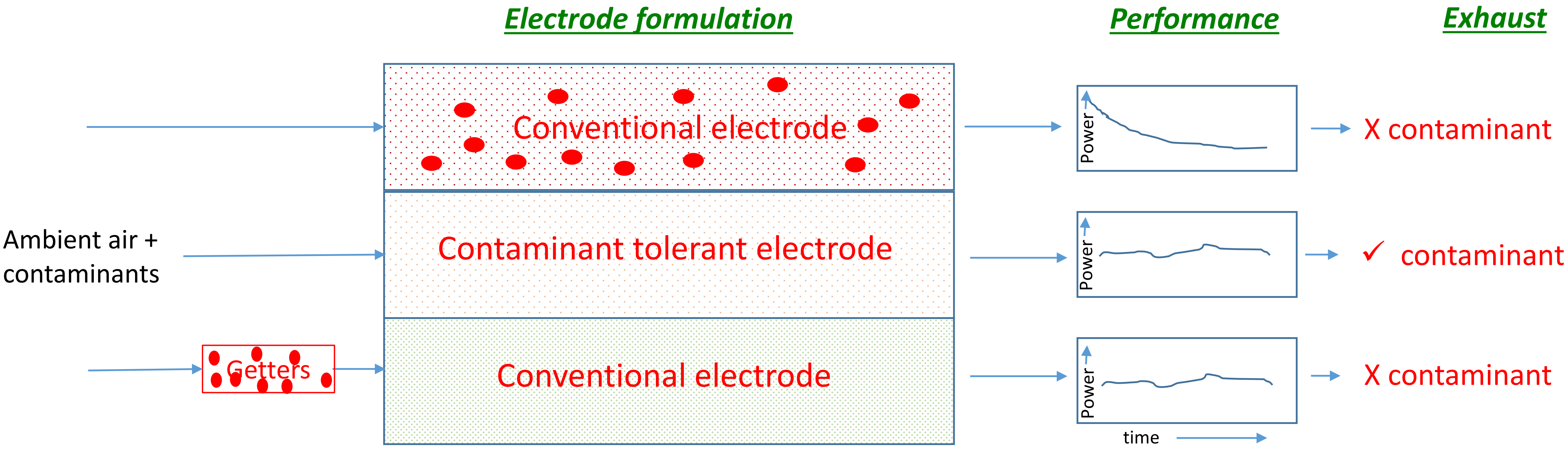
- Develop mechanistic understanding of contaminant interactions (chemical, electrochemical and structural) with conventional air electrode materials.

- 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.

Trace Contaminant interactions with Cell components

Three Scenarios considered:



Presence and level of contaminants – dictated by the system configuration and materials selection

Exposure conditions: Electrochemical systems

Levels of Humidity – low (~3%) to High (~90%)
Cathode materials – LSCF, PBSCF, and others
Contaminants – Cr, Si, B, S and others

Fuel cell mode – inlet and outlet conditions
Electrolysis mode – oxygen ion/ proton conductors
inlet and outlet conditions

Accomplishments

- Presence of intrinsic (S) and extrinsic (Cr, Si) trace gaseous contaminants have been identified in ambient air stream.
- Formation, transport and interactions of contaminants with perovskite air electrode has been examined. Chromates, chromites and silicates form in various perovskite electrodes due to favorable and irreversible reaction pathways.
- Getters have been identified, synthesized, and fabricated for the capture of trace S (intrinsic) and Cr, Si (extrinsic) gaseous contaminants.
- Technical approach offers a low cost and scalable pathway for the capture of trace gaseous contaminants present in high temperature fuel cells, electrolyzers and chemical reactor systems.

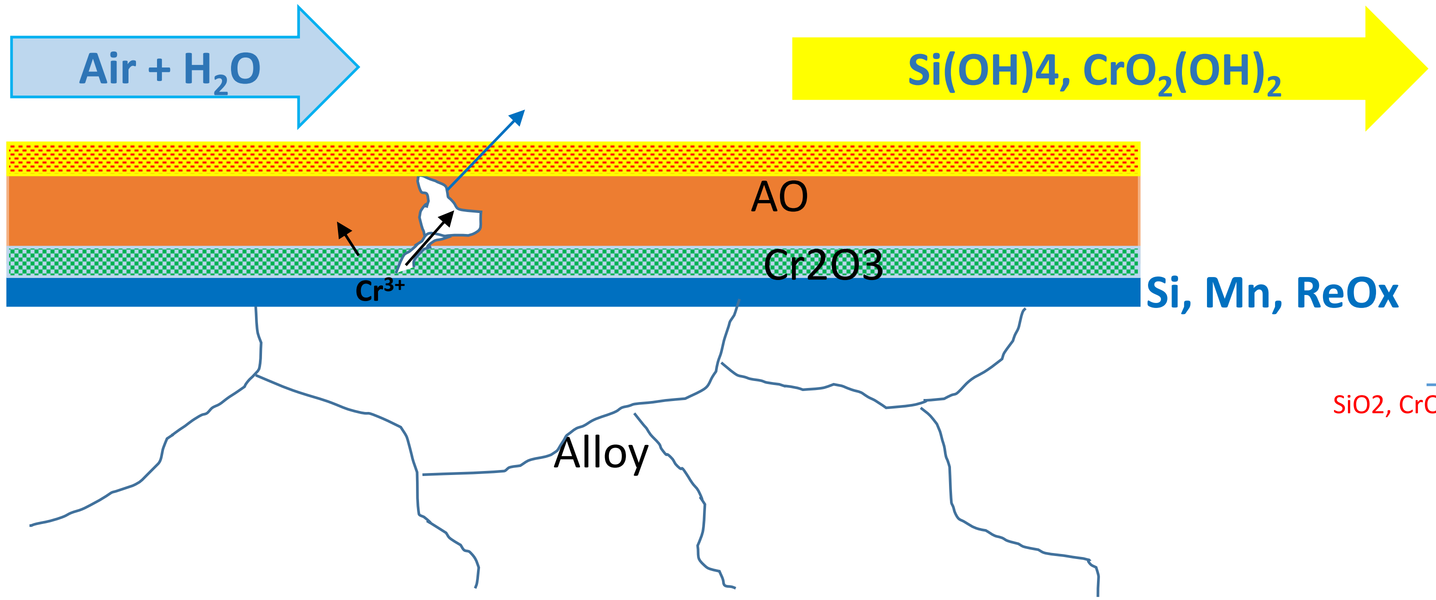
Large range of contaminants   large volume of reactants   longer operating times

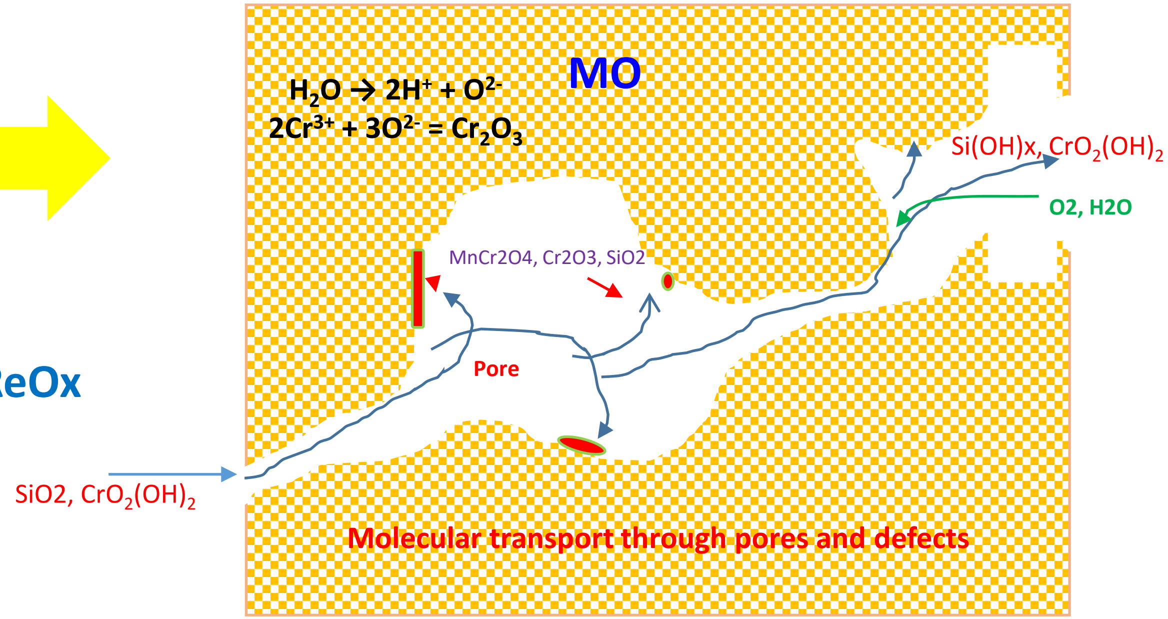
Select publications: Cr evaporation and capture (my group)

1. S. Belko, P. Dubey, K. X. Lee, P. Singh, J. Hong, M. Reisert, and B. Hu "Multi-Contaminant Getter for Trace Airborne Contaminant Capture in Elevated Temperature Electrochemical Systems" 243rd ECS Meeting ,18th International Symposium on Solid Oxide Fuel Cells
2. 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
3. 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
4. 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
5. 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,
6. 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)
7. 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)
8. 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
9. 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
10. 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
11. 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
12. 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
13. 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

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.





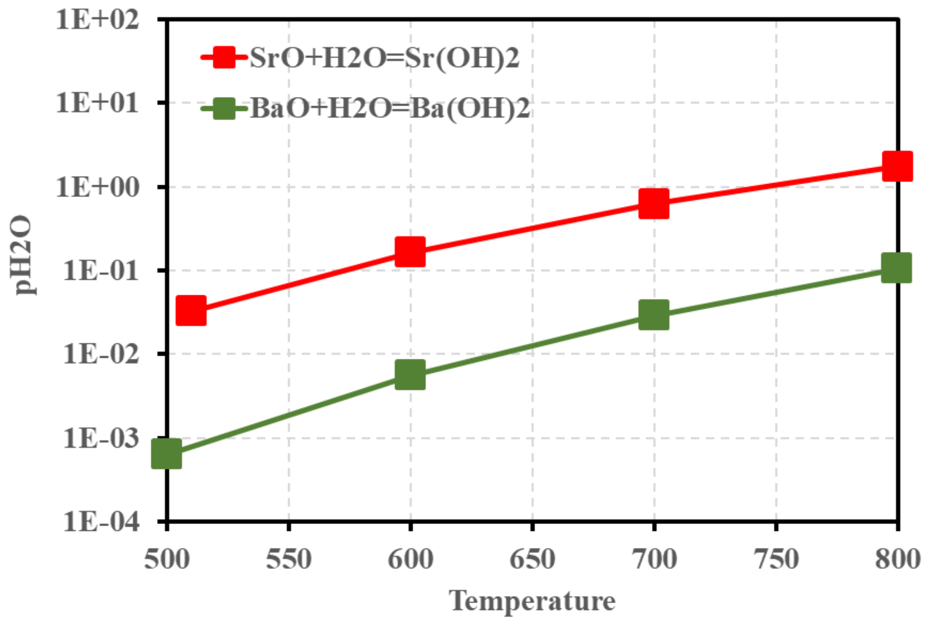
Examine molecular transport of reactants and products through defective surface oxides

BaO and SrO with H2O and gaseous Si species

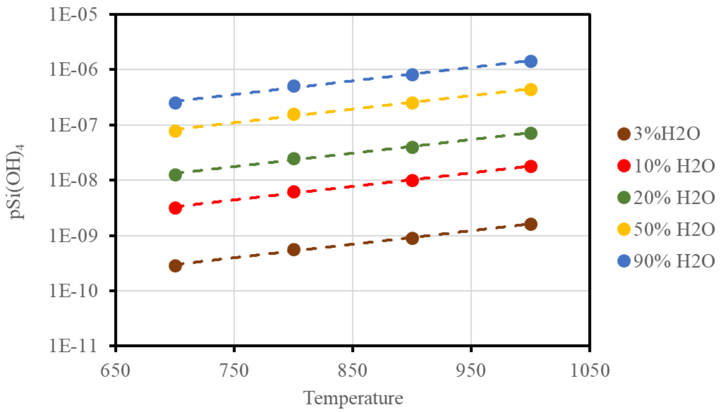
BaO (s) + H_2O (g) = $Ba(OH)_2$ (s)
SrO (s) + H_2O (g) = $Ba(OH)_2$ (s)

At operating temperature $P_{(H2O)} > P_{(H2O)eq}$

Surface segregated BaO and SrO form the respective hydroxide phase in high humidity conditions



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



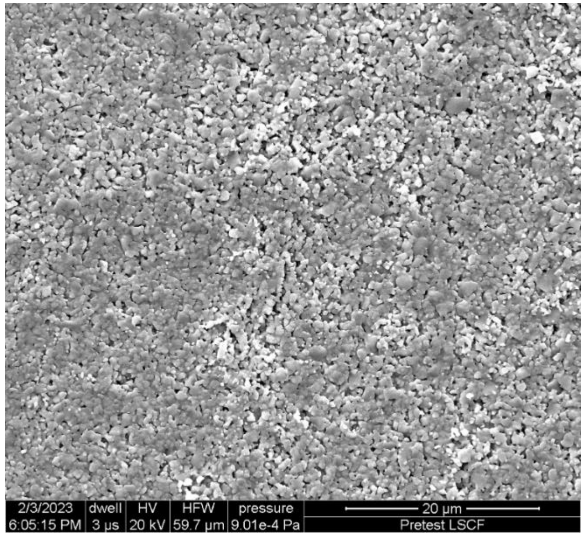
Changes in $Si(OH)_4$ partial pressure with temperature and humidity levels

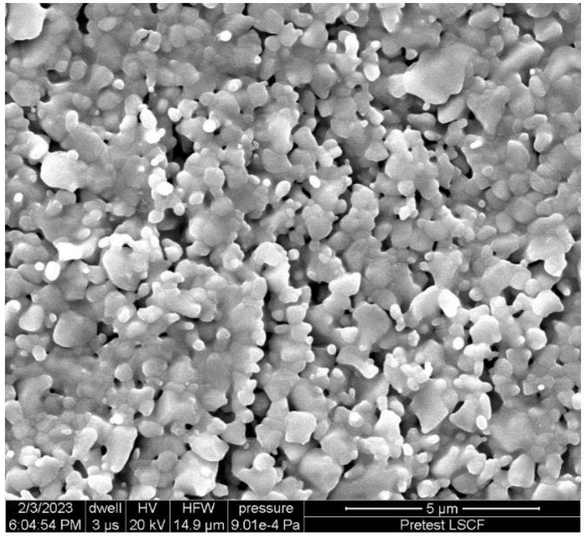
Recommended thermodynamic properties of $Si(OH)_4$(g) at 298.15-2000 K

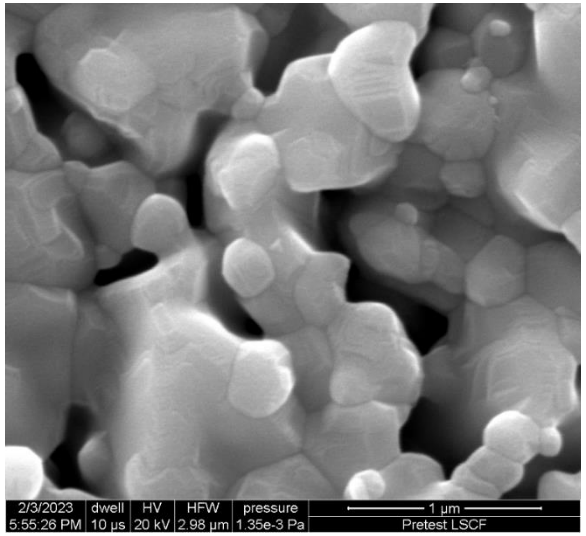
T, K	C_p, J K^{-1} mol^{-1}	$S°$, J K^{-1} mol^{-1}	$H^o_T - H^o_{T_r}$, kJ/mol	$(G^o_T - H^o_{T_r})/T$, J K^{-1} mol^{-1}	$G°$, kJ/mol	$\Delta_f H^o(T_r) + (H^o_T - H^o_{T_r})$
298.15	115.28	338.550	0.000	338.550	−1241.370	−1346.300
Uncertainty		±1.32		±1.32	±2.34	±2.37
500	144.83	406.252	26.687	352.878	−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

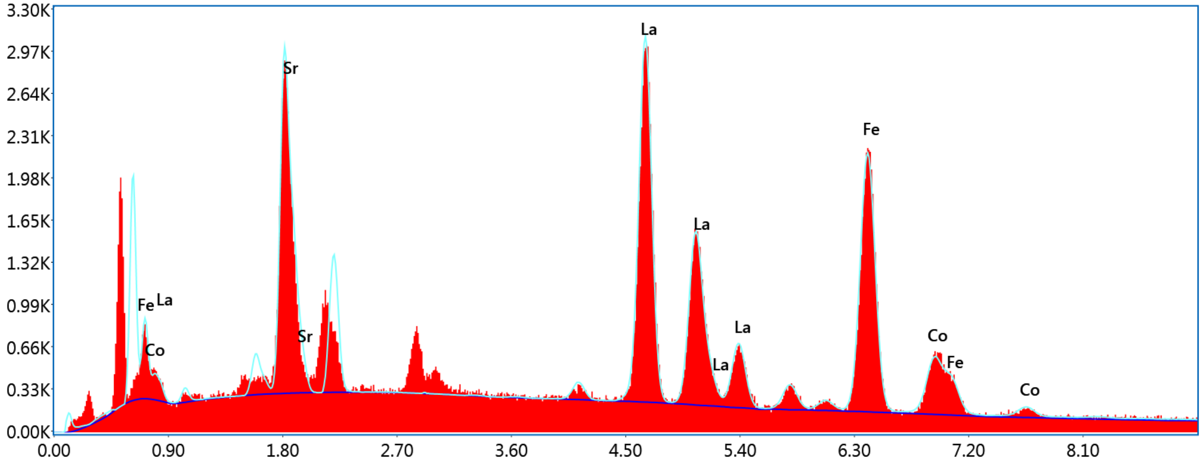
C_p/R (298.15-2100 K) = 27.4945 − 6.22157 × $10^{-3}T$ + 4.34739 × $10^{-6}T^2$ − 9.07719 × $10^{-10}T^3$ − 4.48699 × 10^3T^{-1} + 2.58937 × 10^5T^{-2}

Pretest Morphology of LSCF





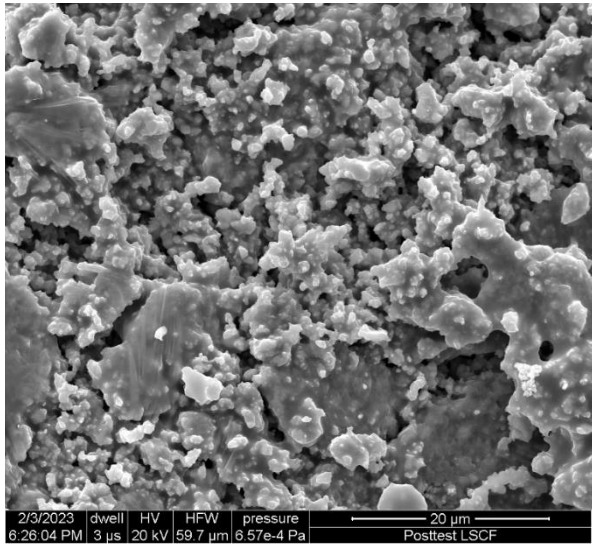


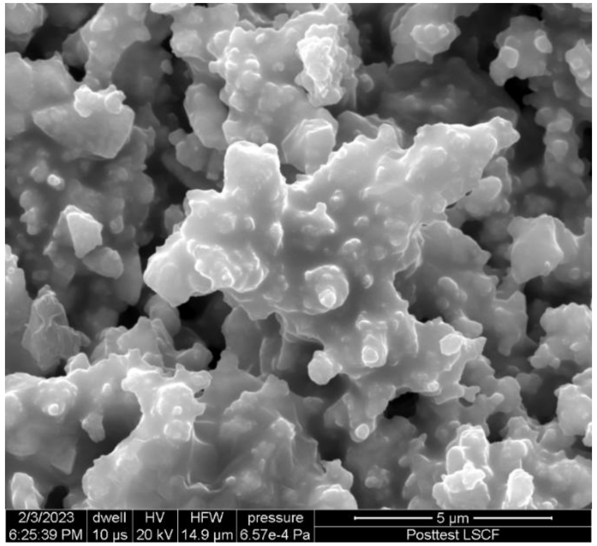


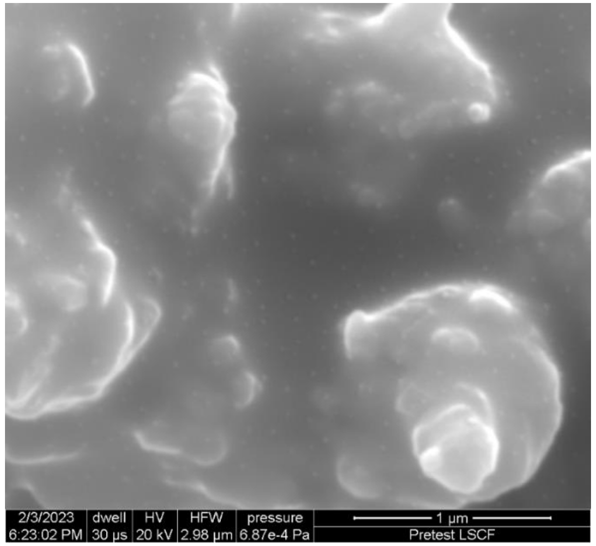
Element	Weight %	Atomic %
Sr L	19.20	19.10
La L	47.60	29.80
Fe K	26.70	41.60
Co K	6.50	9.50

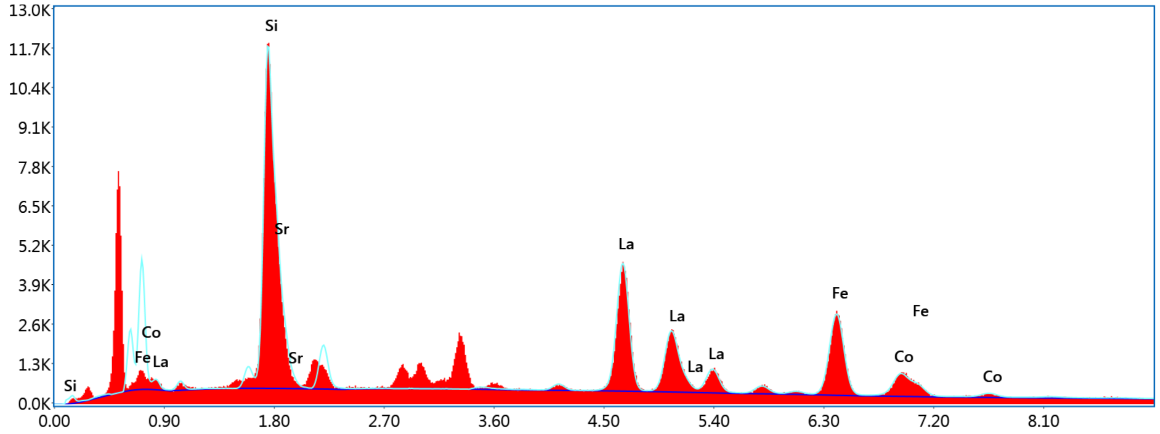
Pretest LSCF sample shows clean surface free of any deposits/ surface debris

Posttest Morphology of LSCF: Si and high humidity environment







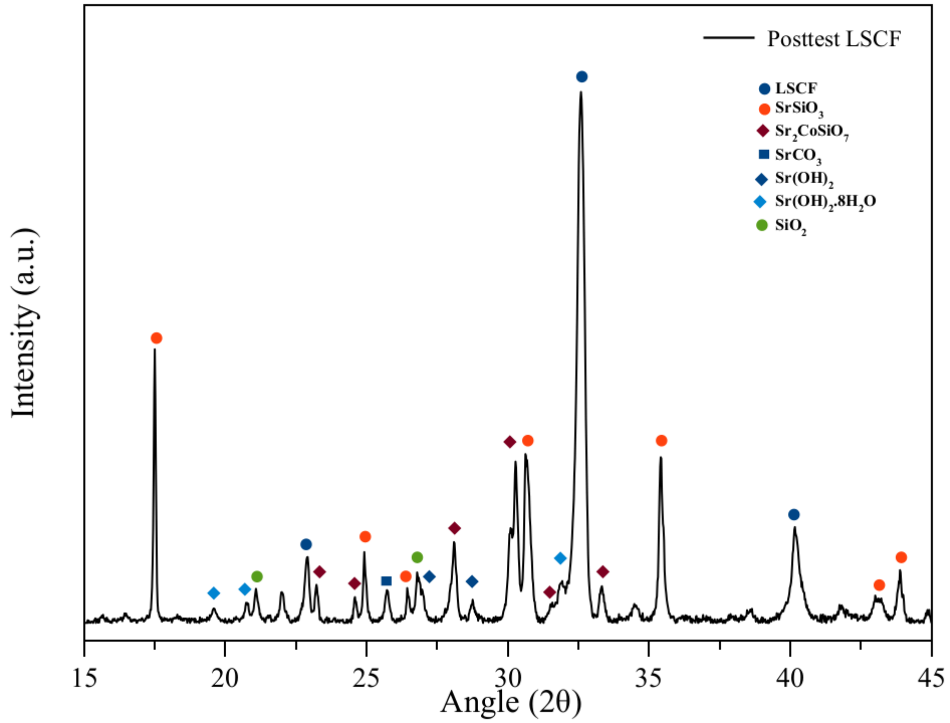


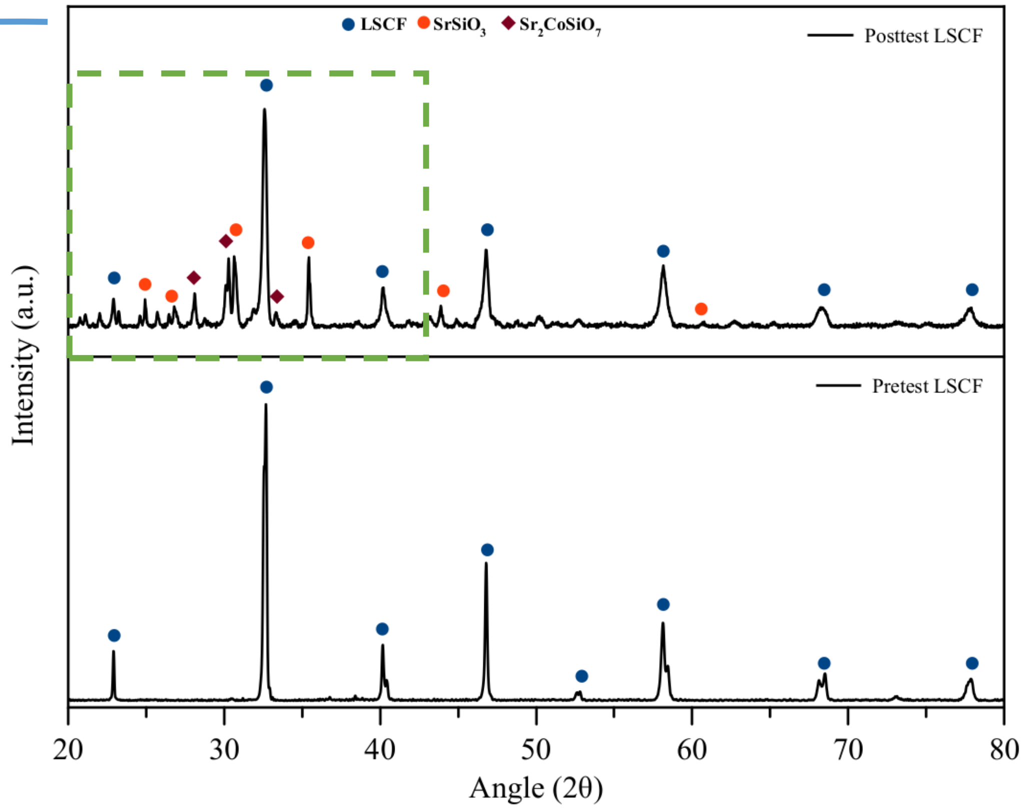
Element	Weight %	Atomic %
Si K	18.80	42.10
Sr L	18.40	13.20
La L	38.40	17.40
Fe K	18.60	21.00
Co K	5.80	6.20

Formation of Si rich layer detected on LSCF surface

Structural Characterization

Slow scan



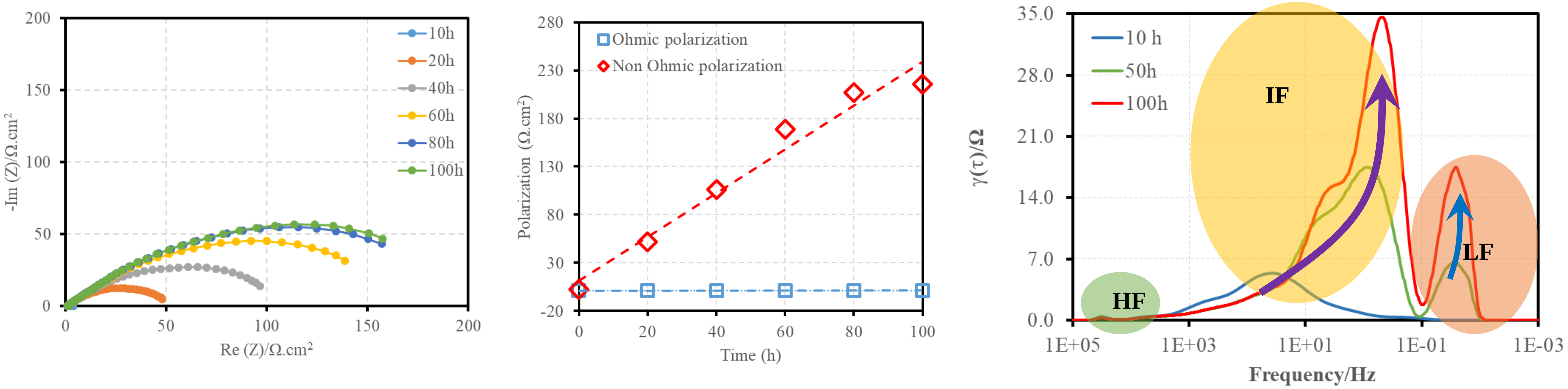


In the post-test sample, the presence of strontium silicate, carbonate, and hydroxide phases were detected, in addition to peaks associated with LSCF.

Bucher, E. Solid State Ionics, 192(1), 480-482 (2011).
Yang, et al. ChemElectroChem 2.2 200-203(2015) .

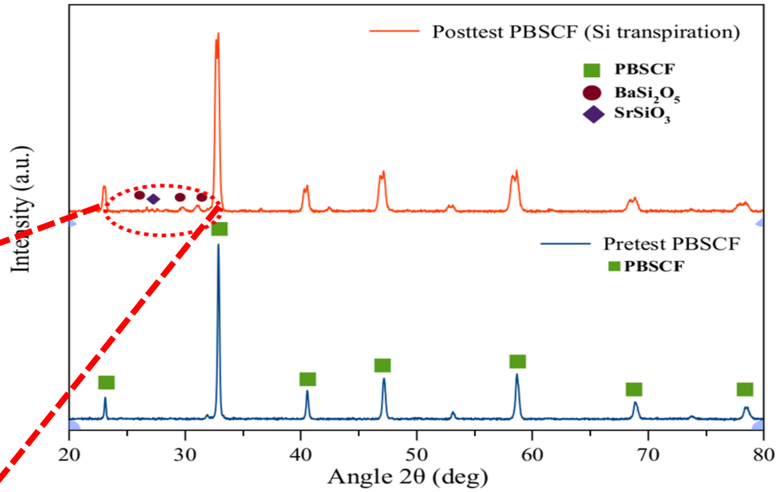
Electrochemical performance degradation

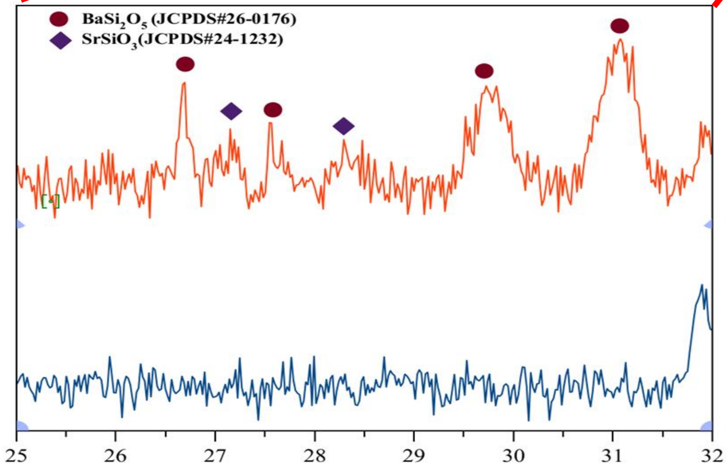
Presence of Si and high humidity



- The cell demonstrates a rapid degradation in performance.
- Non ohmic polarization increases rapidly with time whereas Ohmic polarization remains relatively constant during the test.
- The DRT analysis represents retarded gas conversion and surface exchange processes, suggesting the formation of a resistive Si layer on the LSCF electrode.

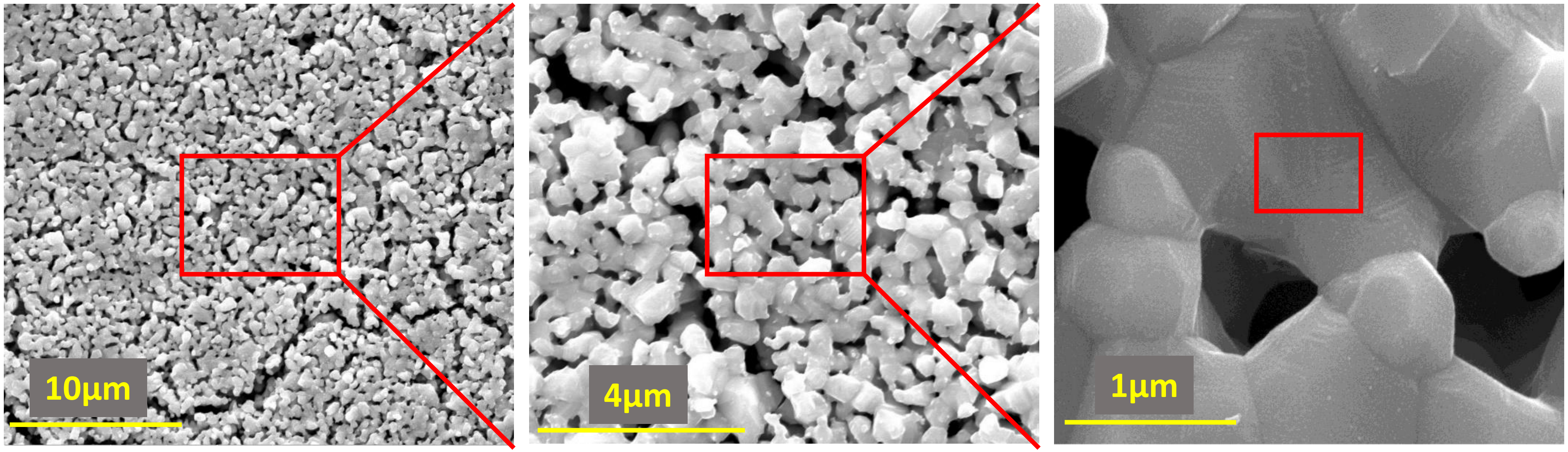
Structural Characterization: PBSCF





Test Conditions
Material tested: PBSCF pellet
Temperature: 800C
Duration 100h
Atmosphere: 90% Steam+ Air
Si Source: High surface area SiO2 powder

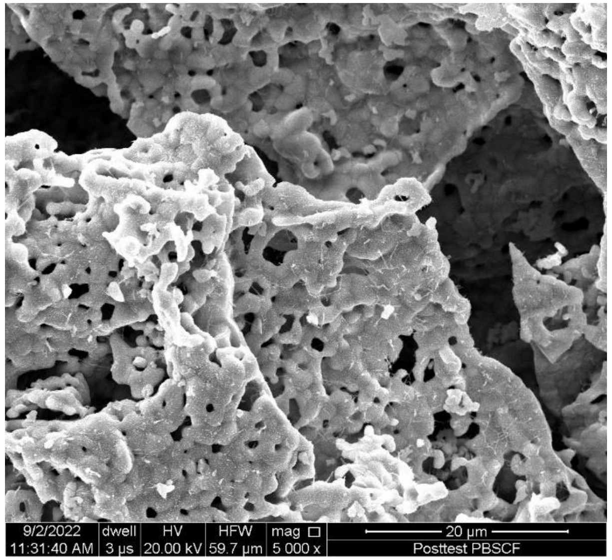
Pretest morphology of PBSCF electrode

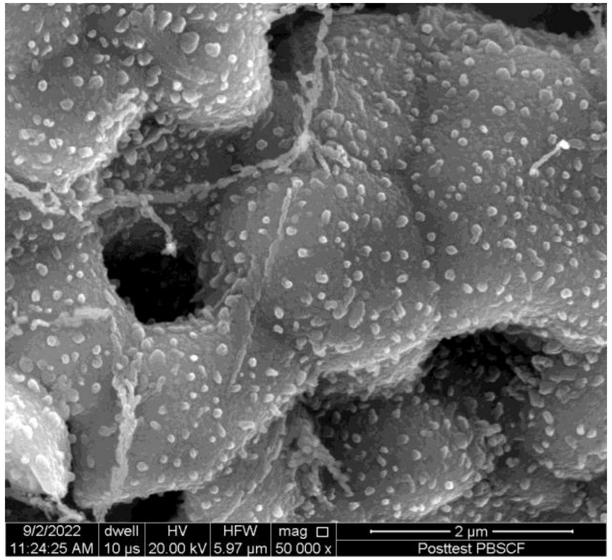


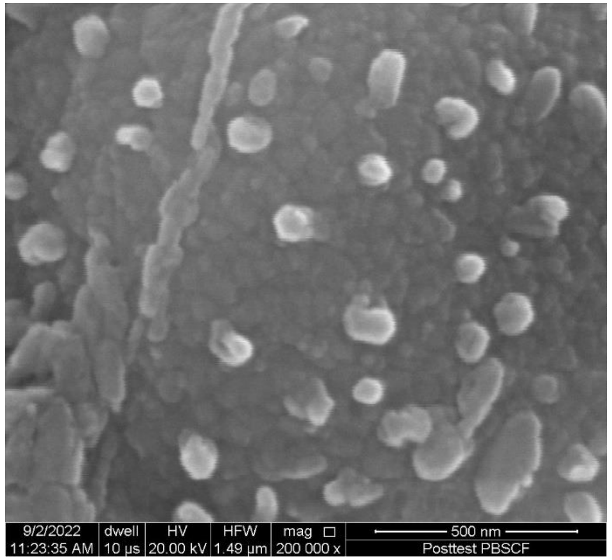
Element	Weight %	Atomic %
O K	16.40	54.00
Sr L	9.00	5.40
Au M	5.90	1.60
Ba L	16.70	6.40
Pr L	27.60	10.30
Fe K	6.10	5.80
Co K	18.40	16.50

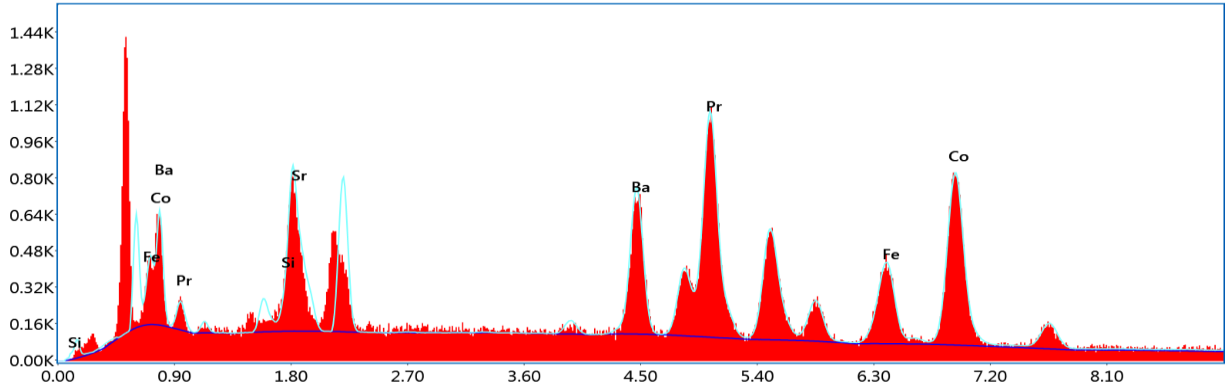
Typical PBSCF surface morphology is observed.

Posttest Morphology of PBSCF: Si and high humidity





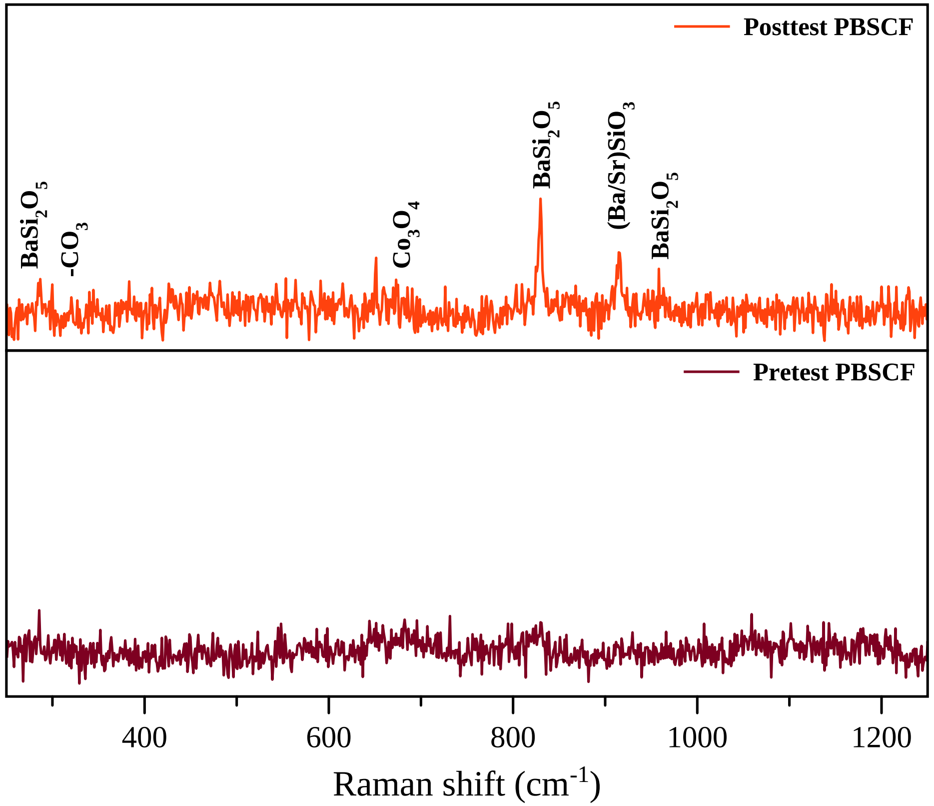




Element	Weight %	Atomic %
Si K	0.80	2.60
Sr L	11.00	11.40
Ba L	20.20	13.30
Pr L	36.00	23.10
Fe K	8.30	13.40
Co K	23.70	36.30

Presence of Si detected a consequence of gas phase transport and deposition

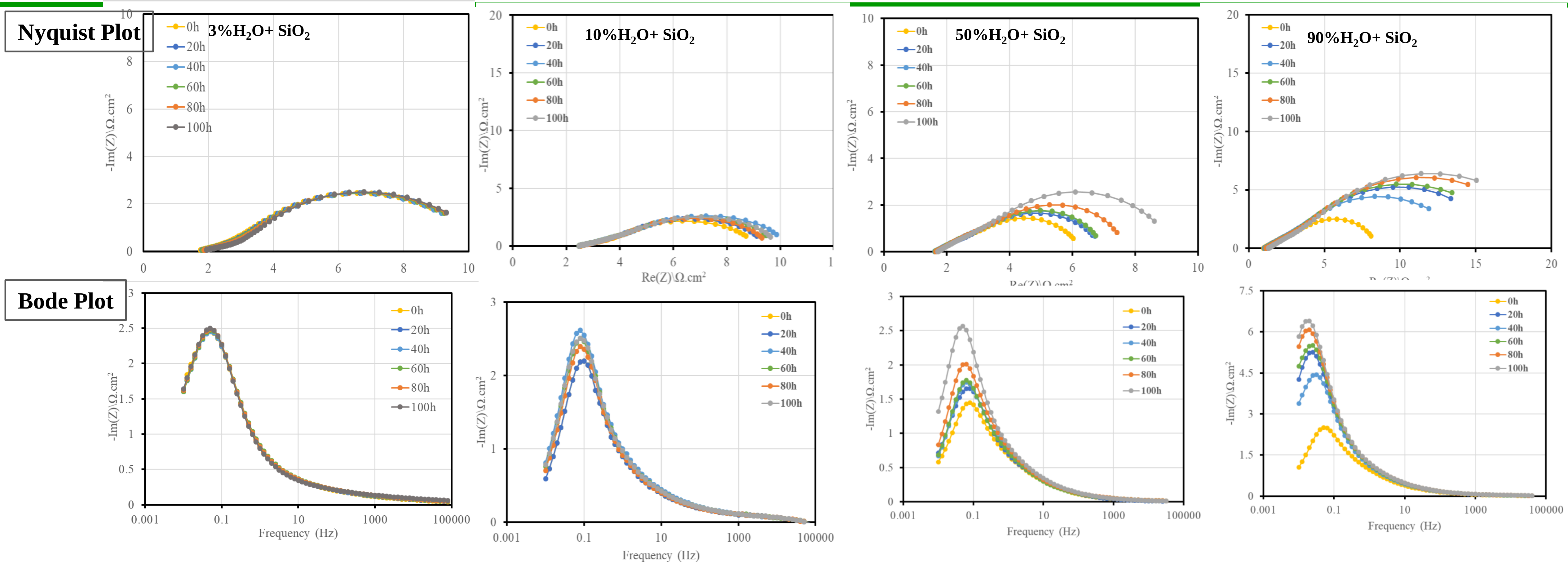
Raman Spectroscopy: Posttest PBSCF



- Posttest Raman spectra shows peaks corresponding to BaSi2O5 and SrSiO3
- Findings of Raman spectra corroborates with the XRD characterization
- SiO2 forms the volatile Si(OH)4 species which get transported to the PBSCF and then react with the surface segregated cations (Ba/Sr) to form the BaSi2O5 and SrSiO3

Li et al., J. Raman Spectrosc. 2014, 45, 672–676

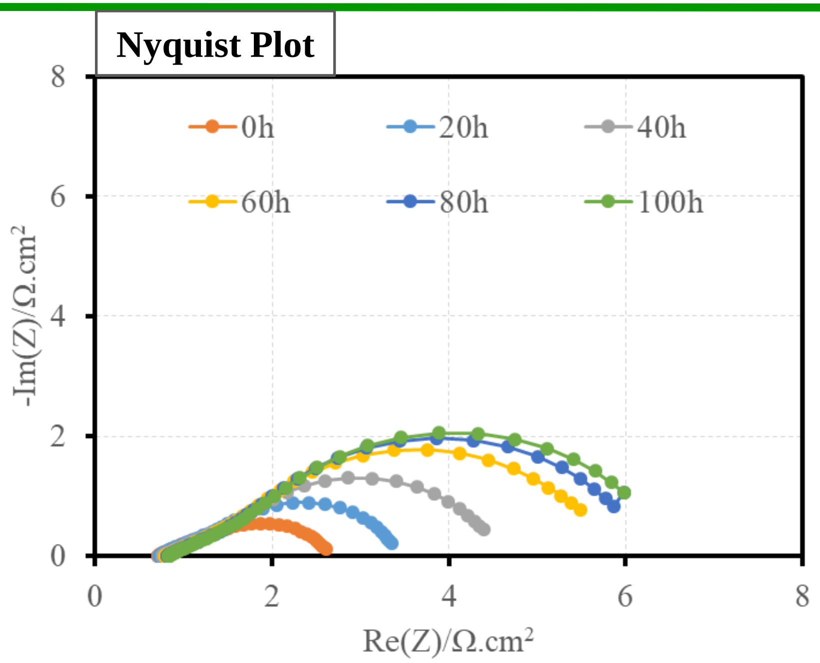
Electrochemical data: performance degradation

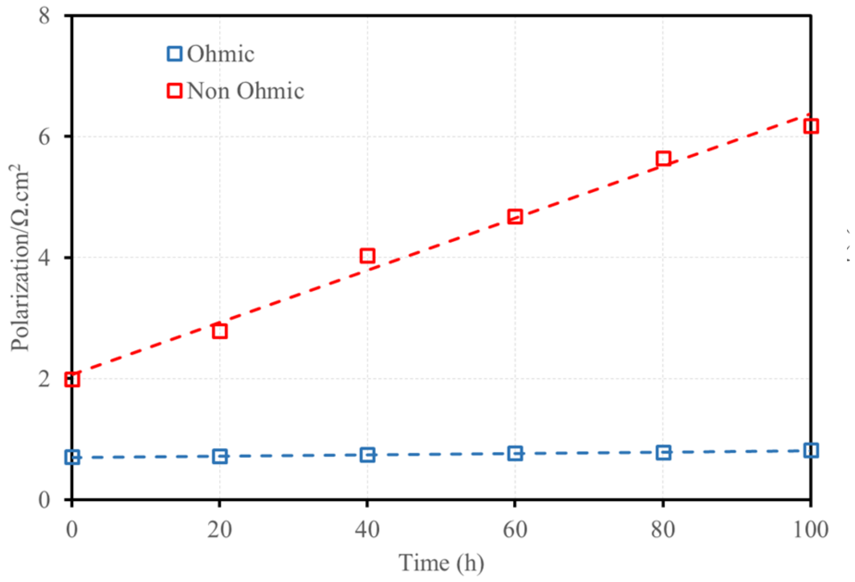


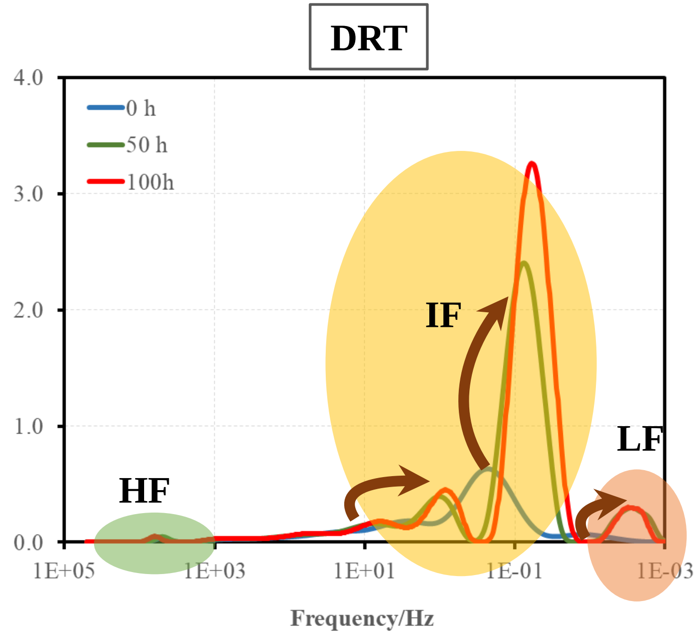
Test Conditions: PBSCF Electrode with different level of humidity; Temperature: 700C; Duration 100h

Atmosphere: X% Steam+ Nitrogen

Electrochemical performance degradation in presence of Si and high humidity





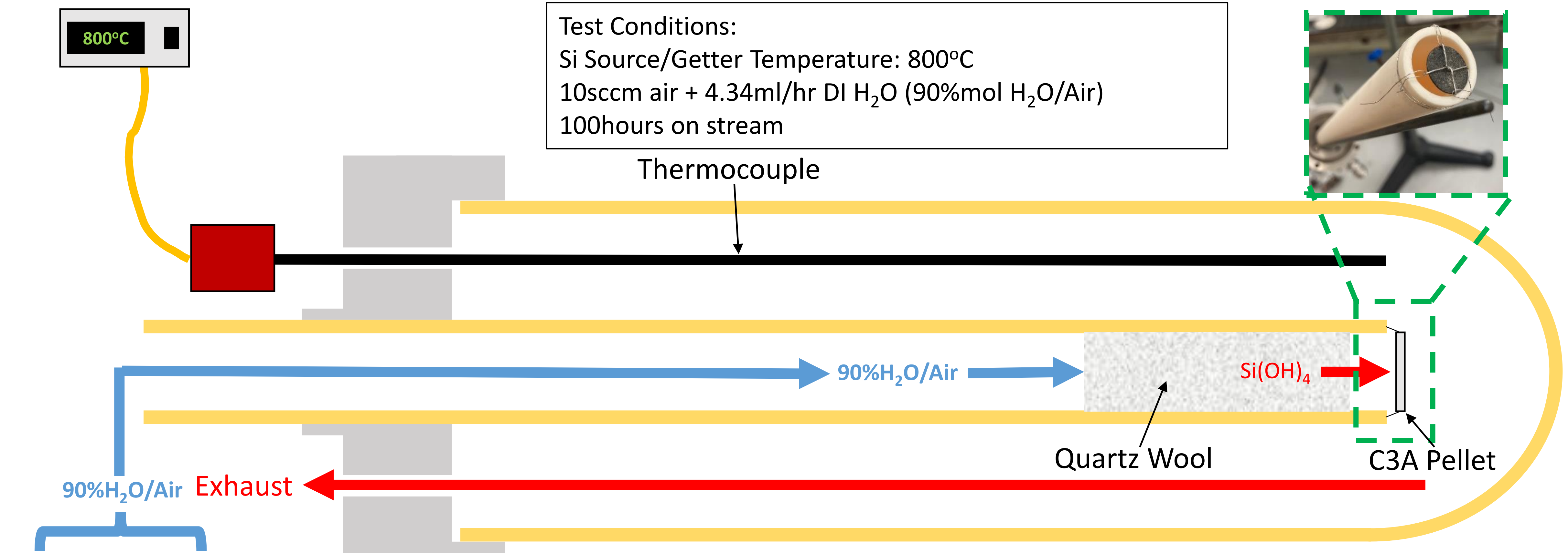


- Cell shows degradation in performance with due to gas phase transport of silica
- Ohmic polarization changes at very slowly whereas non-ohmic polarization increases faster with time during the test
- DRT analysis shows retarded gas conversion and surface exchange processes

Test Conditions:
Material tested: PBSCF Electrode; Temperature: 700C; Duration 100h; Atmosphere: 90% Steam+ Air

Schematic of Si Deposition on C3A Getter

Test Conditions:
Si Source/Getter Temperature: 800ºC
10sccm air + 4.34ml/hr DI H_2O (90%mol H_2O/Air)
100hours on stream

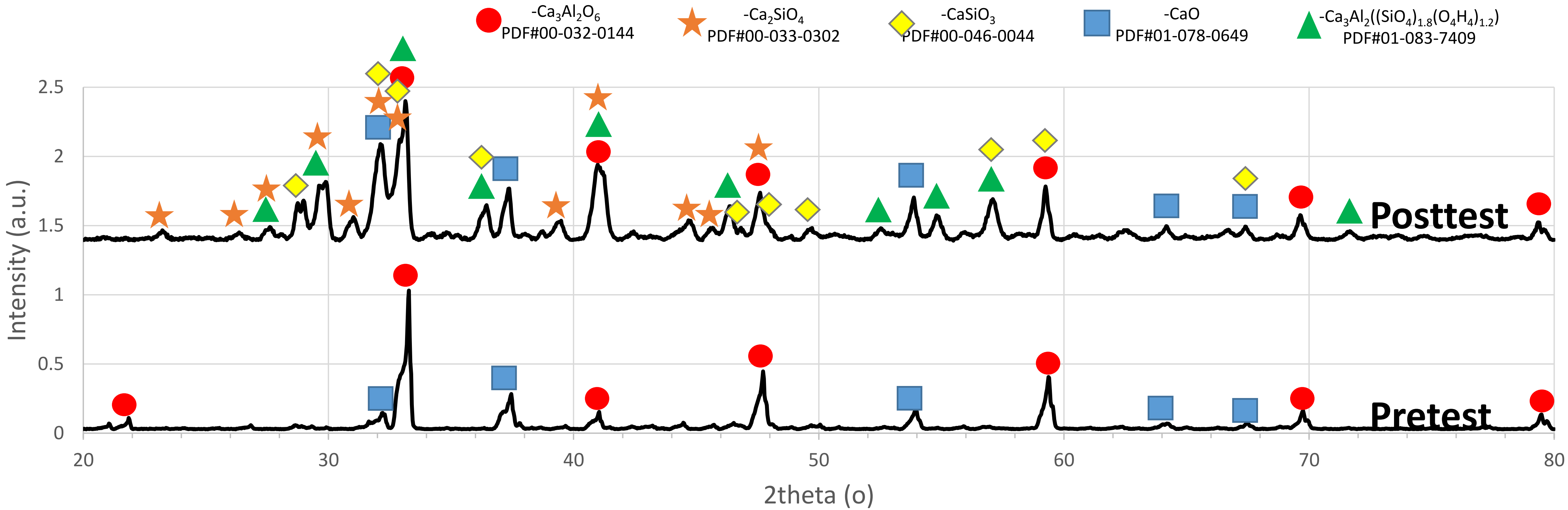


After vaporizing DI H_2O into incoming air, 90%H_2O/Air is sent through quartz wool to react according to reaction:

$$SiO_{2\,(s)} + 2H_2O_{\,(g)} \rightarrow Si(OH)_{4\,(g)}$$

Si vapors are transported from the Si source to a uniaxially pressed and sintered C3A pellet to react

Si Deposition on C3A Getter

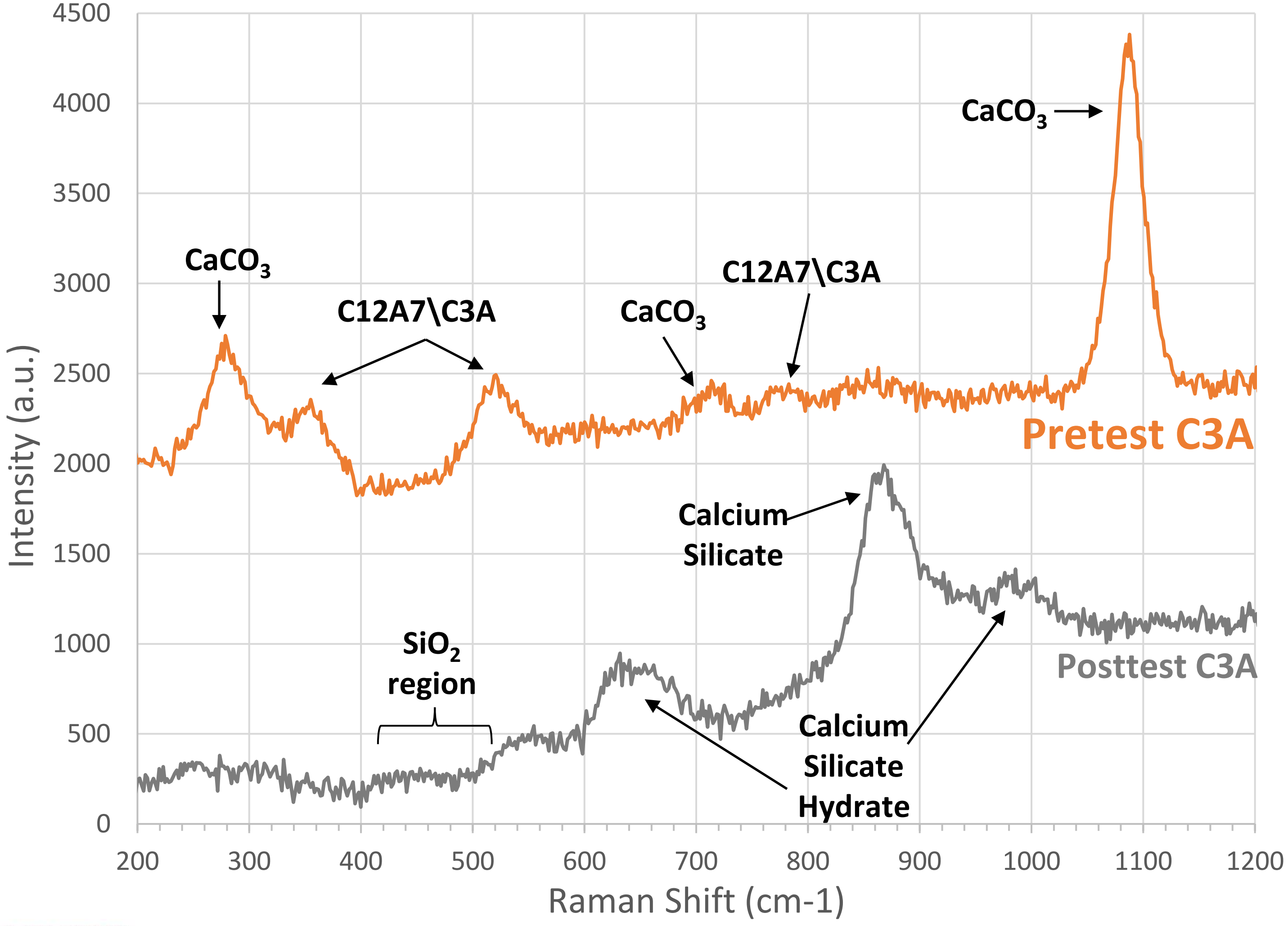


For C3A pellet after sintering at 1300°C in air for 2hours, the major phases in the pellet are $Ca_3Al_2O_6$ and unreacted CaO.

After exposure to Si vapor at 800°C for 100hours, the sample shows the presence of calcium aluminum silicate hydrate and calcium silicate, supporting Raman spectra of posttest C3A getter.

Raman Spectroscopy of C3A Pellet

Exposure atmosphere: 90%H_2O – 800ºC – 100hr



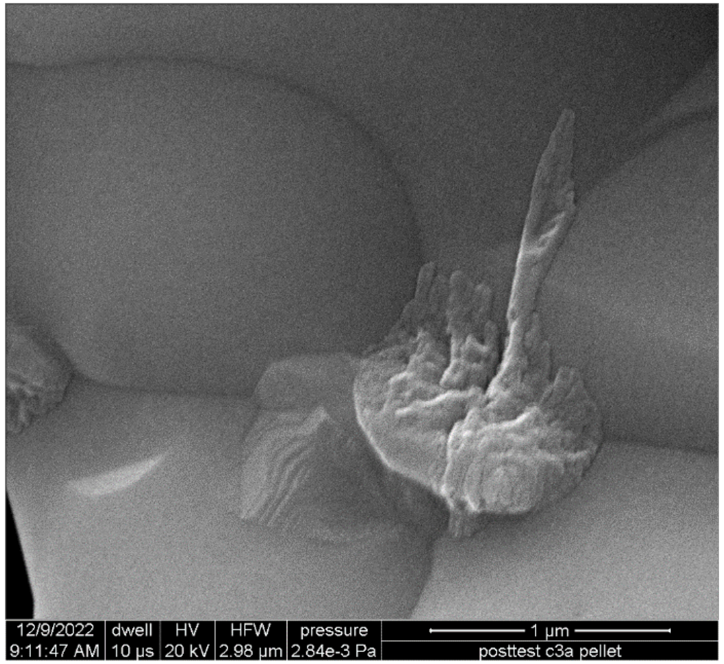
Raman spectra of pretest C3A getter shows peaks for $CaCO_3$ due to CaO reacting with atmospheric CO_2 when cooling to RT after sintering C3A to substrate.

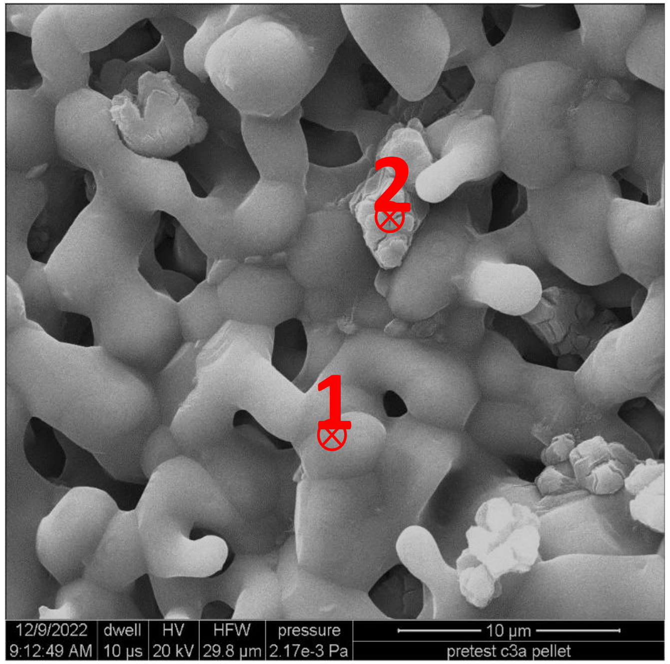
Posttest C3A shows peaks associated with calcium silicate. Amorphous SiO_2 or $CaCO_3$ were not detected.

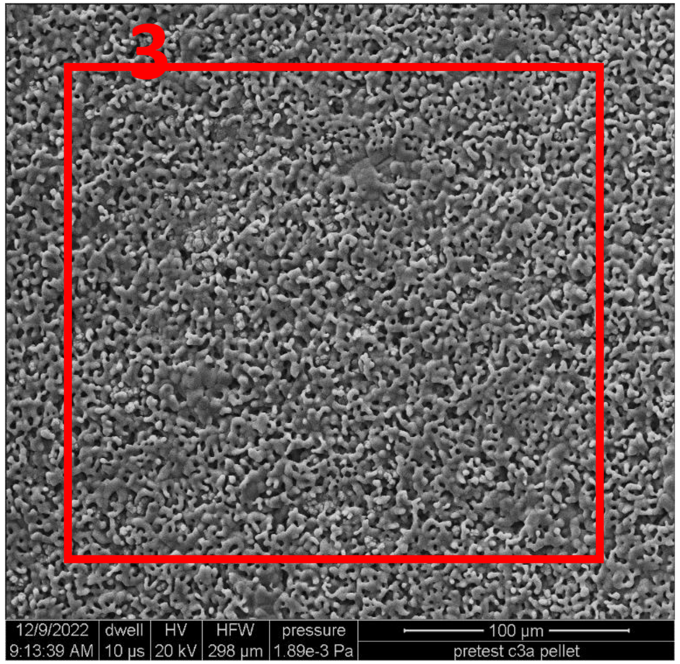
Si vapor species react with C3A to form silicate compounds.

Si Deposition on C3A Pellet

Pretest Surface morphology and chemistry (SEM/EDS)







EDS#1

Element	Weight %	Atomic %
Al K	31.60	40.70
Ca K	68.40	59.30

EDS#2

Element	Weight %	Atomic %
Al K	6.90	10.00
Ca K	93.00	90.00

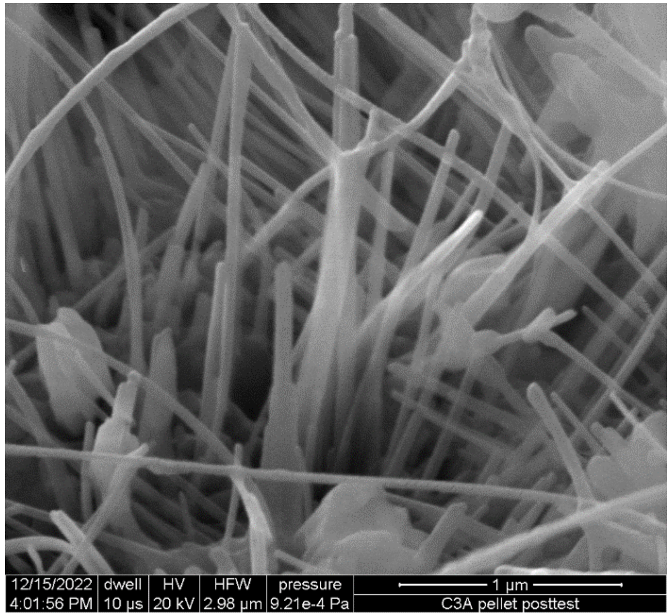
EDS#3

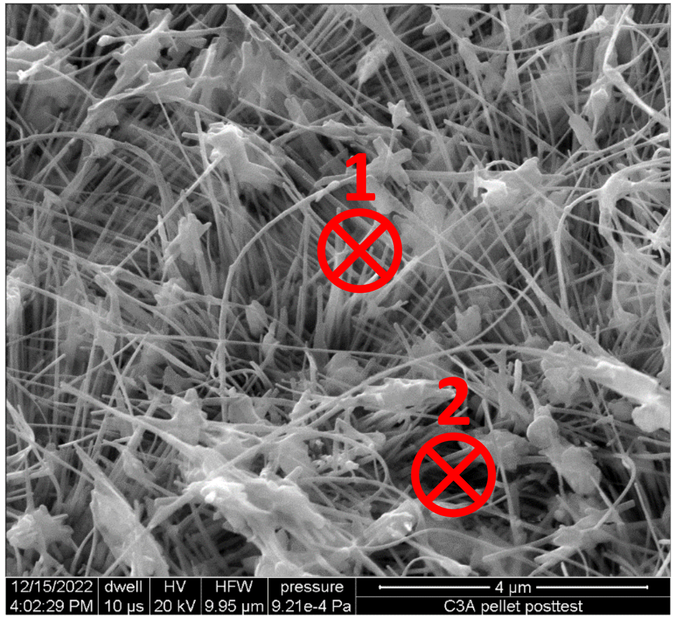
Element	Weight %	Atomic %
Al K	24.10	32.00
Ca K	75.90	68.00

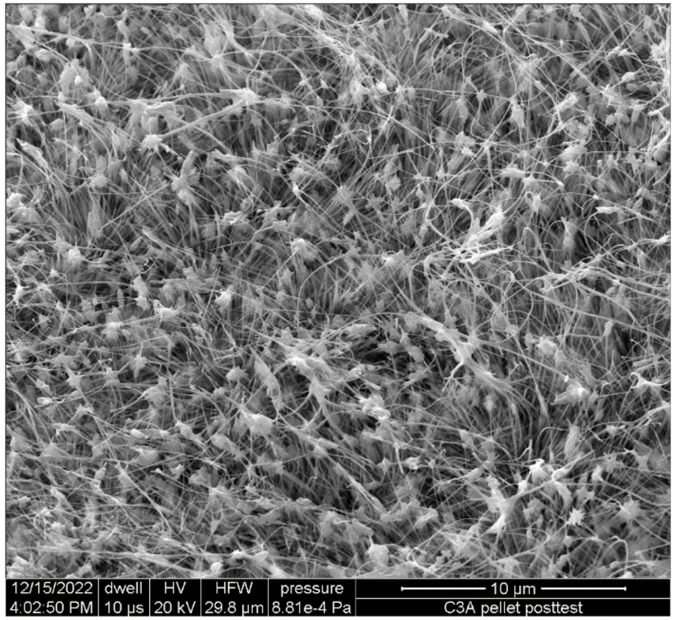
After sintering, the C3A pellet shows sintered particles with a porous surface. EDS analysis of the sintered particles shows reaction products formation and the presence of unreacted CaO.

Si Deposition on C3A getter

Posttest: Air-90%H_2O ; 800^{o}C ; 100hrs.







EDS1

Element	Weight %	Atomic %
Al K	1.40	1.80
Si K	29.80	37.50
Ca K	68.80	60.70

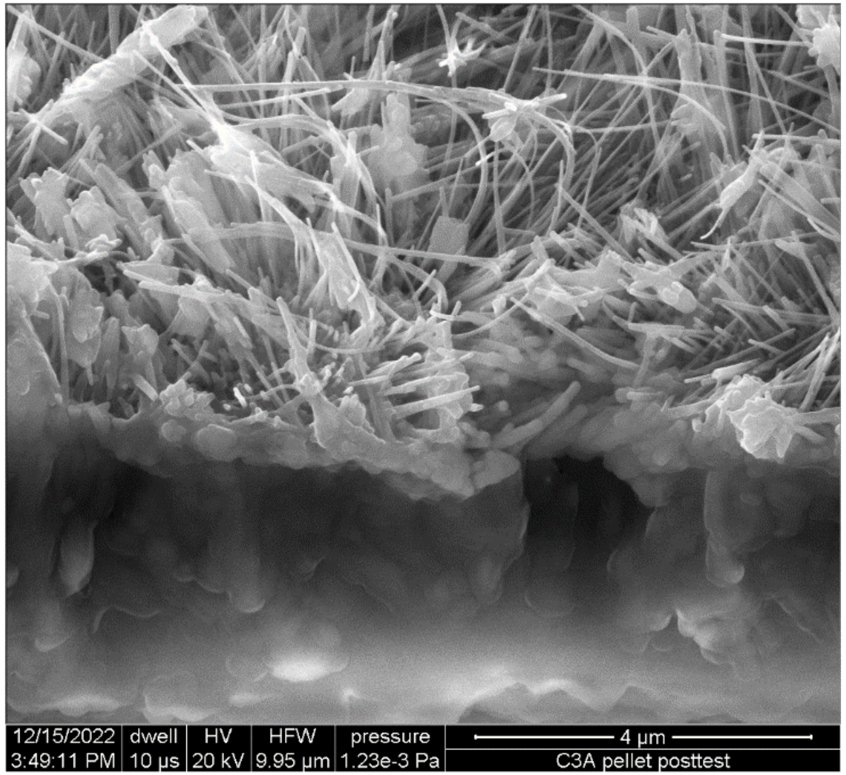
EDS2

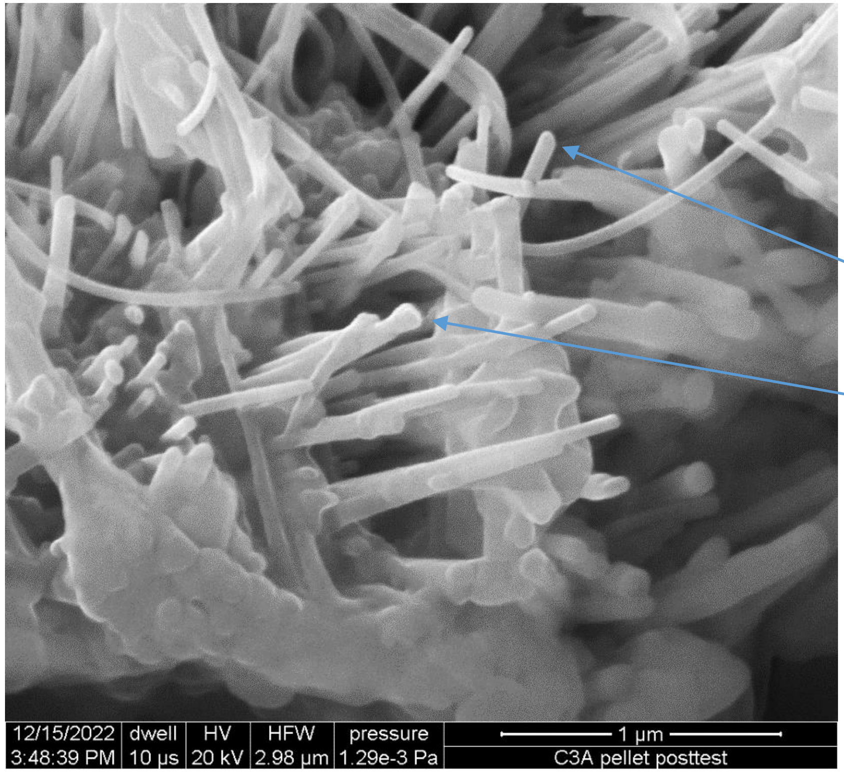
Element	Weight %	Atomic %
Al K	1.20	1.50
Si K	35.30	43.60
Ca K	63.50	55.00

Elemental analysis of the C3A posttest sample shows formation of agglomerates and rod like structures with Si.

Si Deposition on C3A Pellet

Posttest – 90%H_2O – 800^oC – 100hr

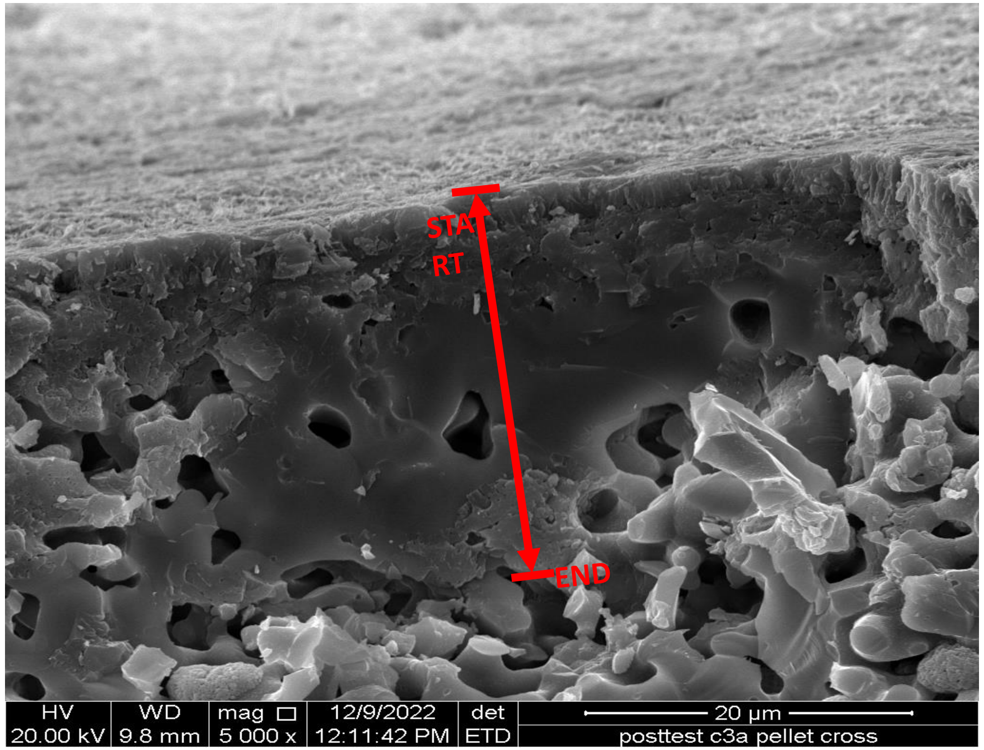


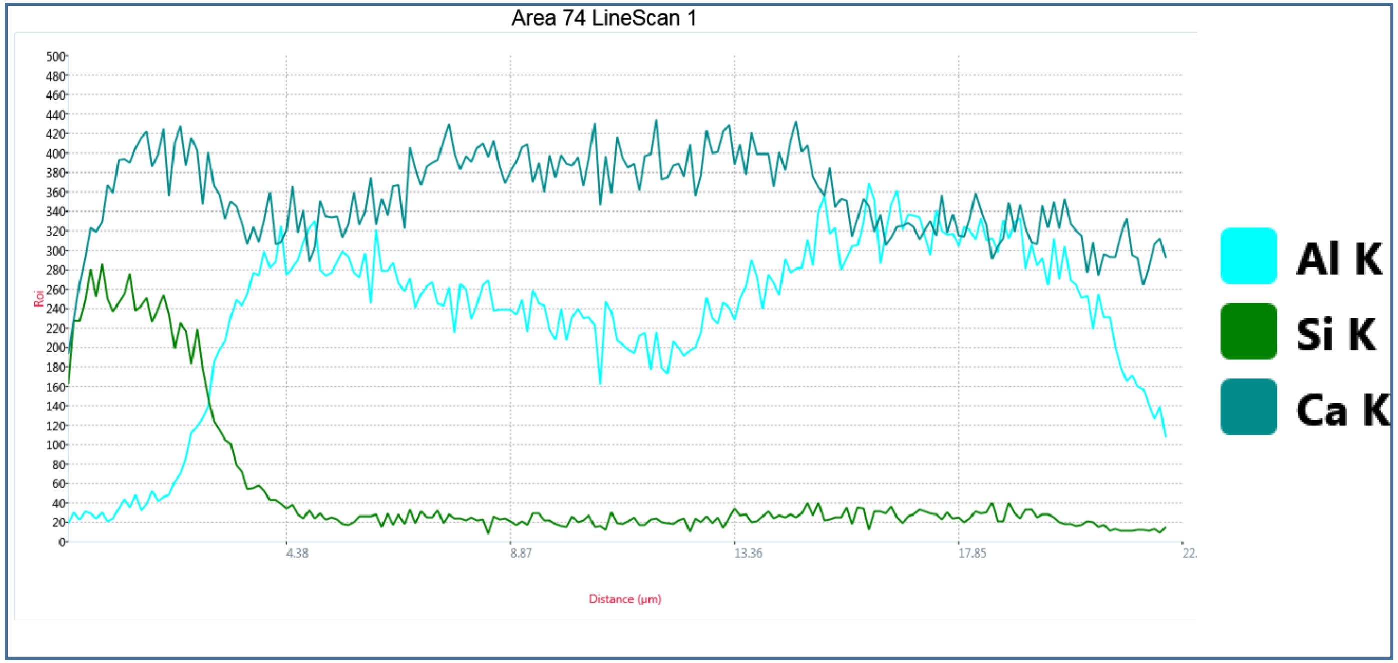


Surface morphology obtained at 45^o angle shows outward rod like growth from the surface. It is postulated that the growth is promoted by the vapor feed at the tip of the rod when calcium reacts with the incoming $Si(OH)_4$.

Si Deposition on C3A Pellet

Posttest Cross-Section SEM/EDS





LineScanEDS of pellet cross-section shows the lack of Al at the surface, while sub-surface C3A has a Ca:Al mol ratio of ~1:1.

Calcium diffuses to the surface of the pellet to react with $Si(OH)_4$.

Conclusions

- **Presence of intrinsic (S) and extrinsic (Cr, Si) trace gaseous contaminants have been identified in ambient air stream.**
- **Formation, transport and interactions of contaminants with perovskite air electrode has been examined. Chromates, chromites and silicates form in various perovskite electrodes due to favorable and irreversible reaction pathways.**
- **Getters have been identified, synthesized, and fabricated for the capture of trace S (intrinsic) and Cr, Si (extrinsic) gaseous contaminants.**
- **Technical approach offers a low cost and scalable pathway for the capture of trace gaseous contaminants present in high temperature fuel cells, electrolyzers and chemical reactor systems.**

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Thank you