Materials and Approaches for the Mitigation of SOFC Cathode Degradation in SOFC Power Systems

Prabhakar Singh

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

WORK PERFORMED UNDER AGREEMENT DE-FE 0023385 and 0027894

18th Annual SOFC Program Review Meeting
June 12, 2017

Technical Contributors

UConn	Prabhakar Singh	Professor
	Rampi Ramprasad	Professor
	Steven Suib	Professor
	Boxun Hu	Assistant Research Professor
	Ashish Aphale	Post-doctoral fellow
	Aman Uddin	Post-doctoral fellow
	Sridevi Krishnan	Post-doctoral fellow
	Su Jeong Heo	Graduate Student
	Junkai He	Graduate Student
	Yanliu Dang	Graduate Student
	JunHo Song	Graduate Student
	Justin Webster	Undergraduate Student
	Seraphim Belko	Undergraduate Student
UAlabama	Manoj Mahapatra	Assistant Professor

Program Managers: Drs. Patcharin N. Burke and Jason Lewis, NETL

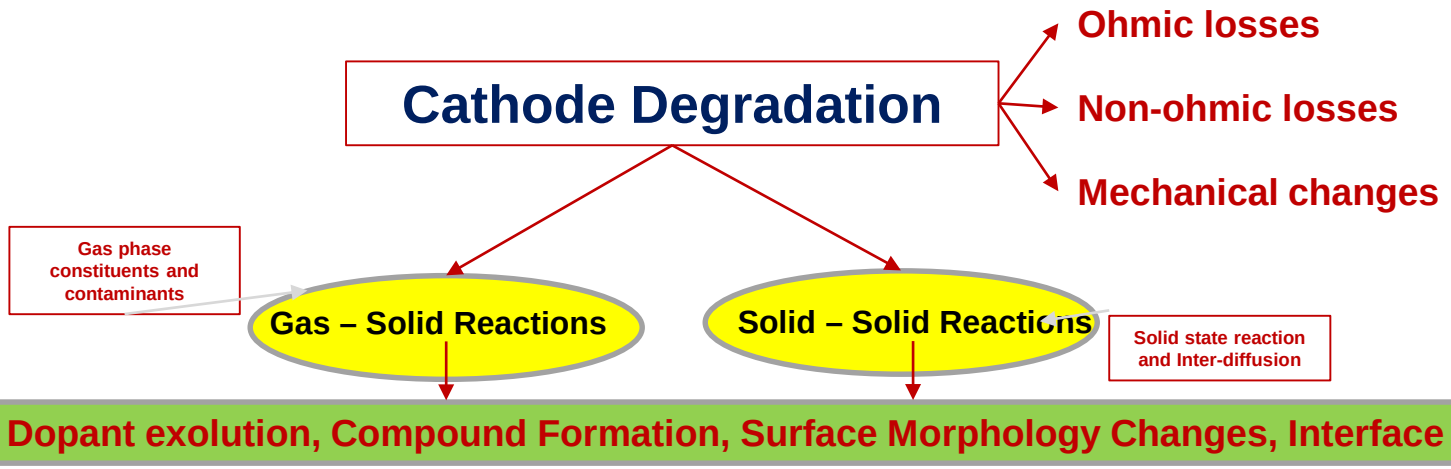
Outline

- Accomplishments
- Background
- Experimental
  - Getter optimization, process scale up and stability evaluation
  - Evaluation of getter performance
  - Fabrication and long term testing of Cr Getter
  - Electrochemical testing – BOP & In-Cell simulation
  - Characterization-SEM-EDX, XRD, and FIB-TEM
  - High surface area (HSA) getter materials
  - Sensor Development for in-situ Cr monitoring
- Results and Discussion
- Future Work
- Acknowledgements

Long term SOFC Degradation – Role of Cathode

A Universal Degradation Phenomena for HT Electrochemical Systems

- SOFC
- SOEC
- OTM



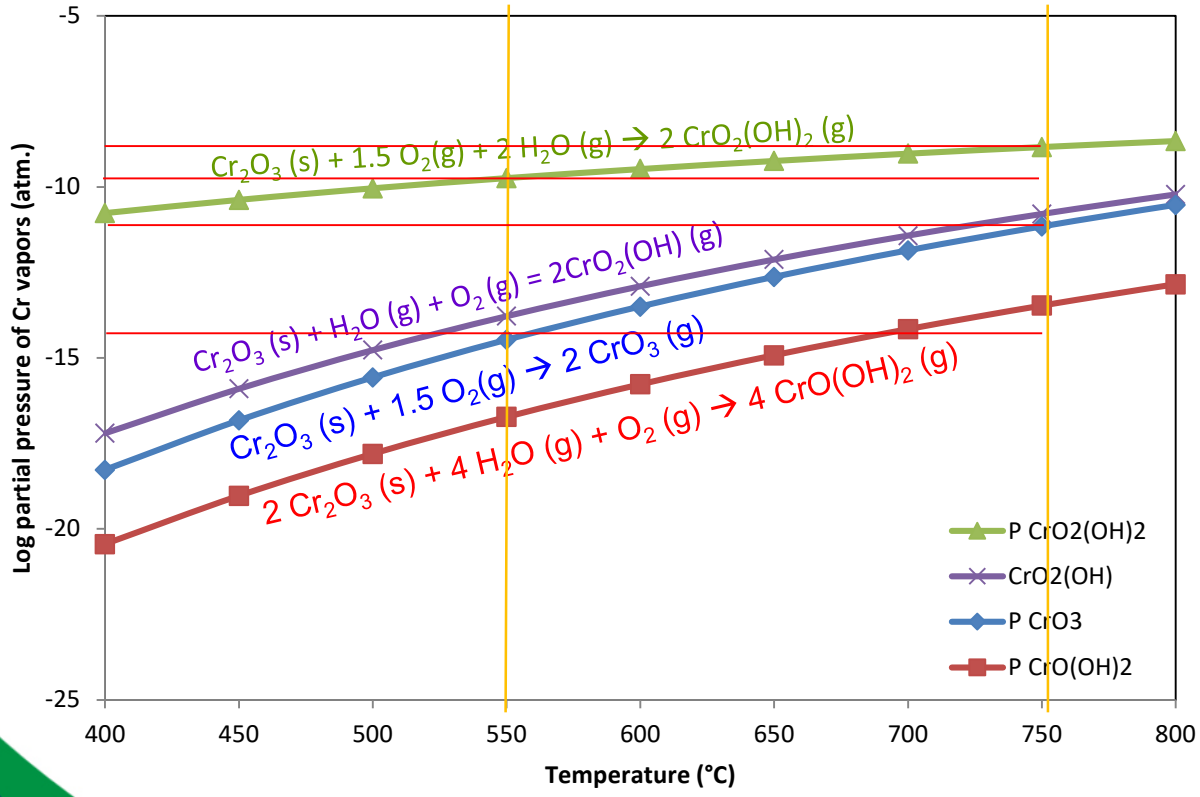
Gas	Concentration
Oxygen	20.9 v%
Nitrogen	78 v%
Water	<1 to 3 v%
Carbon dioxide	350 ppm
Sulfur dioxide	<1 ppm
Noble gases	<1 v%
Particulate matter (PM)	<50 µg/m^3

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

Chromium Evaporation at Low & Intermediate Temperatures

Oxidation and electrochemical poisoning

Gaseous Cr species formation and transport remains a significant issue at lower temperatures similar to high temperature operation conditions. Presence of H_2O in air will lead to high partial pressures of Cr species.



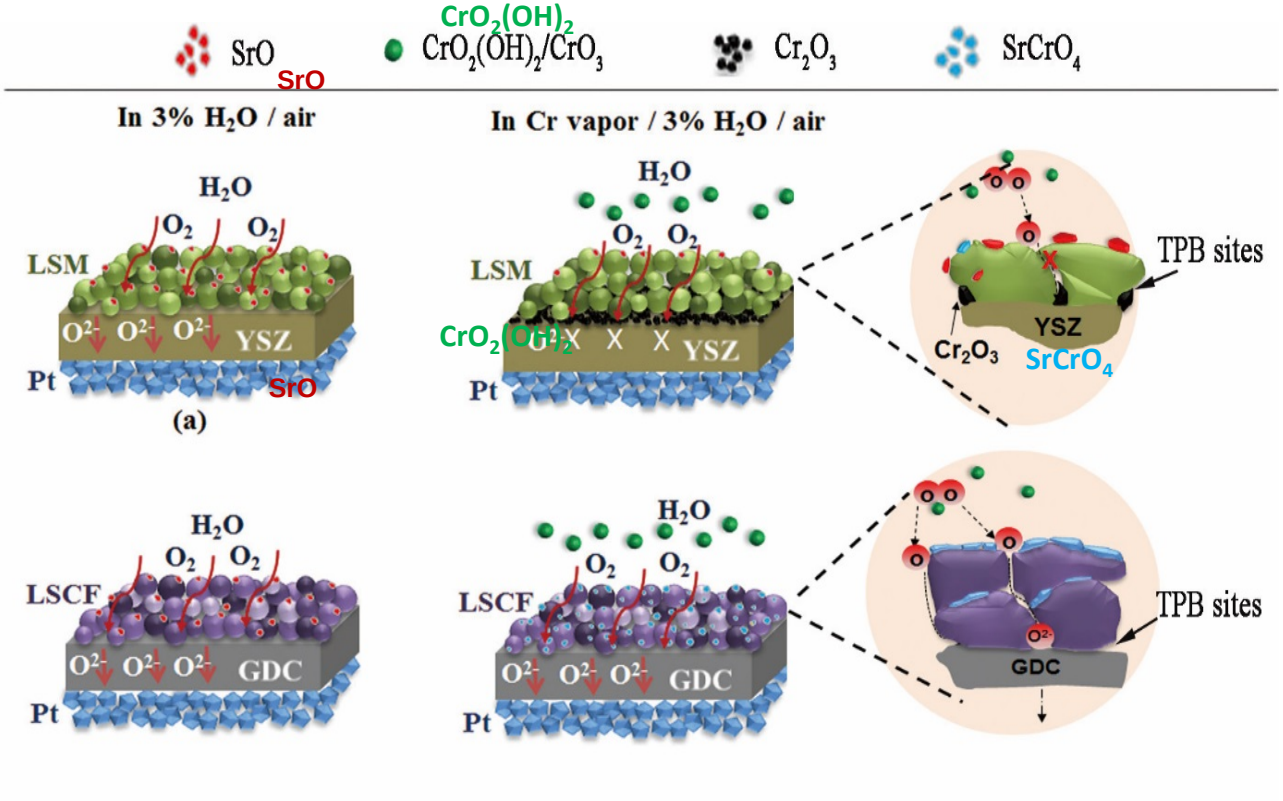
Air + 3%H2O atmosphere
P_{O_2} = 0.21 atm.
P_{H_2O} = 0.03 atm.

Paralinear oxidation
Electrode poisoning

- Alloy oxidation rate increases.
- Lowering of temperature doesnot significantly lower the Cr vapor pressure in humidified air as indicated by smaller slope.
- Significant reduction will, however, be obtained in dry air as indicated by larger slope.

Background – Chromium Poisoning of Cathodes

Morphology evolution in the presence of water and chromium vapor



B. Hu, S. Krishnan, C. Liang, S. J. Heo, A. N. Aphale, R. Ramprasad, P. Singh, . Int J Hydrogen Energy , 2017

Project Objectives

Develop, Validate and Transfer Technology Related to Materials and Approaches for the Mitigation of SOFC Cathode Degradation in SOFC Power Systems

Long Term Bulk, Interfacial and Surface Stability

Dopants, Electric polarization, Gas phase contaminants (H_2O, CO_2, SO_2, Cr-vapor species, stoichiometry)

Tools: EIS, DC conductivity, XRD, SEM, X-ray absorption spectroscopy, XPS, SIMS, TEM, HTXRD

Compound formation (Solid-solid/solid-gas reactions)
dopants exolution and oxides segregation at surface
- ✓ oxides and compounds at interface
- ✓ crystal symmetry
- ✓ microstructure
- ✓ Micro-cracking and/or delamination

Bulk, Interfaces, Surface Stability

Electrode – Electrolyte / Electrode - IC

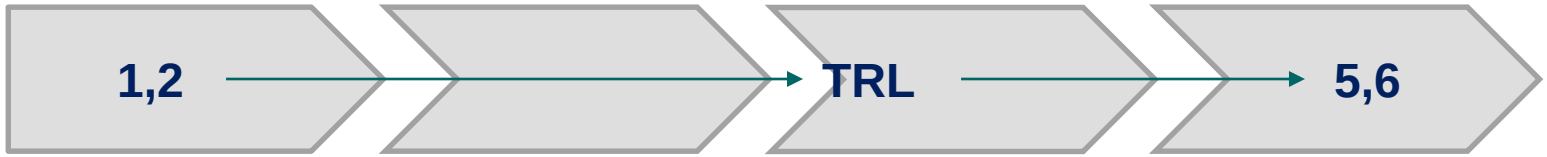
Couple/ Symmetric / Full cell/ configurations

Air side contaminants:
Water,CO2, SO_2, Oxide vapors
Other contaminants

In-situ, Ex-situ Bench top tests

Accomplishments

- Cr capture successfully demonstrated from BOP/ In-cell sources
- Cr getter identified, synthesized, tested and characterized
- Synthesis process scaled up to 1kg/batch using lab equipment
- Design studies performed for 40,000 hrs. getter life
- Cr getter provided to PNNL, LG, Cummins, Ceres for testing
- Laboratory findings provided to SOFC industries
- Cathode degradation mechanisms identified
- Getter operation validated at low temperatures
- Alternate HSA getter has been identified and synthesized.



Concept validation: Materials, synthesis, testing, characterization

Scale up, testing and validation, technology transfer

Accomplishments-Technical

- Suitable metal oxides have been selected for co-getter materials using thermodynamic calculations.
- Processes have been identified for the synthesis of HSA materials
- As-synthesized HSA materials have been characterized using SEM, TEM and EDS techniques.
- In-situ electrochemical and ex-situ transpiration tests have been conducted to validate co-getter efficacy for Cr and S capture.
- Getter design is being further optimized by CFD computational analysis.
- New sensor design have been examined to test the sensitivity of Cr.

- Developed chromium getter shows excellent affinity for capturing gaseous Cr^{6+}. Experiments are in progress on validating the capture of Sulfur and Sulfur- chromium species, respectively.
- Pre- formed and “in-situ” getter preparation demonstrated
- Electrochemical and transpiration tests show excellent blockage of Cr vapor from entering into cathode electrode.
- Getter materials, support structure and HSA getter deposition processes are being developed and optimized.

- Graduate / Undergraduate students being trained - 7
- Post-doctoral fellows - 3
- Outreach: Middle and High School, STEM, International academic institutions
- Publications in peer reviewed journals

Background: Getter

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

Cr getter critical property	Performance of new Cr getter against baseline state of the art Cr getter	Test conditions (Temp, time, atm)
Phase Stability	Superior: New Cr getter shows no phase changes and interaction with humidity and CO2 present in air.	RT-980C, Ambient air
Reaction products	As processed getters consist of several oxide phases containing Sr and Ni (Sr9Ni7O21, Sr4Ni3O9 and Sr2Ni4O5).	Powder synthesis process and transpiration, electrochemical testing at 850C for up to 500 hrs in Air -3%H2O
Microstructures	Stable powder, coating and substrate microstructures obtained New Cr getter retains its microstructure after high temperature exposures (850C) in humidified air. Literature review does not provide background information on the SOTA.	During processing up to 980C in air During bench top testing at 850C for up to 500 hrs in humid air
Thermochemistry	Similar or Superior: Based on thermochemical models developed	
Physical Properties	Similar or Superior: Based on resistance to ambient air (NAAQS)	
Product morphology	Porous powder coating on ceramic substrates	During processing up to 980C in air During bench top testing at 850C for up to 500 hrs in humid air
Cr Conc. profile	Superior: Capture Cr in the first 1500 - 3000 micron. Reproducible results	During bench top testing at 850C for up to 500 hrs in humid air
Substrate	Configuration include honeycomb, foam and fibrous structure, Substrate materials include Cordierite, Mullite, zirconia and alumina.	
Ease of fabrication	Conventional powder preparation and coating techniques	pre-formed /In-situ getter formation

Novelty and Innovation

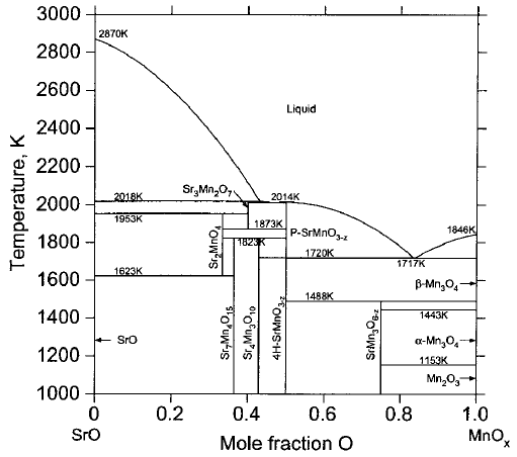
- **Design flexibility for integration in wide range of SOFC systems configuration**
- **Flexibility of operation from 600-900°C**
- **Use of conventional non-strategic and non-noble low cost metal oxides for getter synthesis**
- **Ease of getter synthesis and fabrication**
- **High Cr capture capacity through tailored high surface area powder and coatings**
- **Replaceable unit with getter health monitoring and sensing**

The innovation will also find application in related high temperature electrochemical systems such as OTM and SOEC for the prevention of Cr assisted performance degradation. The proposed approach for Cr capture can also be applied to oxycombustion and other advanced combustion techniques for the reduction of Cr vapor in the exhaust gas stream.

Getter Chemistry Optimization and Scale up

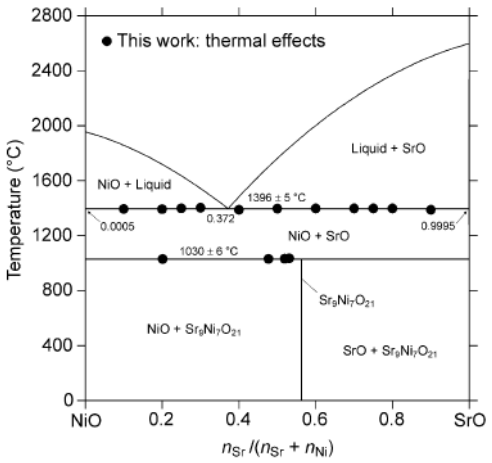
Validation and testing

Materials Selection- Phase diagram



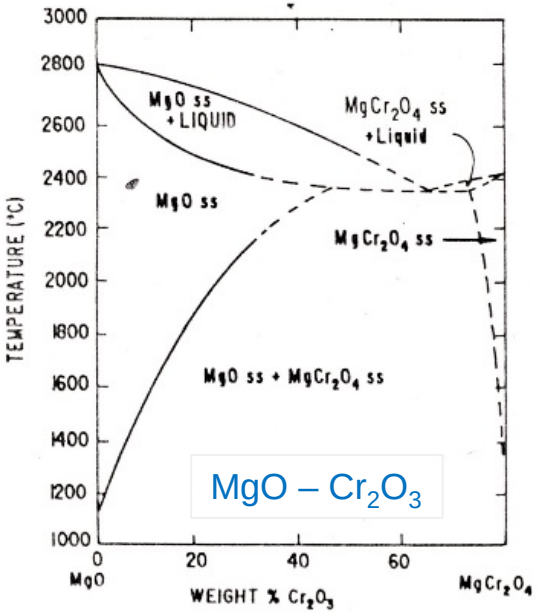
SrO - MnOx

JPEDAV (2004) 25:311-319



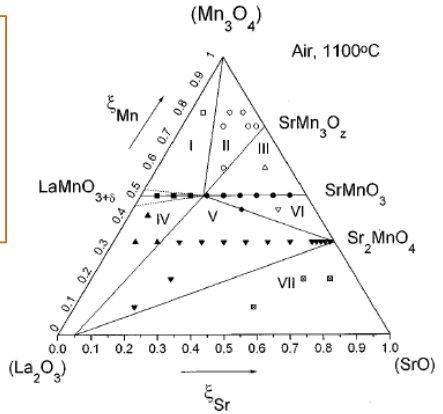
SrO - NiO

M. Zinkevich / Journal of Solid State Chemistry 178 (2005) 2818–2824



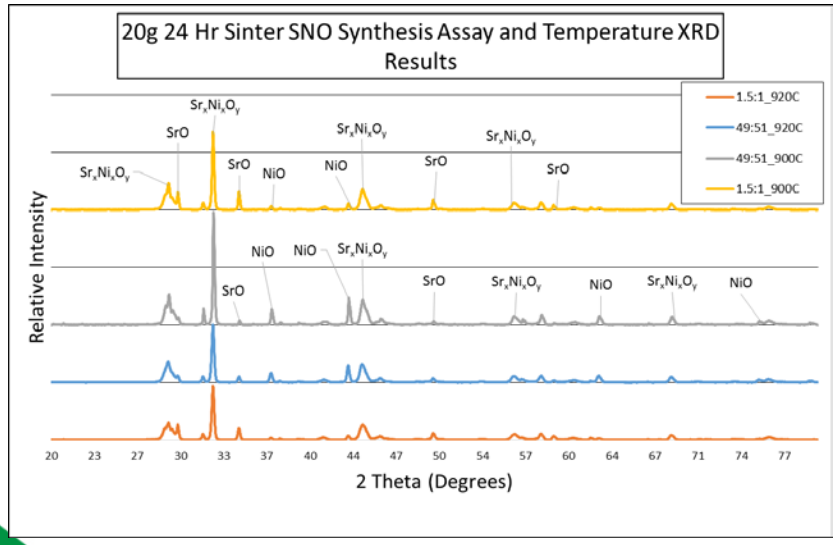
MgO – Cr_2O_3

Oxide solid solutions and mixtures from Alkaline earth and Transition metal group are preferred and considered over single phases due to chemical stability and resistance to interactions with gas phase impurities.



Large-Scale Getter Material Synthesis

Objective: Produce a large batch of SNO for industrial application
Approach: Scale up smaller 20g batches of SNO to produce 1kg batch.
Rationale: Using results from initial 20g and 100g batches, 250g batch is prepared to produce SNO with desired composition. XRD results from assay and temperature comparison of 20g batches were used to optimize 250g batch.



Previous Work : 20g batches were used to optimize powder composition of large batch with respect to initial assay and sinter temperature. Optimal composition and temperature were found to be 49:51 Sr to Ni ratio sintered at 900°C as shown.

Alternate Synthesis Processes

Synthetic Method	Advantages	Disadvantages
Microwave	Fast, high surface area	Lack of affinity
Sol-gel	Simplicity, high surface area	complex
Impregnation	Doped ions and form secondary coating layer	Need two steps
Hydrothermal	Uniform crystal size	Low surface area, high energy needed
UCT	Form porous thin layer with HSA	complex

Process Flowchart

Batch

Weigh out 347.9g $Sr(NO_3)_2$ and 498.0g $Ni(NO_3)_2$ separately.

Dissolve

Add $Sr(NO_3)_2$ to 500ml of DI water into 2000 ml beaker and begin mixing and heating. Add $Ni(NO_3)_2$. Heat @ 80°C until fully dissolved.

Precipitate

Titrate 300 ml of NH_4OH into solution or enough to bring pH above 8.75.

Dry

Heat at 80°C while maintaining pH above 8.75 through titration.

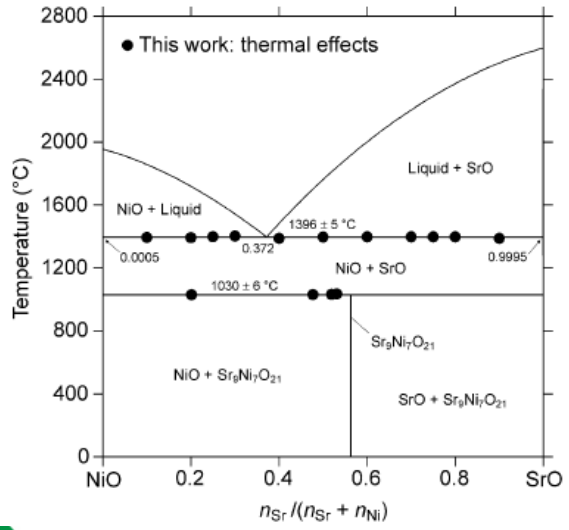
Finish drying in oven set at 80°C for 72 hours. After 72 hours remove from oven and crush into small particles using mortar and pestel.

Sinter

Place powder in furnace. Begin calcination process. Ramp oven to 500°C @ 3°C/min. Hold for four hours. Ramp oven to 900° C @ 3°C/min. Hold for 48 hours. Quench to Room Temperature.

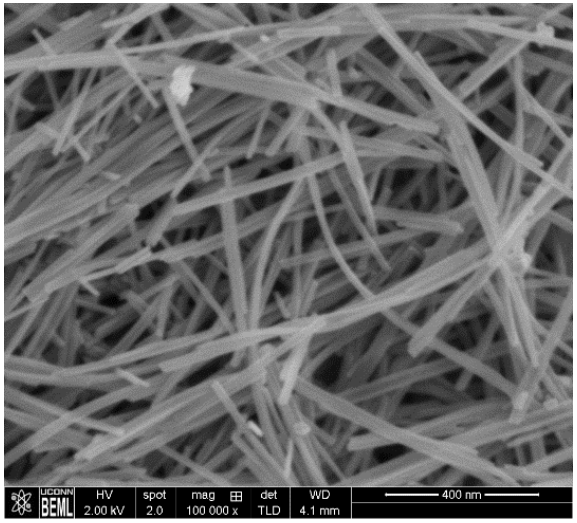
Analyze

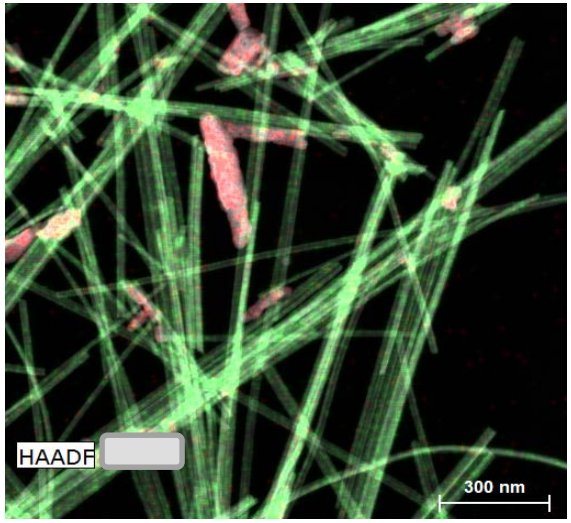
Perform characterization using XRD and particle size analysis.

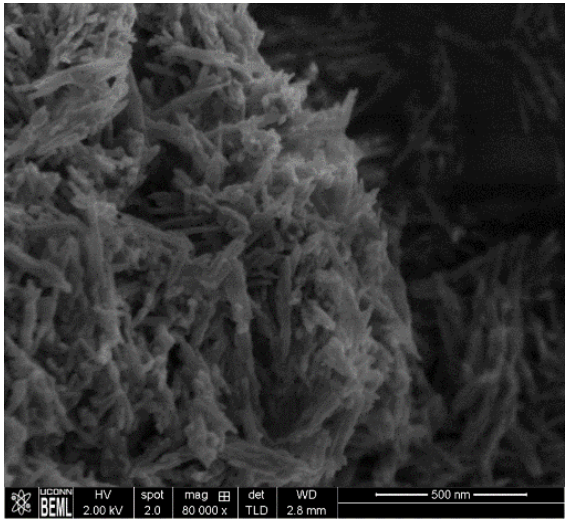


Synthesis Methods for High Surface Area Getter

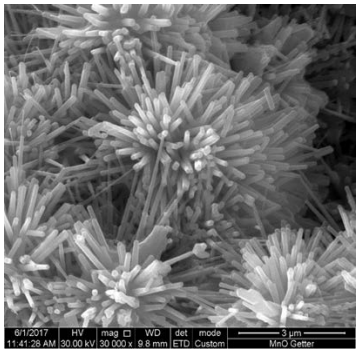
MO_x nanofibers



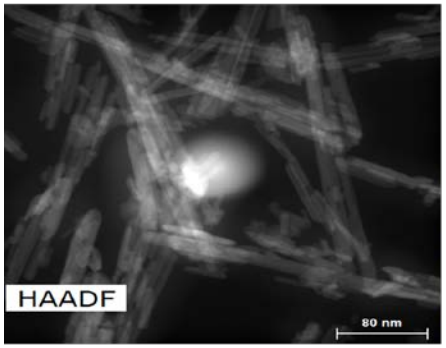




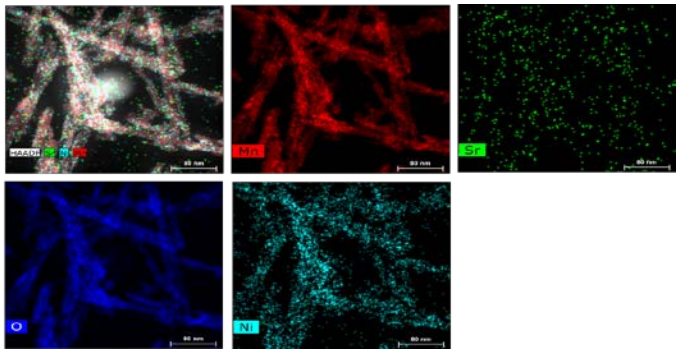
Microwave Method



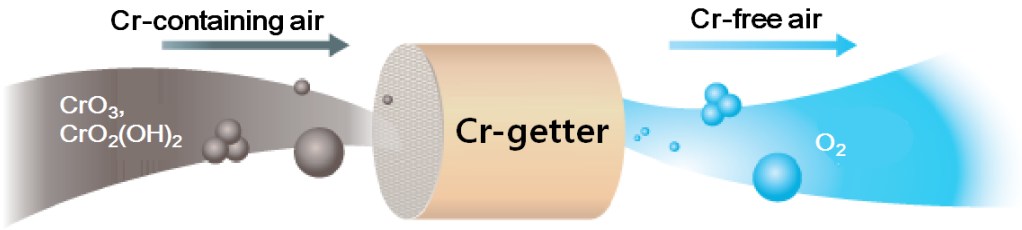
Impregnation Method

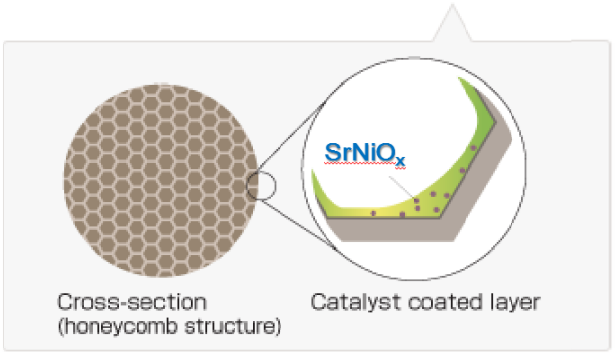


Hydrothermal method



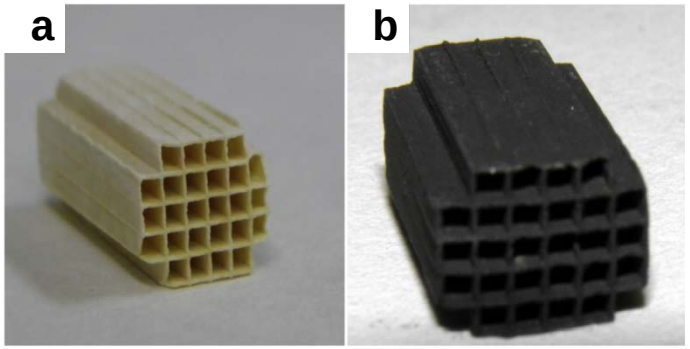
Honeycomb/ Foam Substrate Getters





Dip-coating from suspension

Schemes of Cr getter with honeycomb structure surface-coated with $SrNiO_x$



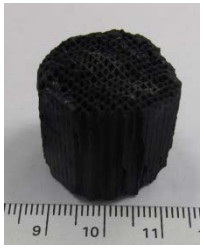
Filter coated with SrNiOx: (a) before and (b) after

High surface area and porous SrNiOx coating (10-30 μm)

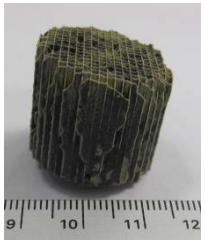
Coating Optimization: Slurry coating of honeycomb

1st coating **2nd coating** **3rd coating**

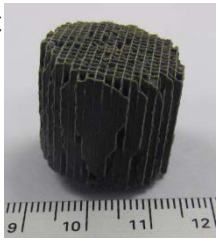
After RT drying



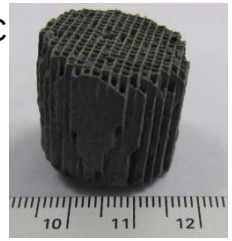
After 900C heat treatment for 5 hour



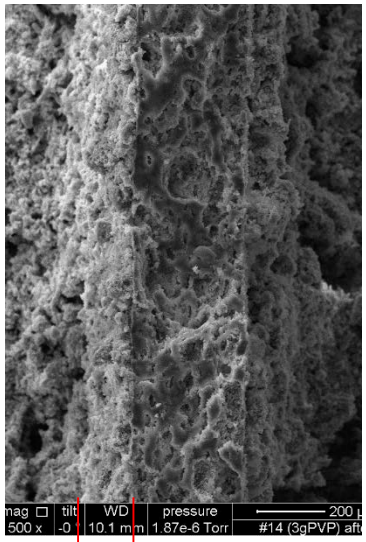
After 850C heat treatment for 5 hour



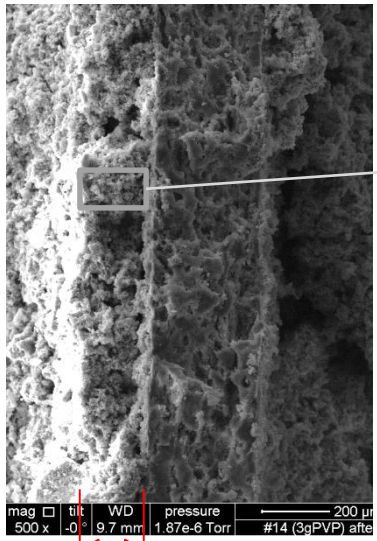
After 900C heat treatment for 5 hour



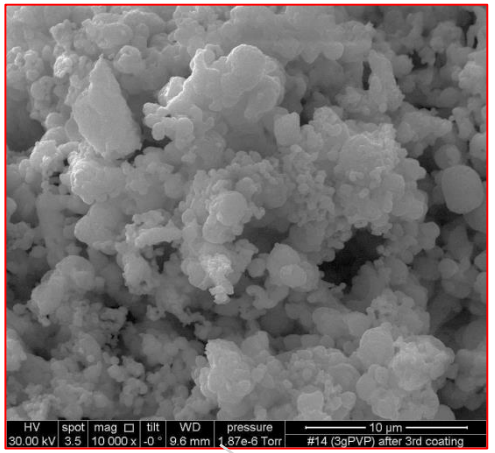
Coating	#5
SNO	10g
Durban	1.2ml
PVP	3g
Cement	1g
Solvent 50ml	50%/50% Water/Ethanol



40µm



50-60µm



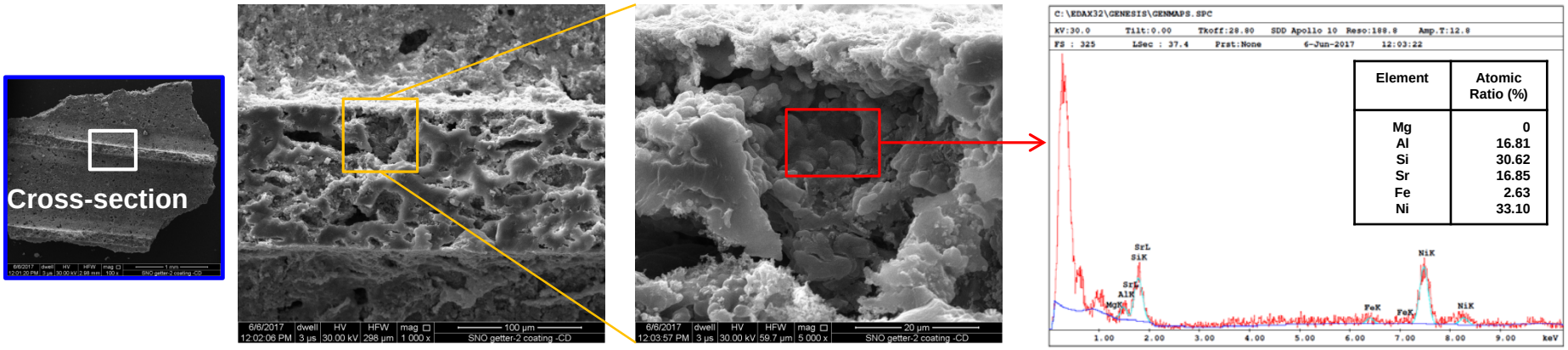
EDS Quantitative Results

Element	Wt%	At%
AlK	13.84	30.57
NiK	32.35	32.84
SrK	53.81	36.60

- After 3rd coating, coating thickness: 40-60 µm.
- Coating is porous.

Coating Optimization: Slurry coating of honeycomb

Cross section



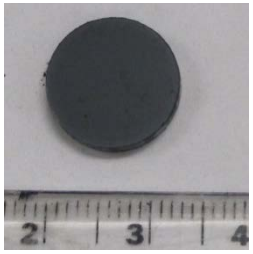
SEM images of the cross-section of the Cr getter and elemental analysis by EDS.

Pores in the substrate (cordierite) contain Sr and Ni
It is suggested that the SrNiOH penetrated into the holes cause strong adhesion between the coated layer and the substrate.
The SrNiO layer is ~10 – 15 µm in thickness.

Stability of Getter Materials

Before sintering

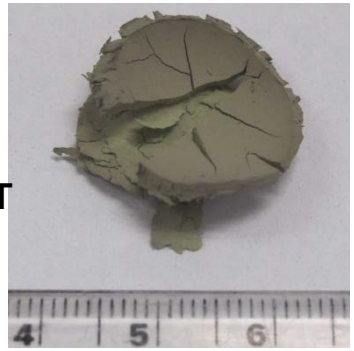
850˚C (20h)



After sintering

1000˚C (20h)

post sintering
24h in air at RT



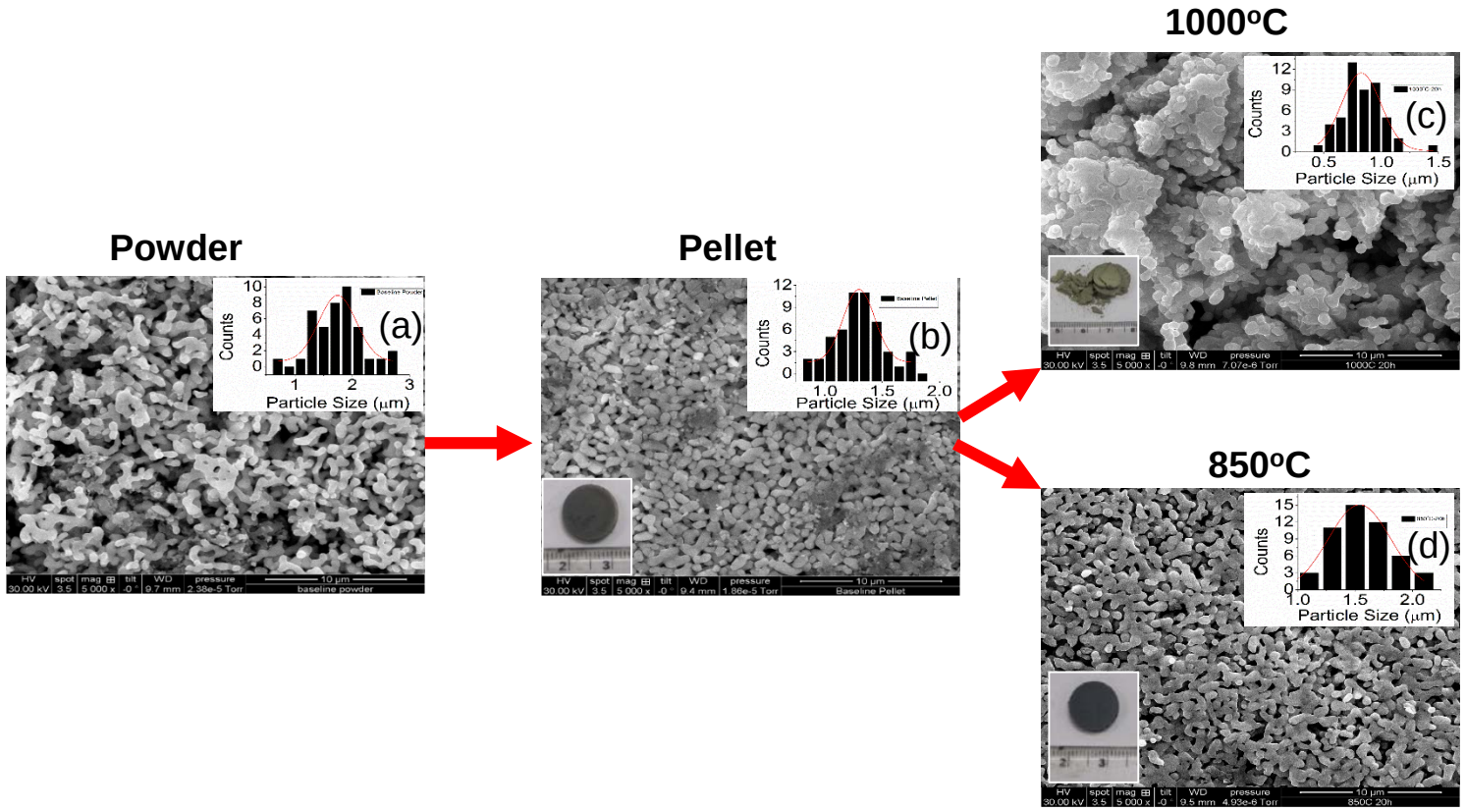
- **Evaluate the stability of SrNiOx**
- **Validate in-cell getter to capture Cr from IC source**

- Sintering at 850˚C for 20h: No change in color and shape of the pellet
- Sintering at 1000˚C for 20h: Pellets became brown and the shape was intact immediately after removal from furnace at room temperature, but after 24h the pellets were pulverized completely.

- No/ negligible changes in morphology was observed for SNO sintered at 850^{o}C for 20h
- Particles agglomeration was observed for SNO sintered at 1000^{o}C for 20h

Thermal stability

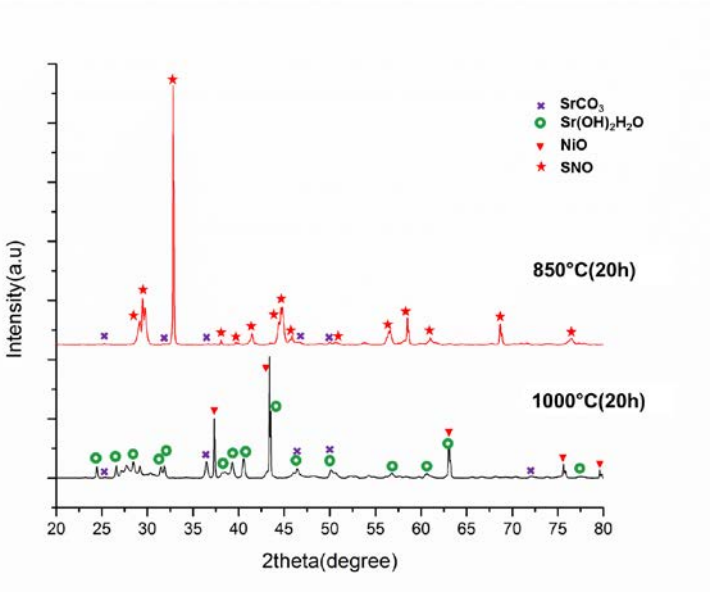
Pellets of SrNiOx sintered at 850°C and 1000°C for 20h



- No change in color and shape of the pellet after sintering at 850°C for 20h
- Sintering at 1000˚C for 20h leads to pulverization of SNO powders. Initially the pellets turn brown in color immediately after taking out of the furnace with changing to green and completely pulverized after 24h left in lab atmosphere.

Post sintering XRD characterization

XRD was conducted after sintering the pellets at 850°C and 1000°C and left in air for at least 24 hours



850˚C (20h)

1000°C (20h)

Lattice volume

Material	Lattice	Volume (Å^3)	Pattern
SrO	FCC	137.51	01-075-6979
$Sr(OH)_2$	Orthorhombic	237.27	00-027-0847
$SrCO_3$	Orthorhombic	259.07	00-005-0418

Molar volume

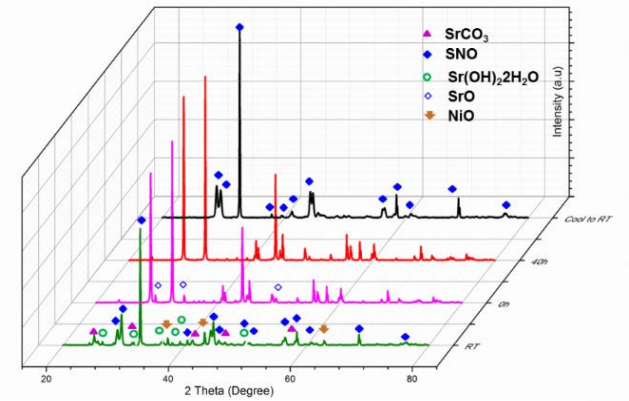
Material	Molar Mass (g/mol)	Density (g/cm^3)	Molar Volume (cm^3/mol)
SrO	103.62	4.70	22.05
$Sr(OH)_2$	121.63	3.63	33.51
$SrCO_3$	147.63	3.74	39.47

- The XRD pattern of 850 °C sintered SNO indicates presence of only $Sr_xNi_yO_z$ phase with presence of minor $SrCO_3$ phase
- In contrast, XRD patterns of pulverized powder (1000°C) shows the presence of $Sr(OH)_2.H_2O$ phase along with the strong peaks of $SrCO_3$.
- Strong peaks of NiO phase appear with absence of SrO phase in XRD patterns of the pulverized samples.

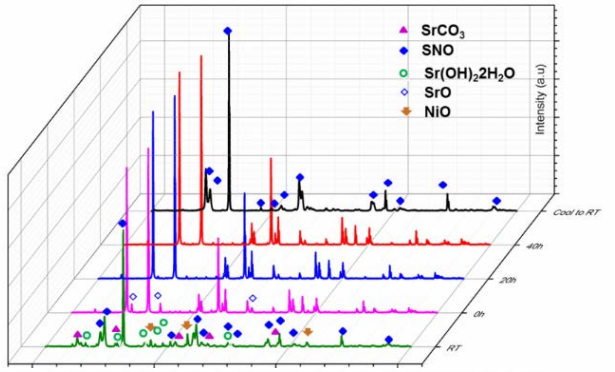
Getter Materials Stability

Phase Stability has been studies by high temperature *in-situ* XRD performed on SrNiOx powder for up to 40h

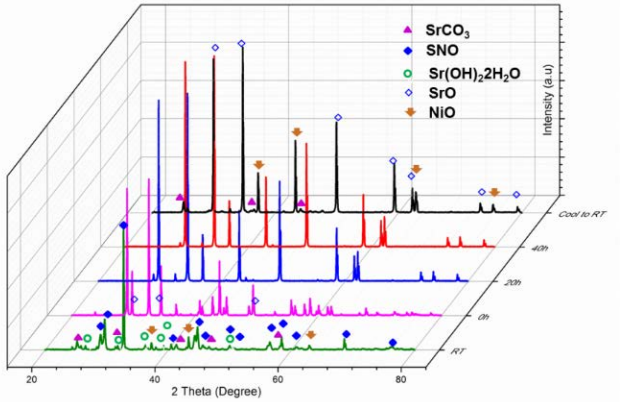
850˚C



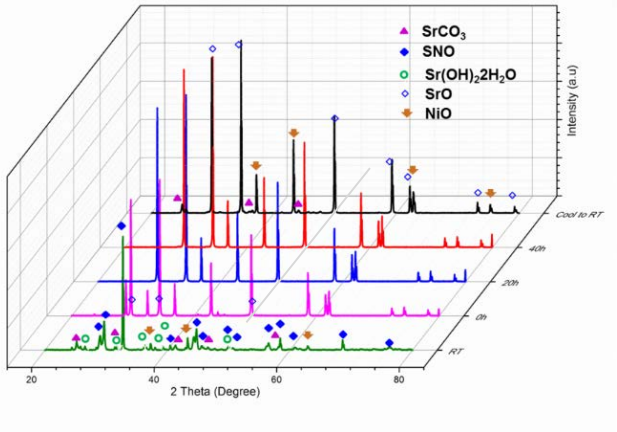
900˚C



950˚C

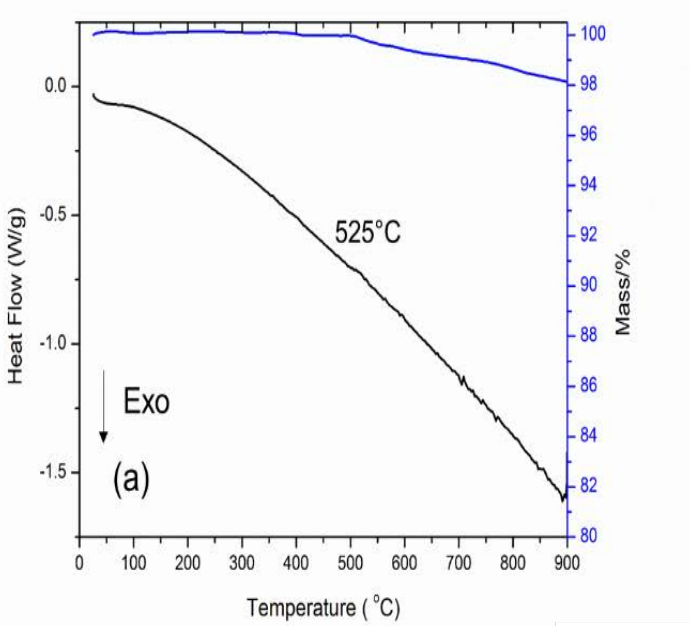


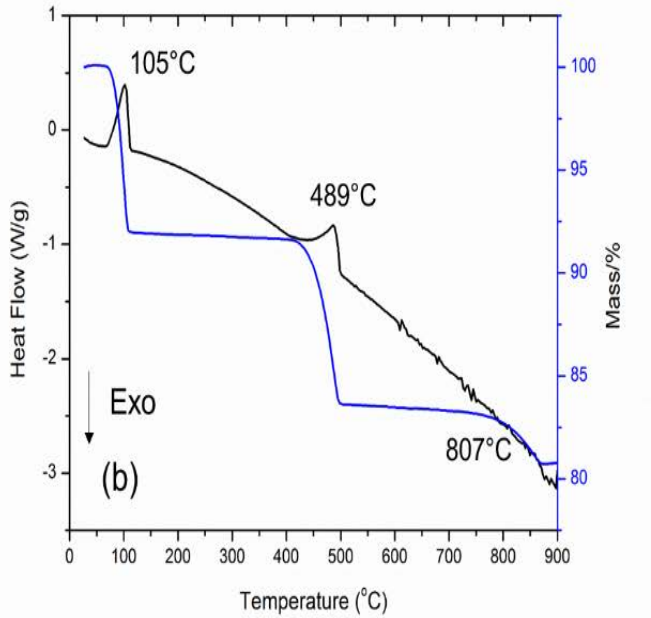
1000˚C



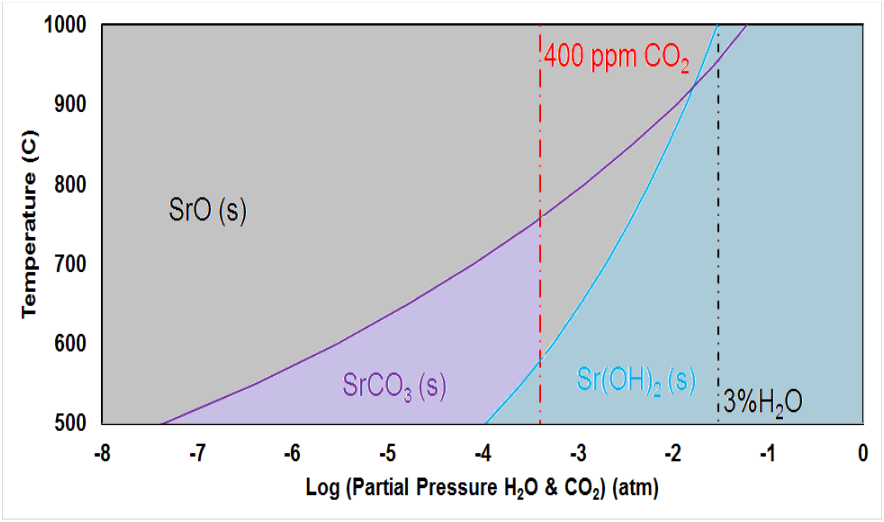
- SrNiOx demonstrated phase stability sintered at 850ºC and 900ºC.
- SrNiOx sintered at 950ºC and 1000ºC dissociates into SrO and NiO phases.

TGA-DTA Analysis

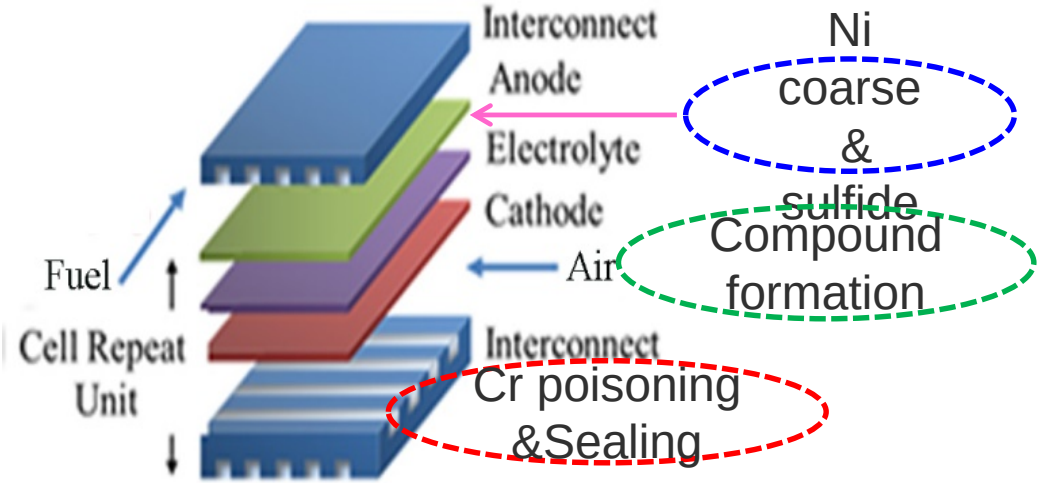




Endothermic peaks at 105 and 489C indicating release of H2O from SNO powder samples sintered at (a) 850C and (b) 1000C (20Hrs)

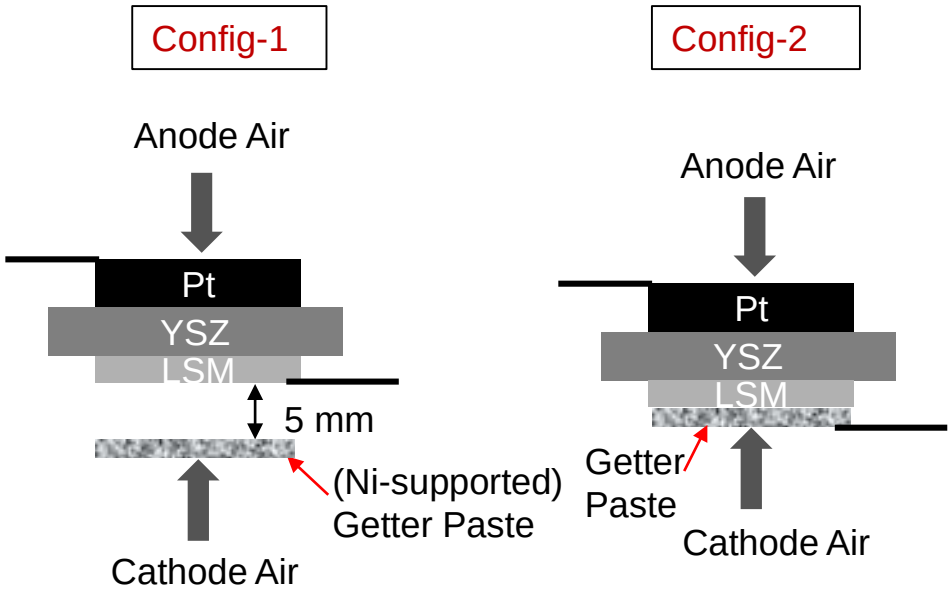


In Stack Cr Capture



Electrochemical Evaluation

Half-cell configuration



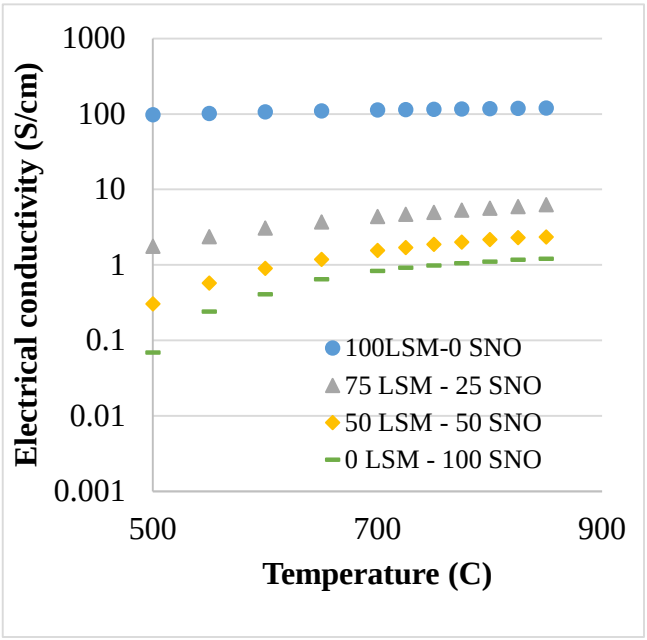
Conditions	
Temperature	850C
Flowrate	150 sccm
Cr Source	Cr_2O_3
Cr Getter	SNO/ LSCF-SNO composite
Bias	-500 mV

- 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

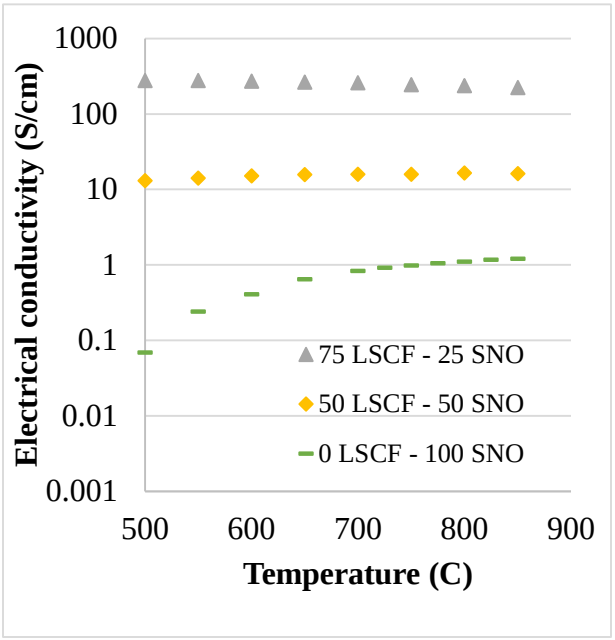
Getter Materials Conductivity

Electrical Conductivity

LSM-SNO



LSCF-SNO

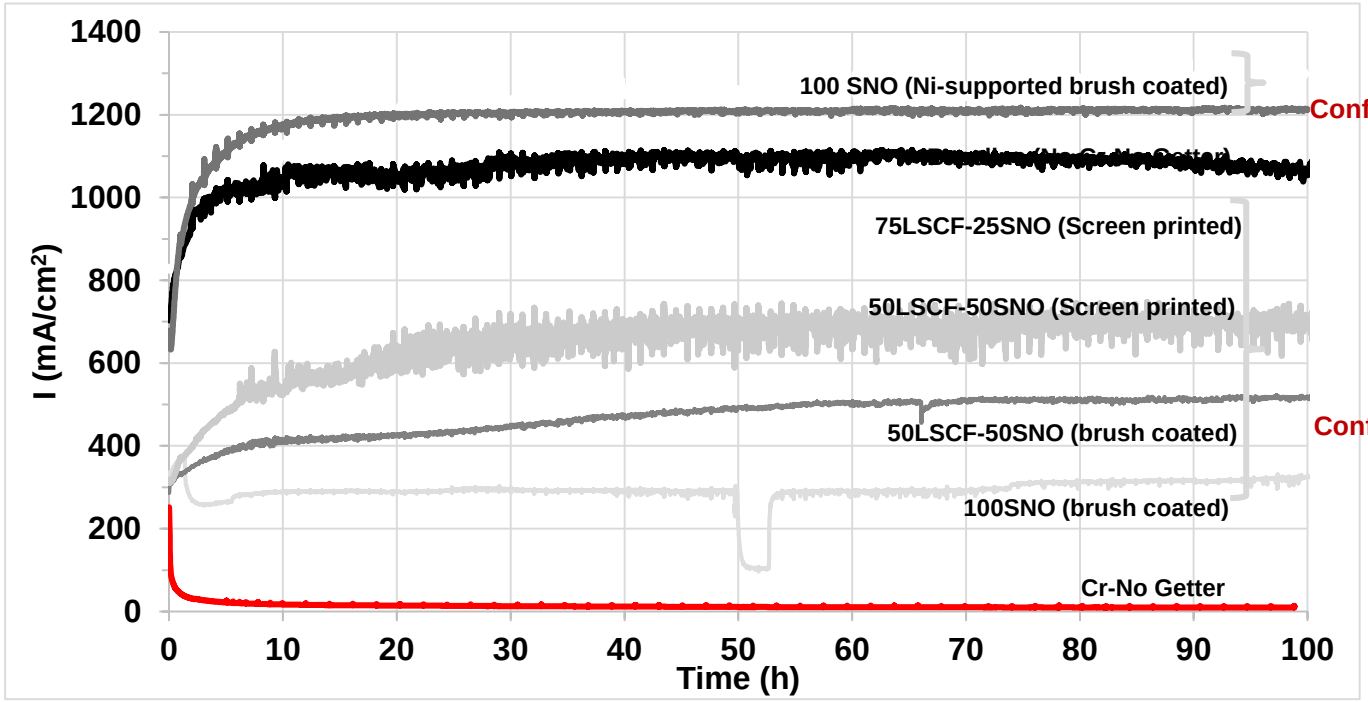


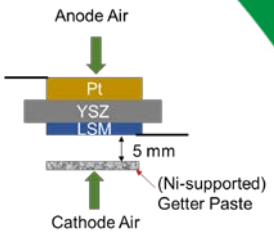
- Electrical conductivity of LSM is approximately 120 S/cm at 850˚C
- Electrical conductivity of SNO is approximately 1.2 S/cm at 850˚C
- Addition of SNO in LSM lowers the conductivity of LSM-SNO composites
- Electrical conductivity of LSCF is more than 800 S/cm at 850˚C[1]
- LSCF-SNO composites display higher conductivity compared to LSM-SNO composites.

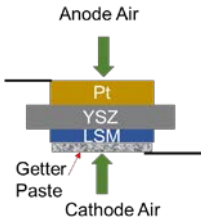
1. Q. Xu et al, Journal of Alloys and Compounds 454 (2008) 460–465

Electrochemical Evaluation

I-t data





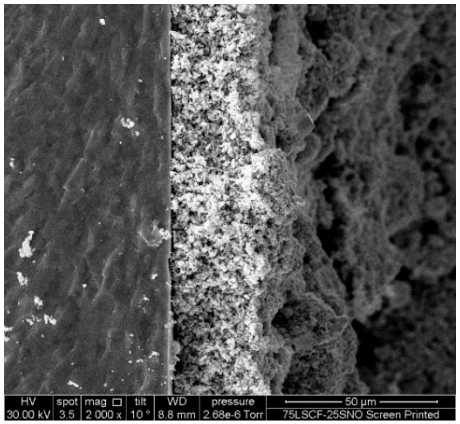


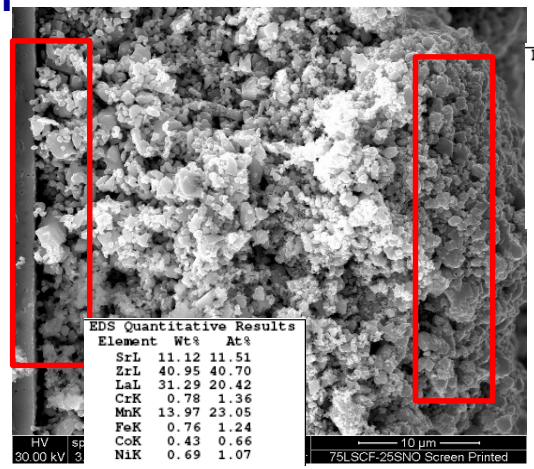
- I-t data shows stable performance for 100h in all the half-cell configurations
- Config-1 shows higher performance because of no direct contact of getter with the LSM cathode
- 75LSCF-50SNO getter shows higher current density (~1100 mA/cm^2) as compared to 50LSCF-50SNO getter (~700 mA/cm^2)

Electrochemical Evaluation

Posttest characterization (SEM)

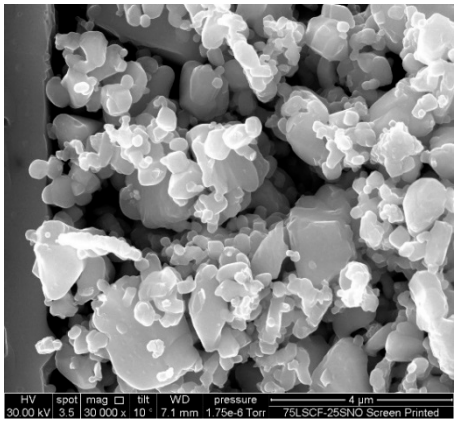
75LSCF-50SNO (Screen printed) Cross-section

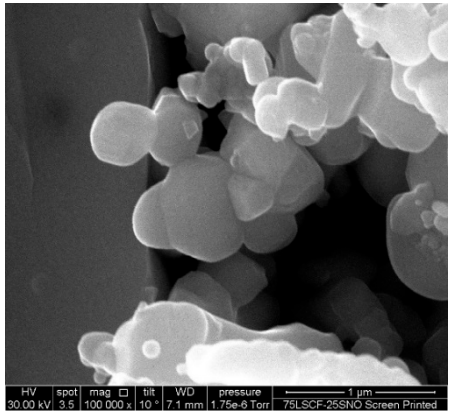




EDS Quantitative Results

Element	Wt%	At%
SrL	21.93	20.39
ZrL	10.46	9.34
LaL	32.01	18.77
CrK	4.99	7.81
MnK	1.26	1.87
FeK	16.10	23.48
CoK	5.86	8.09
NiK	7.39	10.25





- Higher Cr concentration observed at the surface
- Cathode/ electrolyte interface remained free from Cr

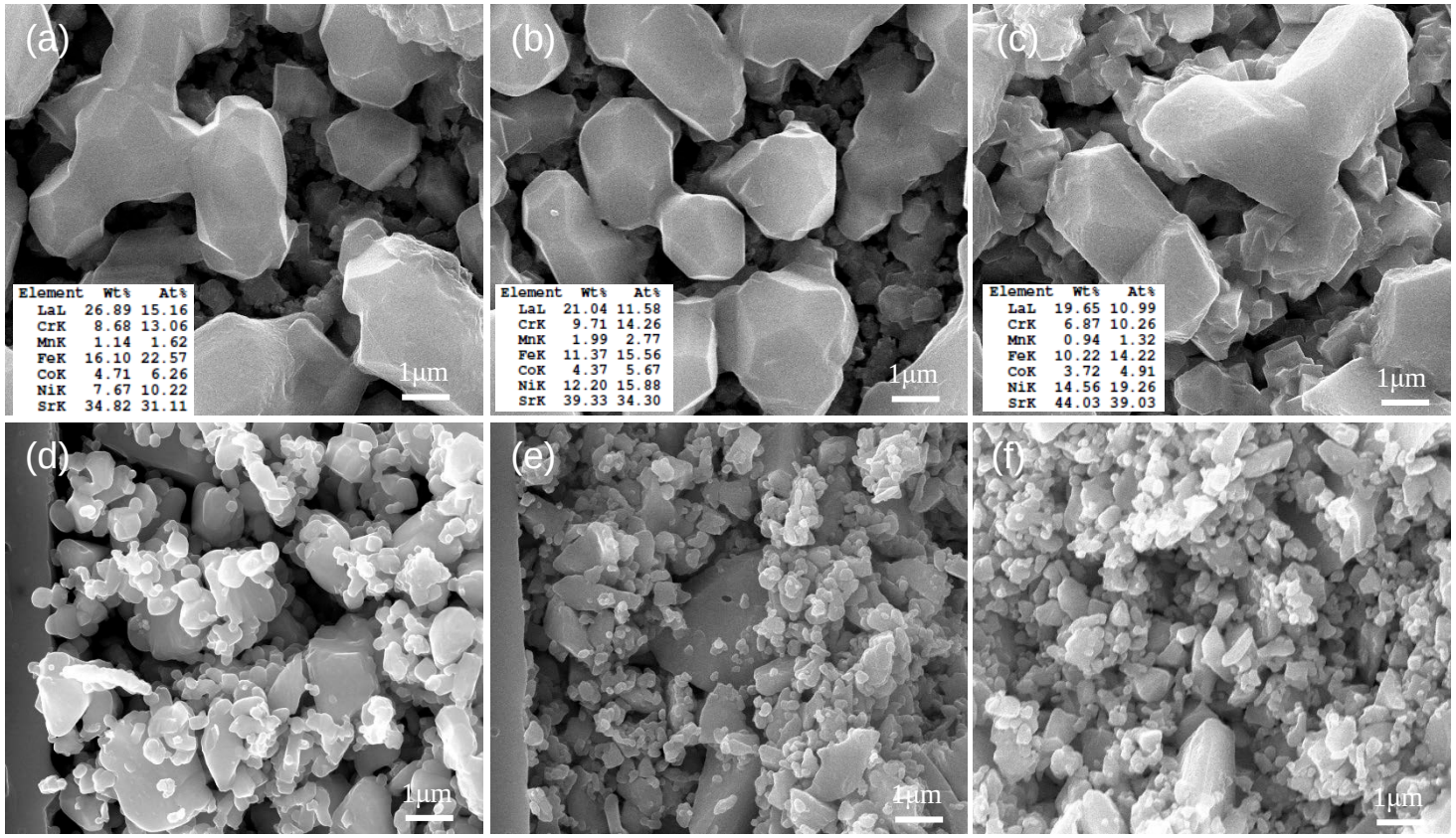
Electrochemical Evaluation

Posttest characterization (SEM)

75LSCF-25SNO (Screen printed) | 50LSCF-50SNO (Screen printed) | 50LSCF-50SNO (Brush coated)

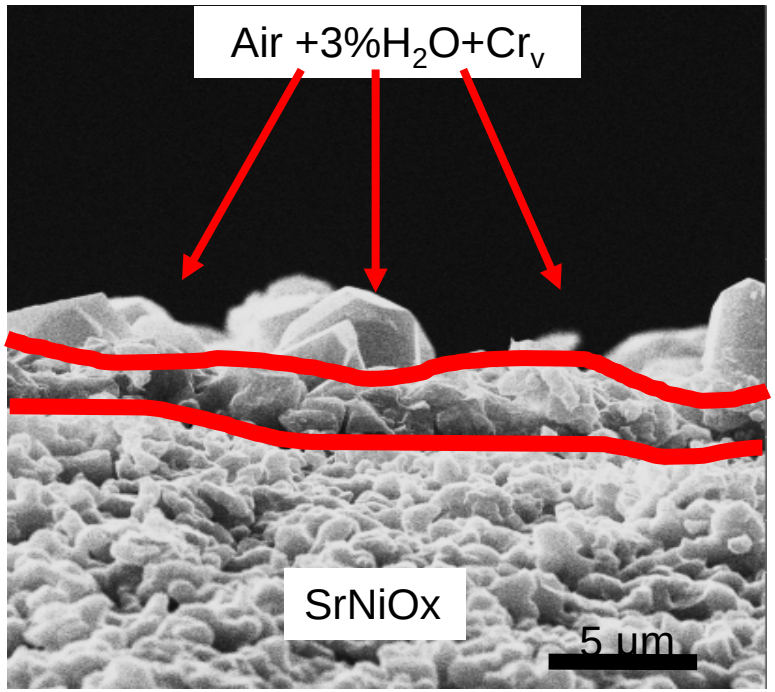
Surface

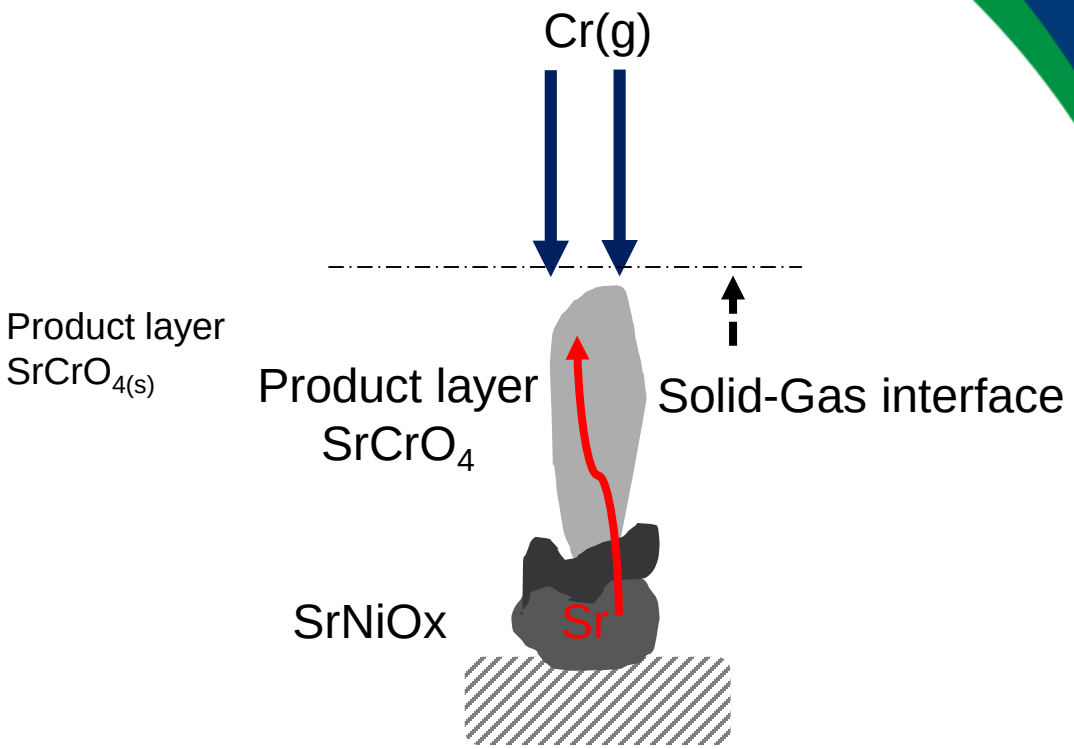
Cross-Section



- All Cr are mostly captured at the surface of the cathode with faceted particle formation
- No Cr or product was found inside cathode or cathode-YSZ interface

Getter reaction and Cr capture



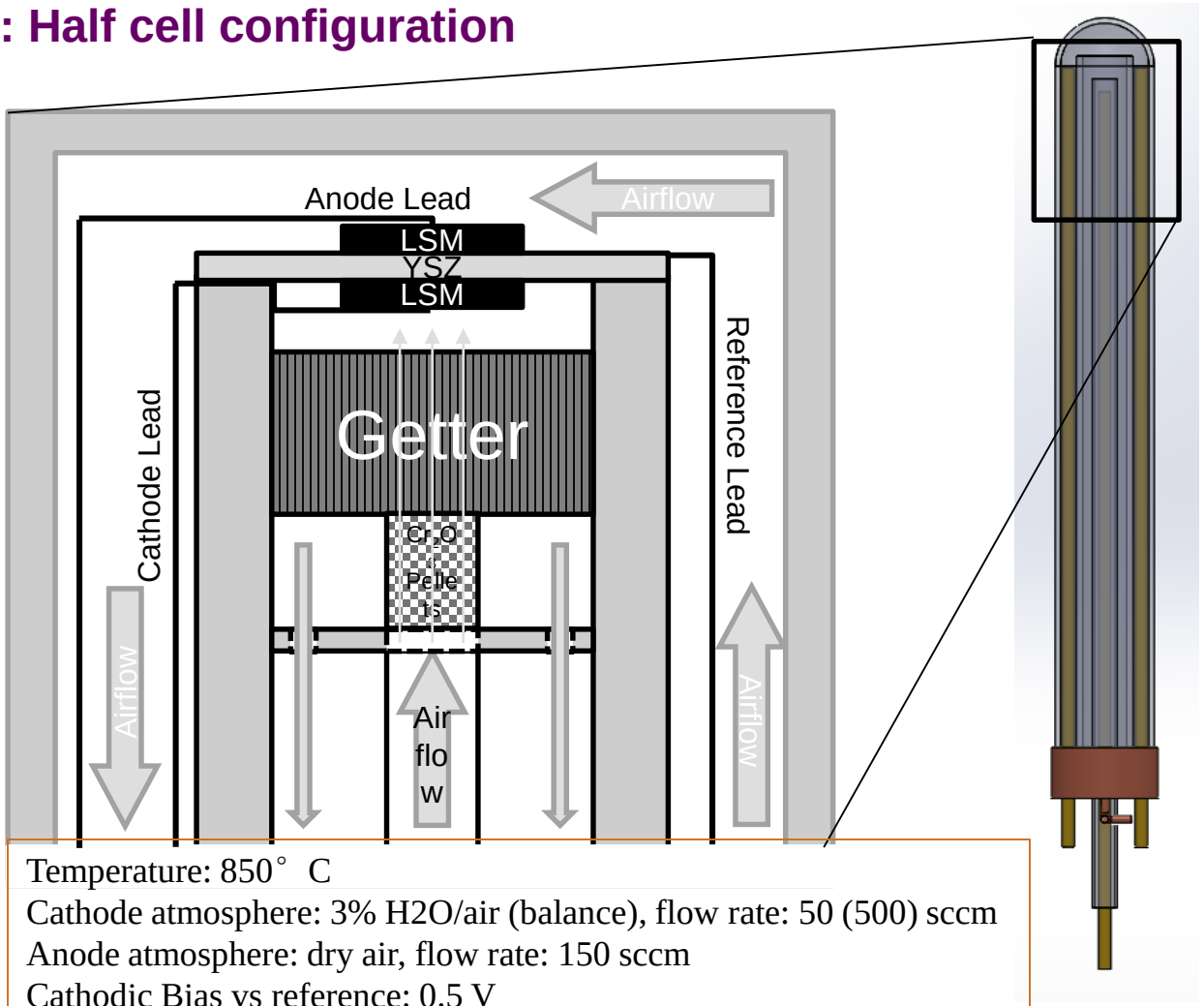


CrO_3 (g) + $Sr_xNi_yO_z$ = $SrCrO_4$+ NiO+ O_2 (g)

$CrO_2(OH)_2$ (g) + $Sr_xNi_yO_z$ + O_2 (g) = $SrCrO_4$ + NiO + H_2O (g)

In-Situ Electrochemical Characterization

Test assembly : Half cell configuration



Temperature: 850° C
Cathode atmosphere: 3% H2O/air (balance), flow rate: 50 (500) sccm
Anode atmosphere: dry air, flow rate: 150 sccm
Cathodic Bias vs reference: 0.5 V
Getter: cordierite /alumina fiber supported SrNiOx

Thermodynamic Analysis

Thermodynamic Analysis

Cr poisoning in SOFC cathodes

- Cr poisoning effects in SOFC cathodes
  - $(La,Sr)MnO_3$
  - $(La,Sr)(Co)O_3$
- Ab-initio thermodynamic with a linear programming approach
- Reaction Energetics of the SOFC cathodes with CrO_3

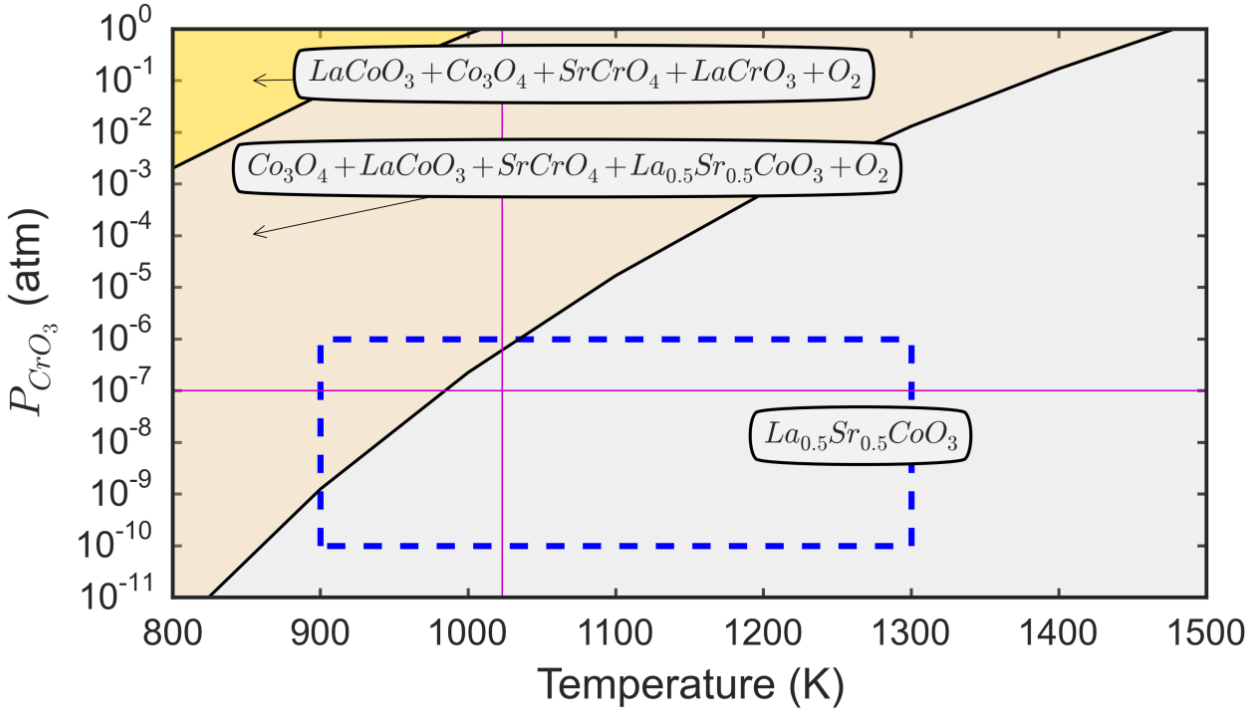
* The structure of the LSCO and LSMO at different Sr concentration have been studied.

* We have identified the minimum energy structures in each of the compositions and they agree well with experiments

* Reaction energetics of CrO_3 with the compounds $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.75}Sr_{0.25}MnO_3$ were studied.

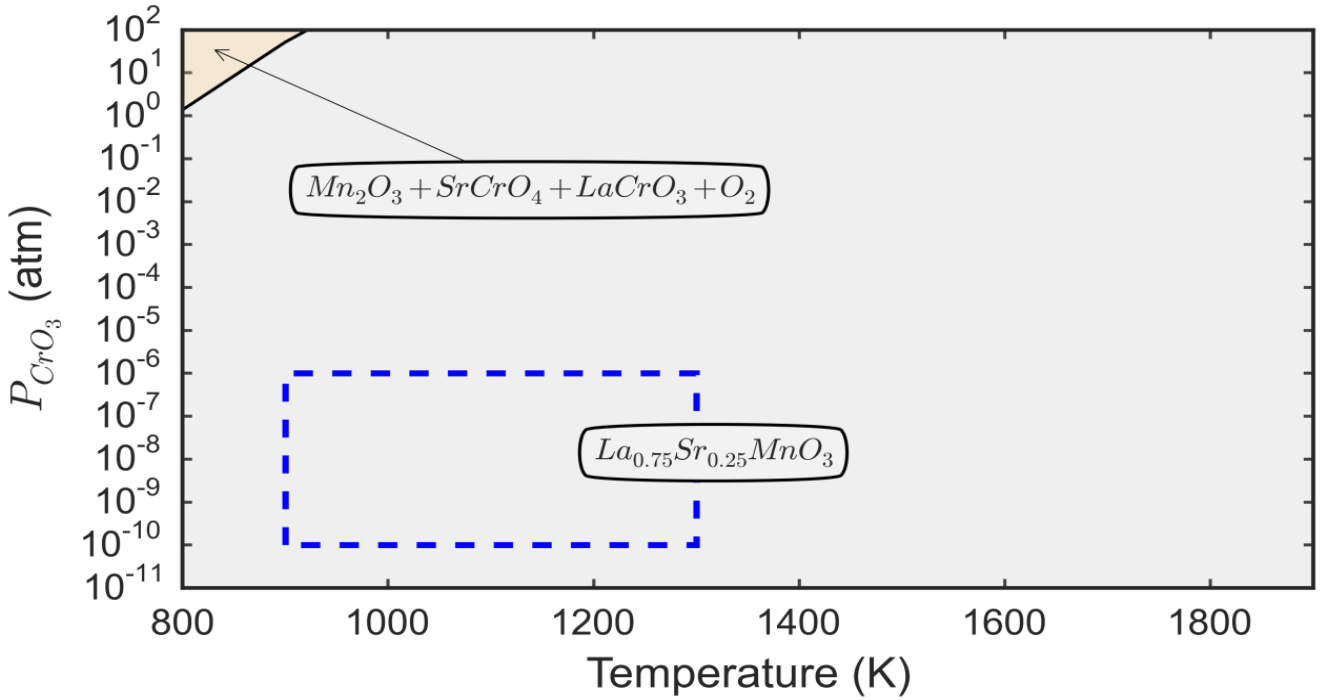
* We find that while LSCO results in reactive products for the experimental window, the LSMO remains unreactive

Reaction energetics of $La_{0.5}Sr_{0.5}CoO_3$ Cubic



Based on the reaction energetics, the formation of these products: $LaCoO_3$, Co_3O_4, $SrCrO_4$, and O_2 are energetically favored in the experimental window.

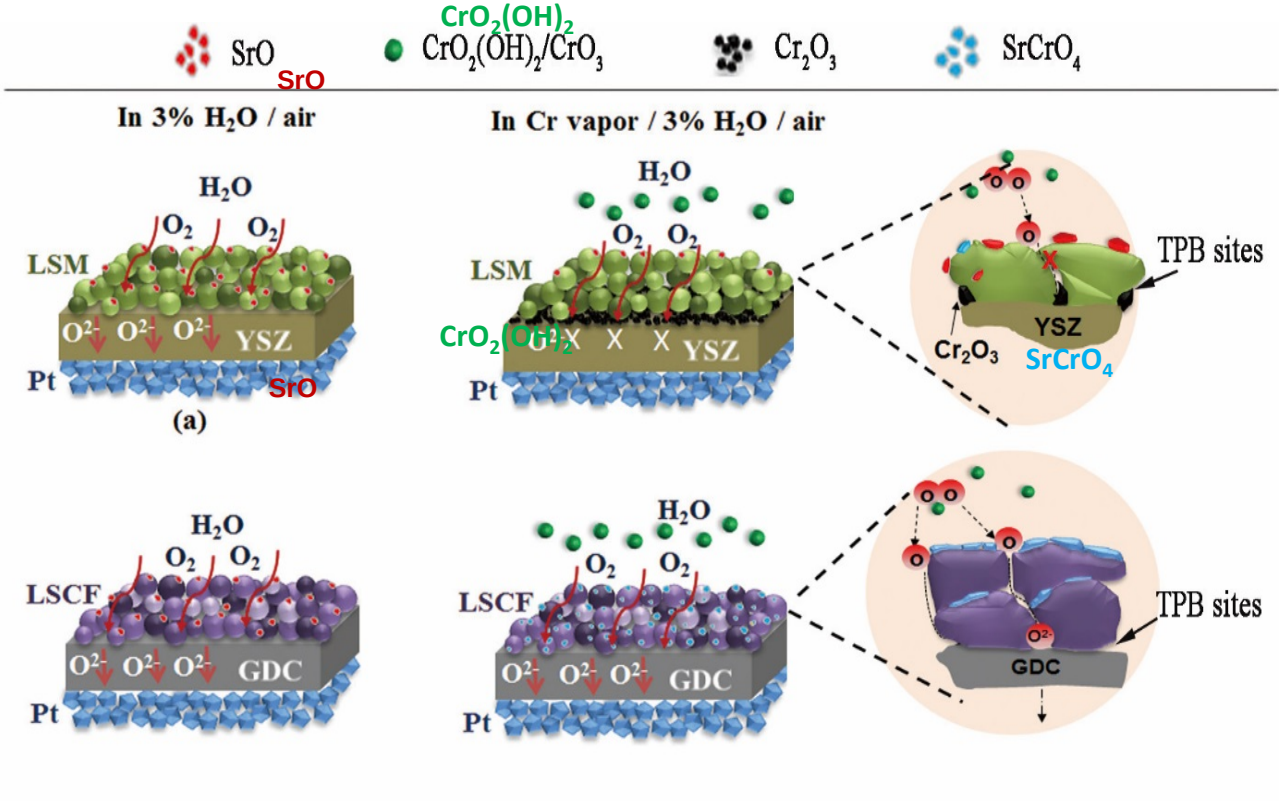
Reaction energetics of $La_{0.75}Sr_{0.25}MnO_3$ Cubic



Based on the reaction energetics, the formation of Cr deposition products are not energetically favored in the experimental window.

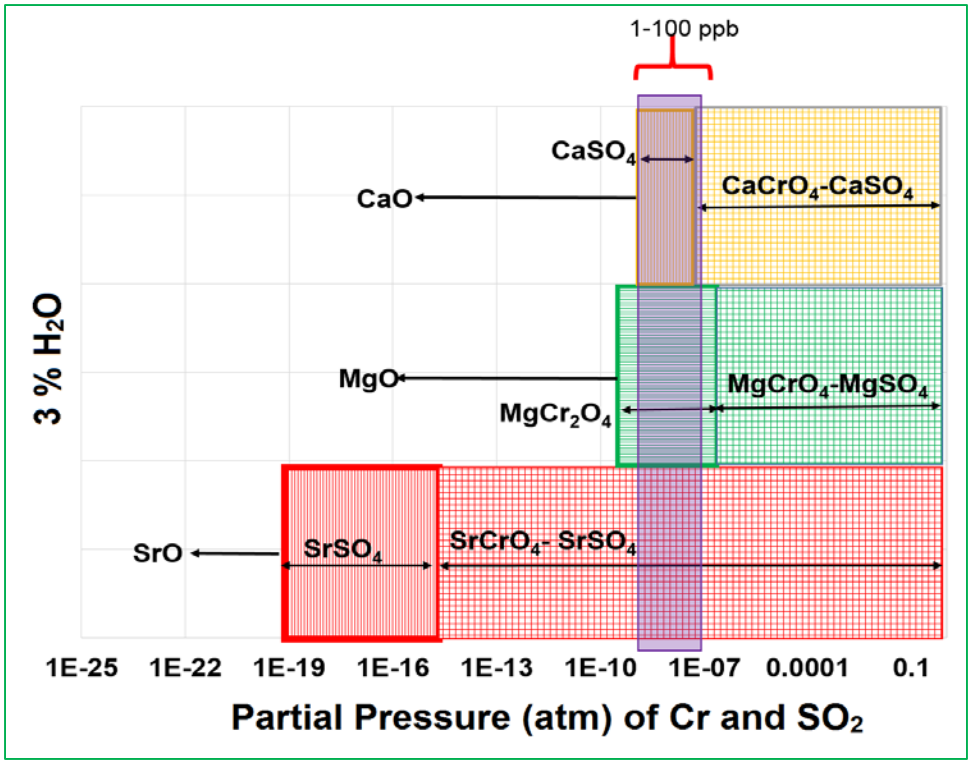
Background – Chromium Poisoning of Cathodes

Morphology evolution in the presence of water and chromium vapor



B. Hu, S. Krishnan, C. Liang, S. J. Heo, A. N. Aphale, R. Ramprasad, P. Singh, . Int J Hydrogen Energy , 2017

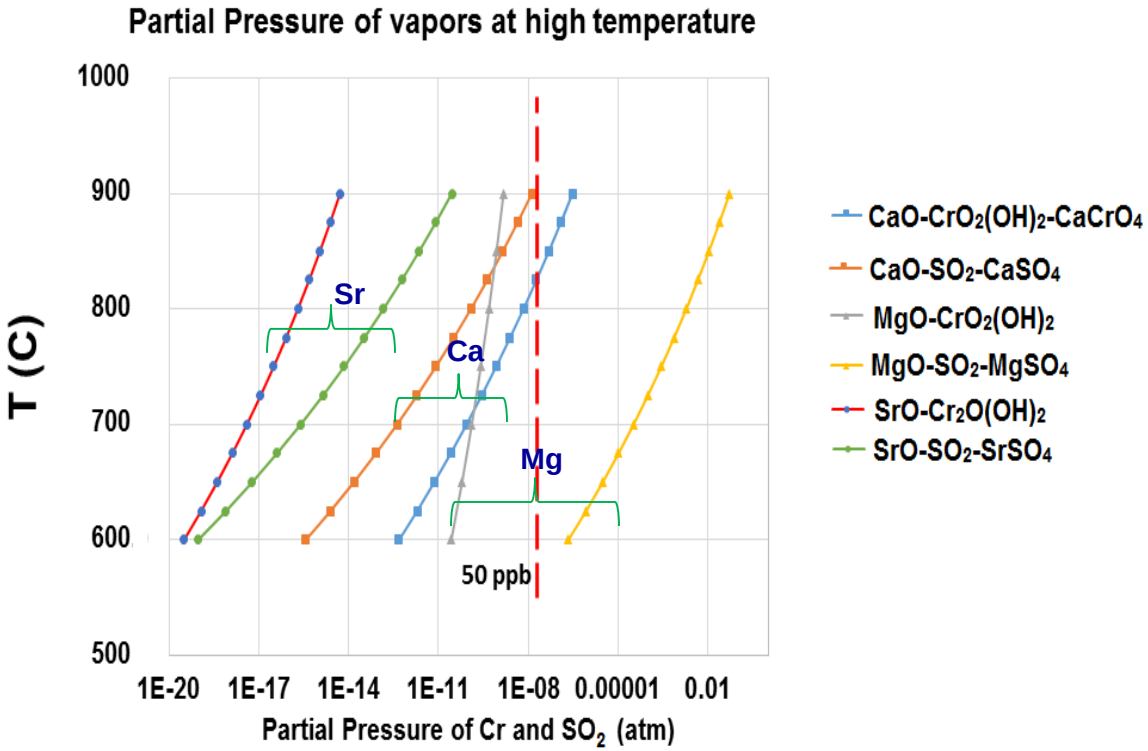
Co-oxidation of Cr and SO_2 on metal oxides



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

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

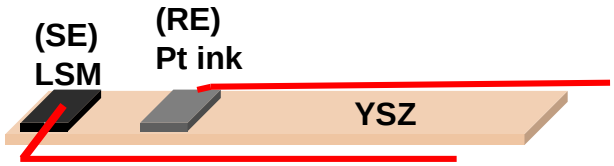
Thermodynamic Calculations of p_{Cr} and p_{SO2} vapors at High Temperatures



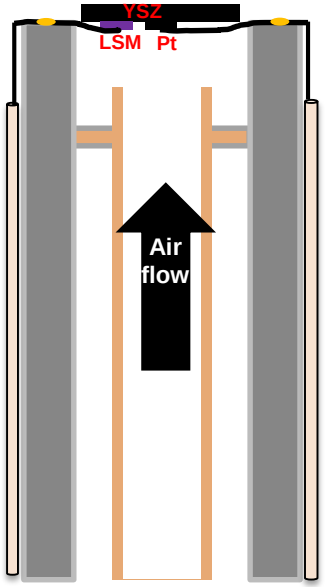
- SrO is better than CaO, and MgO as a getter material for Cr and S capture.
- SrO is capable of forming $SrCrO_4$ and $SrSO_4$ compounds at extremely low concentrations of Cr and SO_2 vapors, even below 1 ppb.

Design and fabrication

- Sensor design:
  - Planar sensor design to monitor the presence of chromium within the getter



Planar (2D) sensor

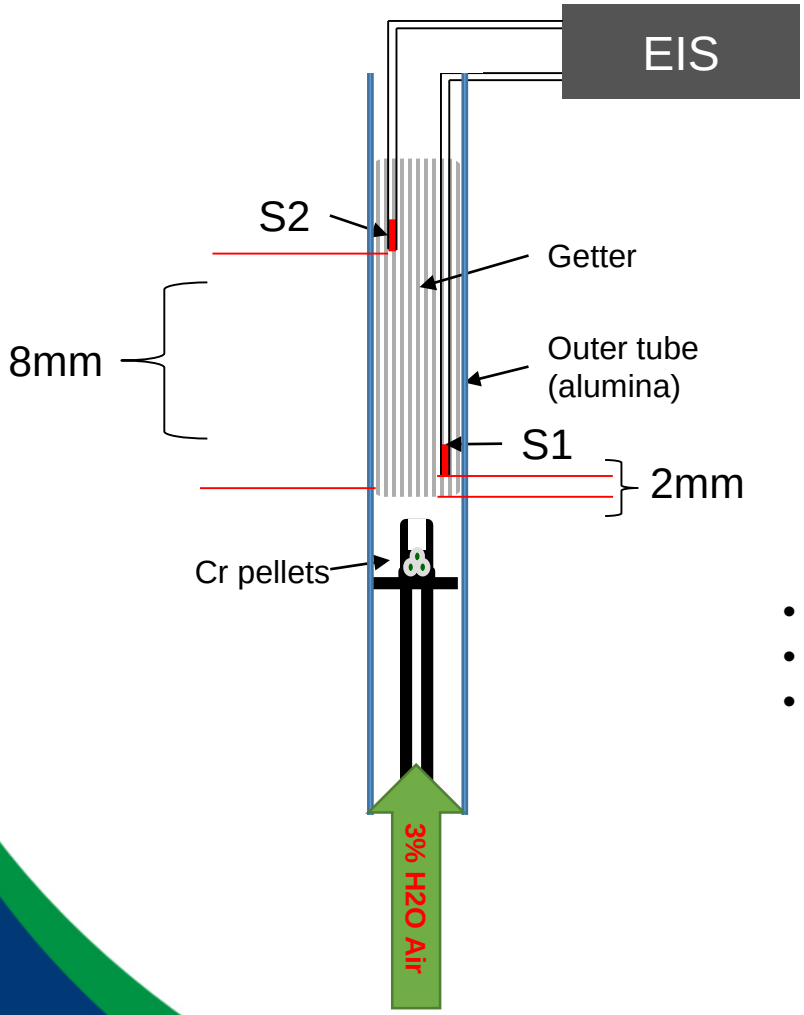


Sensor Fabrication

Sensor Validation

- LSM sintered at 1200 ^{o}C in air and Pt sintered at 850 ^{o}C in air with the ramp rate of 3C/min for 1h
- LSM and Pt ink was brush coated on the YSZ disk as sensing (SE) and reference electrode (RE)

Validation



- S1 is inserted within the getter at about 2 mm from inlet
- S2 is inserted about 8 mm from inlet of the getter
- Observe the changes in polarization resistance and ohmic resistances to determine extent of Cr related degradation

Governing Equations, Boundary Conditions, and Parameters

Mass conservation equation:

$$\frac{\partial \rho}{\partial t} + \nabla.(\rho \mathbf{u}) = 0$$

Momentum conservation equation:

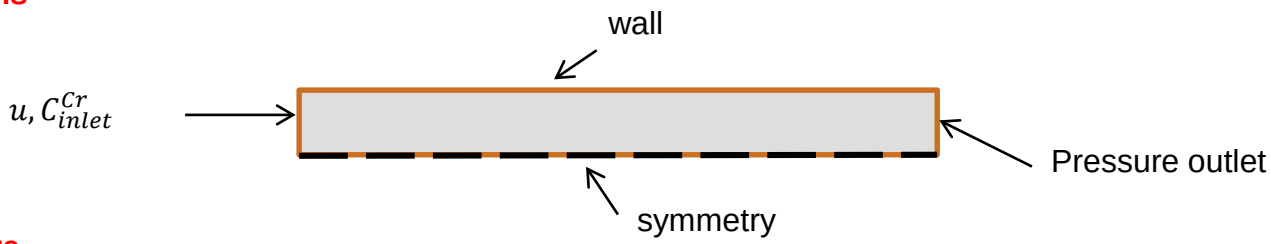
$$\frac{\partial (\rho \mathbf{u})}{\partial t} + \nabla.(\rho \mathbf{u}\mathbf{u}) = -\nabla p + \nabla.\left(\boldsymbol{\mu}^{\boldsymbol{eff}} \nabla \mathbf{u}\right) + \rho \mathbf{g}$$

Species conservation equation:

$$\frac{\partial (C^{Cr})}{\partial t} + \nabla.(\mathbf{u} C^{Cr}) = \nabla.\left(\boldsymbol{D} \nabla \mathrm{C}^{\mathrm{Cr}}\right) + \mathrm{S}_{Cr}$$

S_{Cr}: sink term for Cr.

Boundary Conditions



Numerical Procedure

- Set of equations is discretized using a finite-volume method.
- Discretized equations are solved within the commercially available CFD software, Fluent, by customizing via user-defined functions.
- The software utilizes the well-known SIMPLE algorithm.

Modeling Parameters

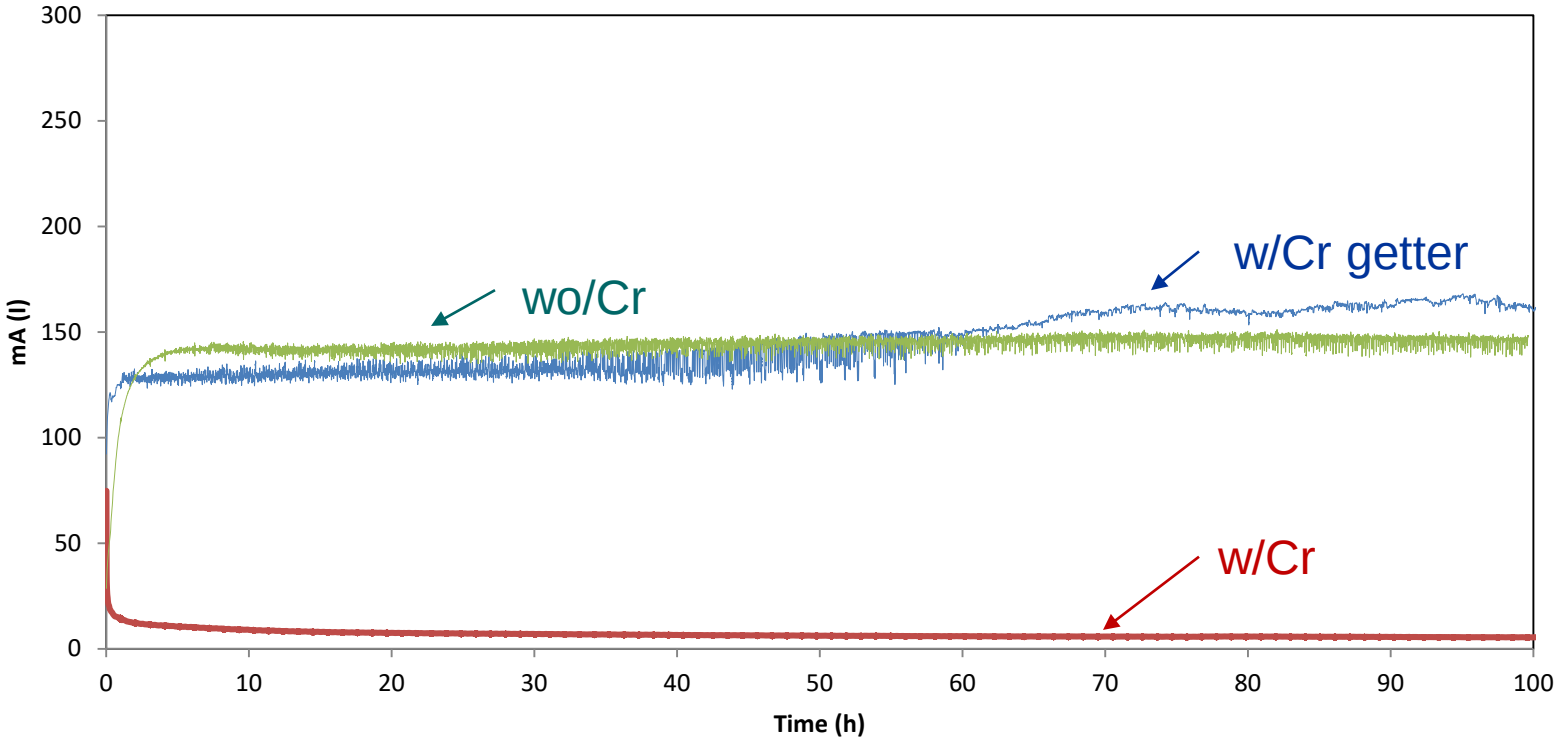
- Modeling Geometry: 50 mm long and 1mm width
- Temperature: 850˚C
- Cr partial pressure 0.1 Pa and 0.001 Pa
- Air density: 0.3139 kg/m^3 at 850˚C
- Gas phase Cr diffusivity: 1.08775e-4 m^2/s
- Solid phase Cr diffusivity: 1e-19 m^2/s
- Solid phase Sr diffusivity: 1e-17 m^2/s

- Getter material: $SrNiO_x$
- $SrNiO_x$ density: 5406 kg/m^3
- $SrNiO_x$ molecular weight: 1.53542 kg/mol

Electrode poisoning at low temperatures

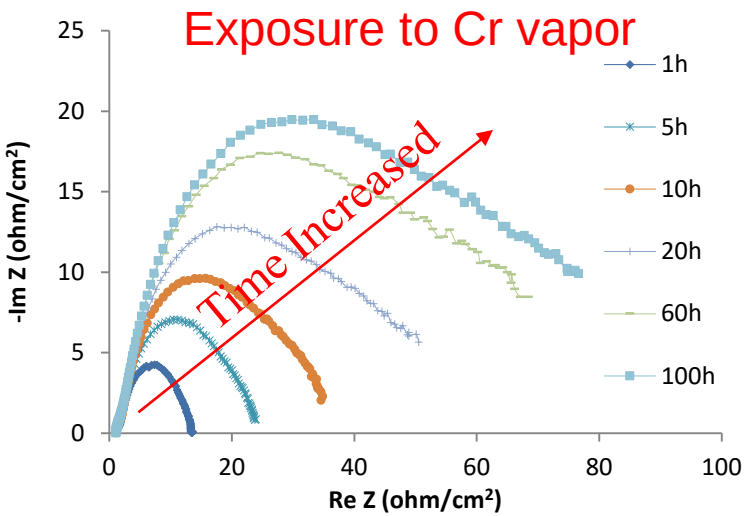
In cell validation

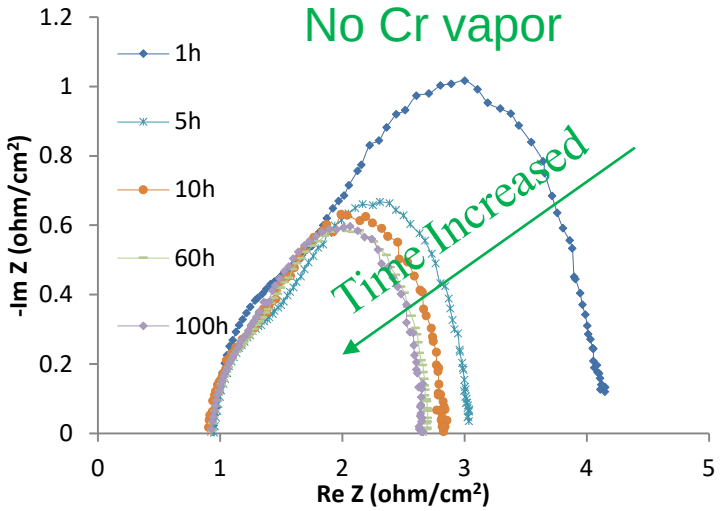
Electrochemical Performance at 650C

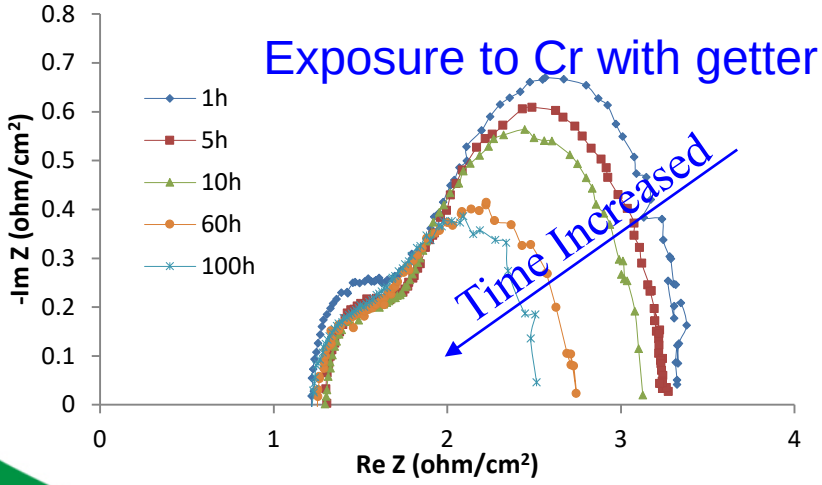


The LSM/YSZ/Pt half-cell exposed to 3% H_2O/air in the presence of Cr vapor shows a rapid drop in the current within the first few hours while the I-t curves from the standard cell (No Cr vapor) and the cell exposure to Cr and followed a chromium getter show similar curve with stable electrochemical performance.

Changes in EIS with/without Cr and Cr/getter



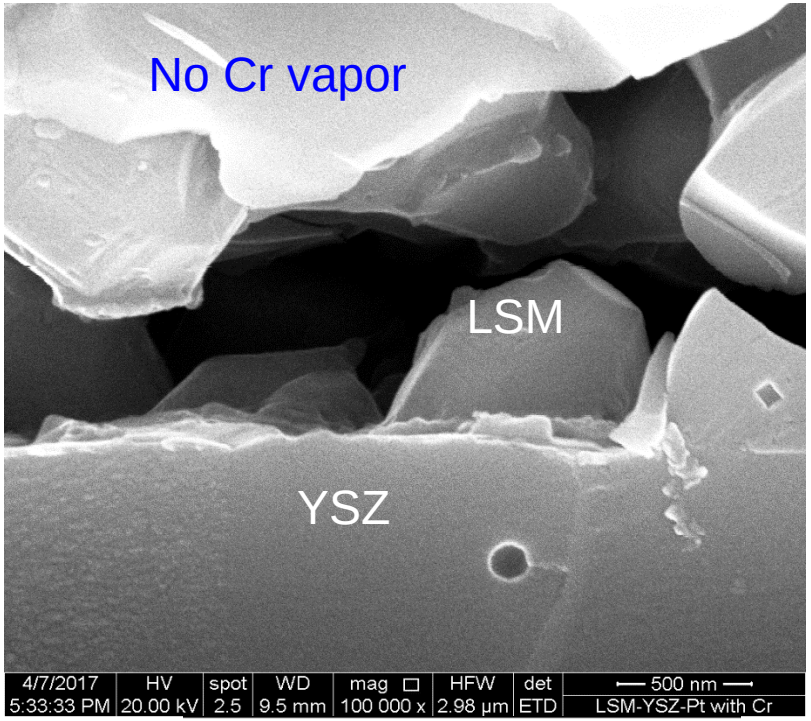




Rp increases with time when cell was exposure to Cr while Rp keeps stable if no Cr species present.

Cr deposition in the cell

Observations: Cr_2O_3 deposits at the LSM/YSZ interface at 650°C when cell was exposed to Cr vapor.



EDS Quantitative Results

Element	Wt%	At%
SrL	19.85	20.60
LaL	53.32	34.90
CrK	0.94	1.65
MnK	25.89	42.85

EDS Quantitative Results

Element	Wt%	At%
SrL	19.19	18.52
LaL	46.55	28.33
CrK	4.96	8.06
MnK	29.30	45.09

Summary

- **Cr capture has been successfully demonstrated from BOP/ In-cell sources**
- **Cr getter materials have been identified and synthesis process have been developed and scaled up.**
- **Synthesis process scaled up to 1kg/batch using lab equipment**
- **Design studies have been performed to obtain 40,000 hrs. getter life**
- **Fabricated Cr getter samples and materials have been provided to PNNL, LG, Cummins, Ceres and others for testing**
- **Laboratory findings have been provided to SOFC industries**
- **Cathode degradation mechanisms have been identified and published.**
- **Getter operation has been validated at low (650C) temperature**
- **Alternate HSA getter has been identified and synthesized.**

Getters can be provided to SOFC industries and research institutions for independent testing and validation

Acknowledgements

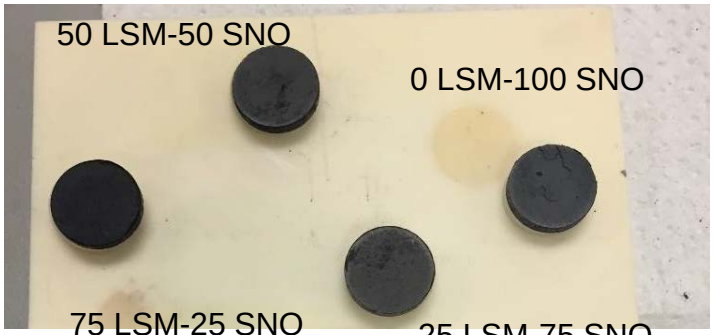
- Drs. Rin Burke, Jason Lewis and Shailesh Vora for guidance and encouragement
- Dr. Jeff Stevenson, Matt Chou and Brian Koeppel (PNNL) for electrical testing and discussion
- Mr. Rich Goettler (LGFCS), Dr. Amit Pandey (LGFCS), Dr. Hossain Ghezel-Ayagh (FCE), Dr. Shubi Mukherjee (CP), Dr. Charles Veseley (CPS), Dr. Lou Carreiro (NUWC) and Dr. Deodeshmukh (Haynes) for engineering and systems related discussion
- Drs. Yu Zhong (FIU), Yoed Tsur(Technion) for thermochemical model
- UConn for providing laboratory facility and support

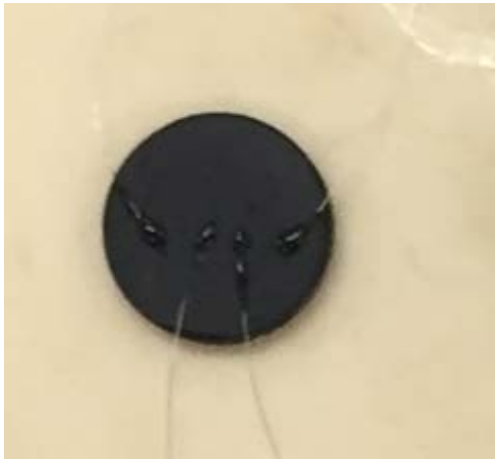
Thank you

Getter Materials Optimization

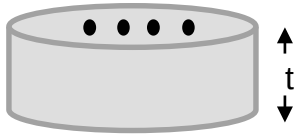
Electrical conductivity measurement: In-cell getter

Composite with LSM – LSCF with SNO





4 point probe method

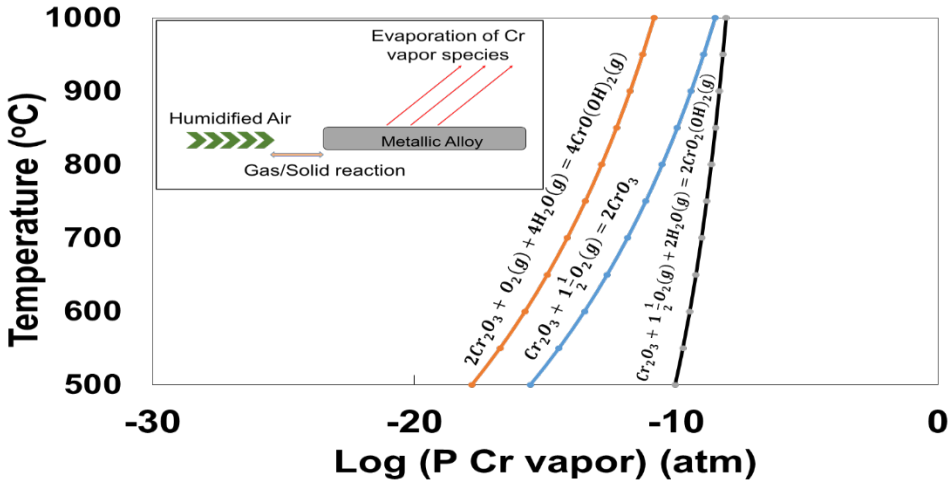


- LSM/ LSCF pellets were sintered at 1200^{o}C
- LSM/LSCF-SNO composite pellets were sintered at 950^{o}C for 1h
- Pt electrodes were attached using Pt paste and sintered at 850^{o}C
- Pellet: Dia: ~12.70mm, Thickness: ~2.07mm, ~Wt: 0.9655g
- 4-probe measurement method applied

Background: Getter

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

Cr getter critical property	Performance of new Cr getter against baseline state of the art Cr getter	Test conditions (Temp, time, atm)
Phase Stability	Superior: New Cr getter shows no phase changes and interaction with humidity and CO2 present in air.	RT-980C, Ambient air
Reaction products	As processed getters consist of several oxide phases containing Sr and Ni (Sr9Ni7O21, Sr4Ni3O9 and Sr2Ni4O5).	Powder synthesis process and transpiration, electrochemical testing at 850C for up to 500 hrs in Air -3%H2O
Microstructures	Stable powder, coating and substrate microstructures obtained New Cr getter retains its microstructure after high temperature exposures (850C) in humidified air. Literature review does not provide background information on the SOTA.	During processing up to 980C in air During bench top testing at 850C for up to 500 hrs in humid air
Thermochemistry	Similar or Superior: Based on thermochemical models developed	
Physical Properties	Similar or Superior: Based on resistance to ambient air (NAAQS)	
Product morphology	Porous powder coating on ceramic substrates	During processing up to 980C in air During bench top testing at 850C for up to 500 hrs in humid air
Cr Conc. profile	Superior: Capture Cr in the first 1500 - 3000 micron. Reproducible results	During bench top testing at 850C for up to 500 hrs in humid air
Substrate	Configuration include honeycomb, foam and fibrous structure, Substrate materials include Cordierite, Mullite, zirconia and alumina.	
Ease of fabrication	Conventional powder preparation and coating techniques	pre-formed /In-situ getter formation


1000
900
800
700
600
500
Temperature (°C)
-30
-20
-10
0
Log (P Cr vapor) (atm)
Evaporation of Cr vapor species
Humidified Air
Metallic Alloy
Gas/Solid reaction
$2Cr_2O_3 + O_2(g) + 4H_2O(g) = 4CrO(OH)_2(g)$
$Cr_2O_3 + 1\frac{1}{2}O_2(g) = 2CrO_3$
$Cr_2O_3 + 1\frac{1}{2}O_2(g) + 2H_2O(g) = 2CrO_2(OH)_2(g)$

Cr getter

Appearance

1. Fabrication Process (coating x2)
: Coating with SrNi(OH)x → sintering at 850 ^{o}C for 1 h → Coating with SrNi(OH)x → sintering at 650 ^{o}C for 1 h

→ Relatively, uniformly coated without any clogging

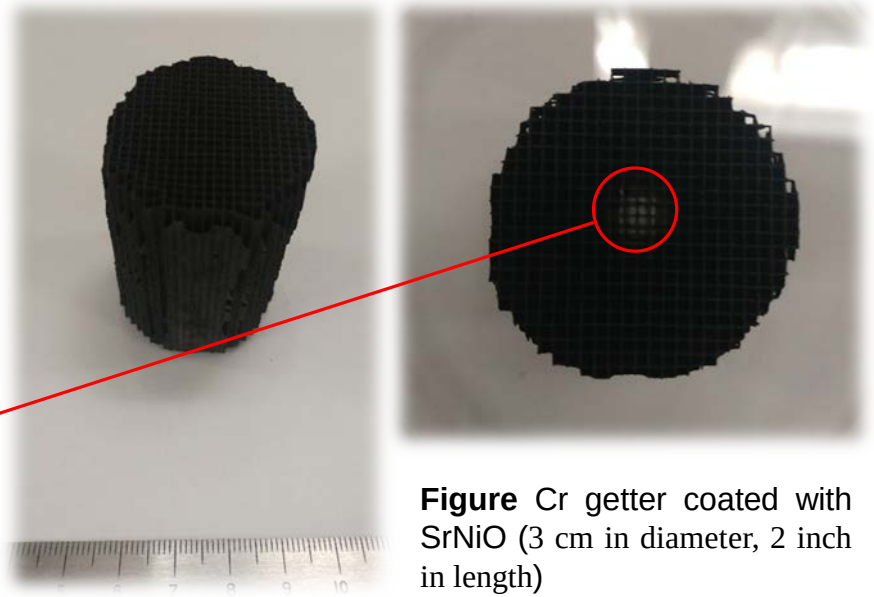
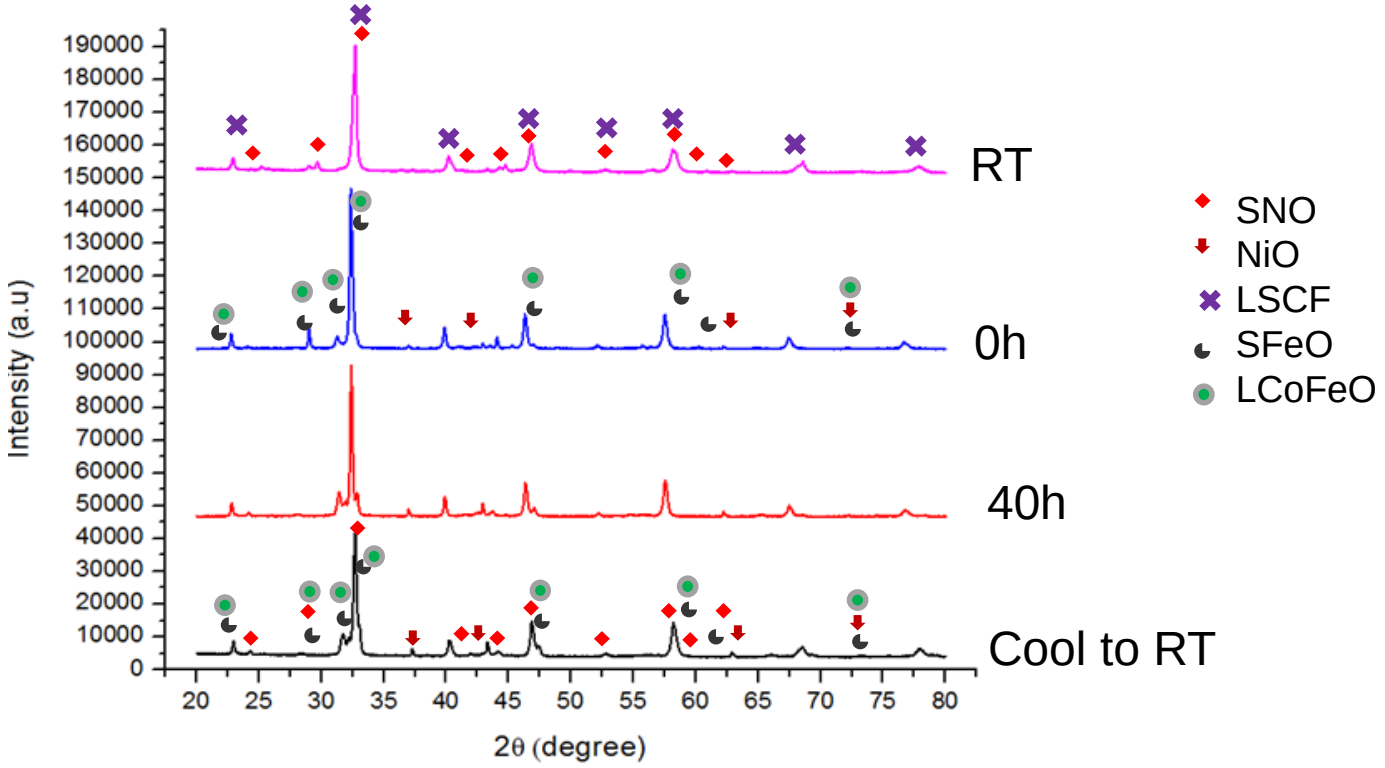


Figure Cr getter coated with SrNiO (3 cm in diameter, 2 inch in length)

2. Expectation from the appearance
   (1) Black color in all positions → Uniformly coated
   (2) No clogging → Uniform and ideal
   (3) No powder dust detached from the getter → Strong adhesion

Getter Materials Stability

High temperature *in-situ* XRD performed on 75LSCF-25SNO powder for up to 40h at 850 C



- SNO does not dissociate into SrO or NiO - indicating phase stability.
- LSCF remains stable throughout the 40h sintering process
- After 40h sintering strontium iron oxide (SFeO)and lanthanum cobalt iron oxide (LCoFeO) appeared in smaller quantity.

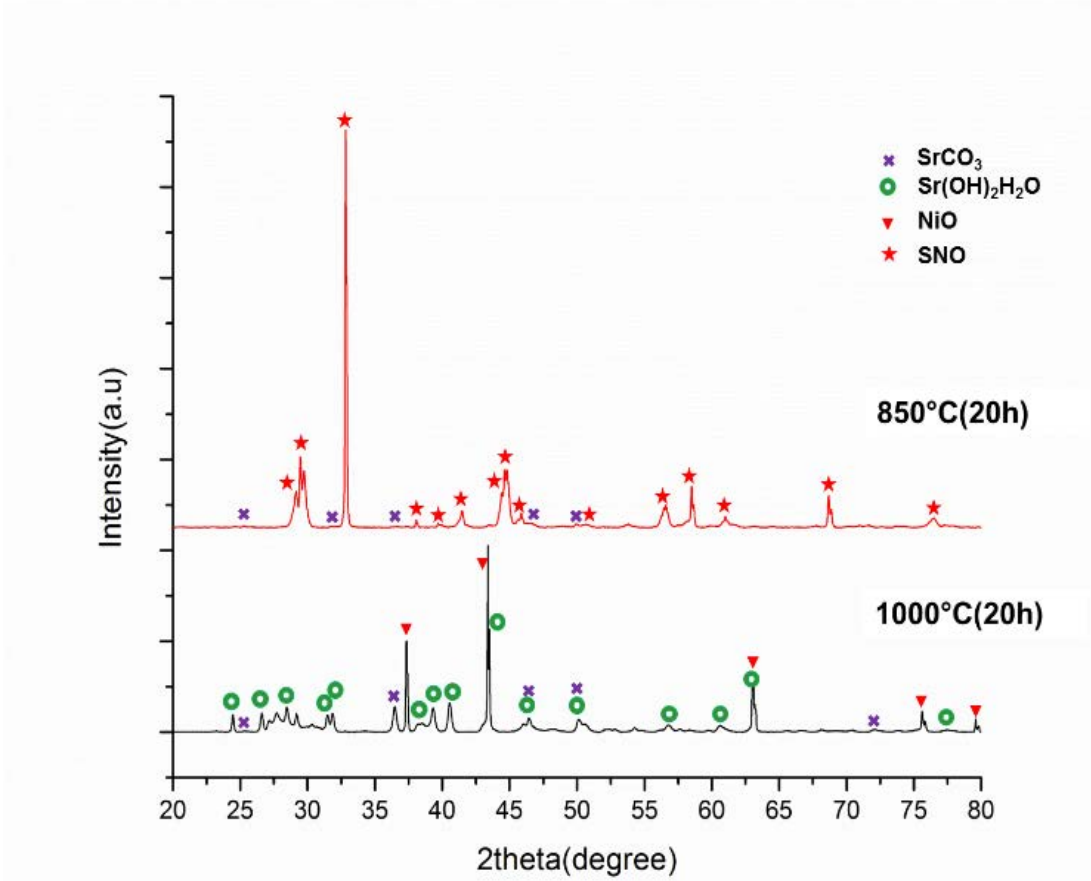
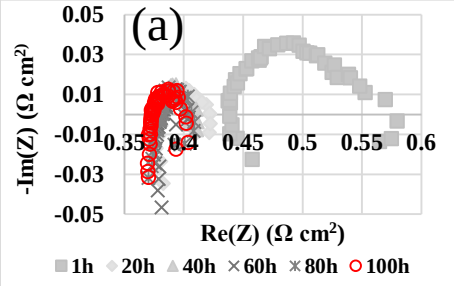


Figure 6. XRD patterns of SNO sintered at 850° C showing stability and showing the formation of $Sr(OH)_2$ and $SrCO_3$ compounds in the pulverized samples sintered at 1000° C for 20h.

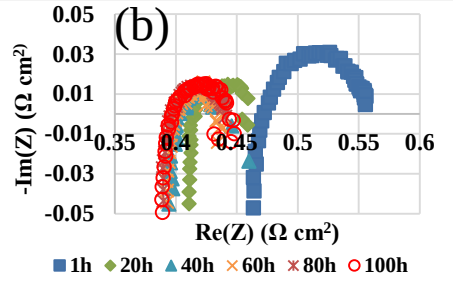
Electrochemical Evaluation

Nyquist plots

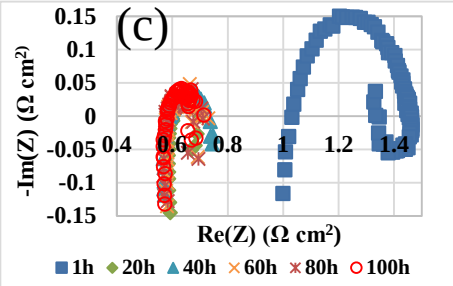
Config-1 100 SNO (Ni supported)



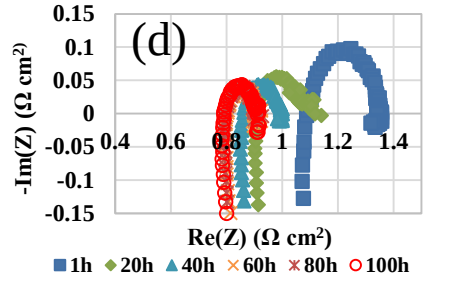
Config-2 75LSCF-25 SNO (Screen printed)



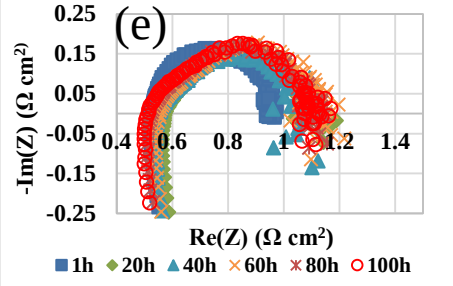
Config-2 50LSCF-50 SNO (Screen printed)

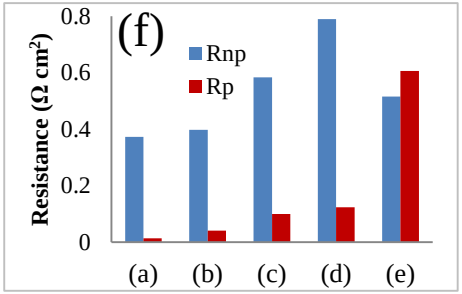


Config-2 50LSCF-50 SNO (brush coated)



Config-2 100 SNO (brush coated)



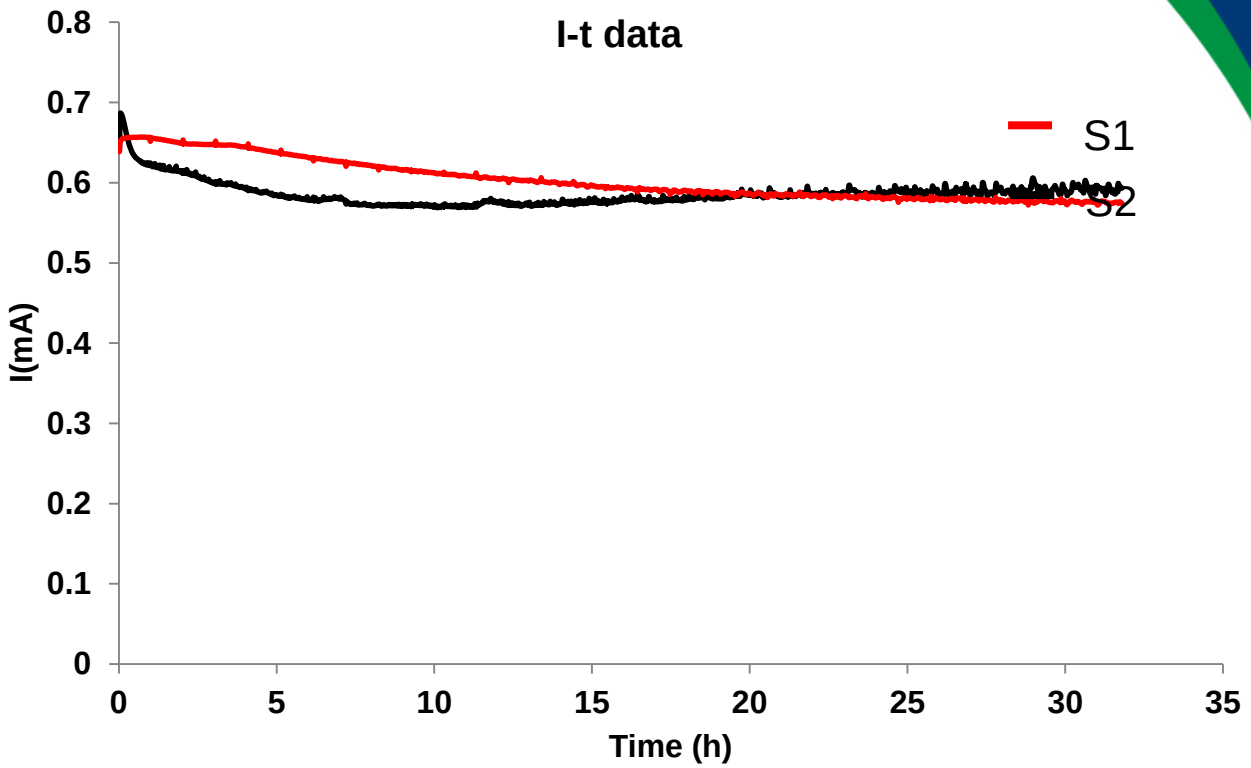


- SNO getter (Config-1) half-cell shows least ohmic resistance and polarization and remained stable throughout
- 75LSCF-25SNO and 50LSCF-50SNO getter with (Config-2) half-cell demonstrated decrease in the ohmic resistance as well as polarization resistance during first 20h and later remained stable
- 100 SNO getter (Config-2) based half-cell has consistent ohmic resistance as well as polarization resistances, 0.6 and 1.5 ohms respectively

Future Work

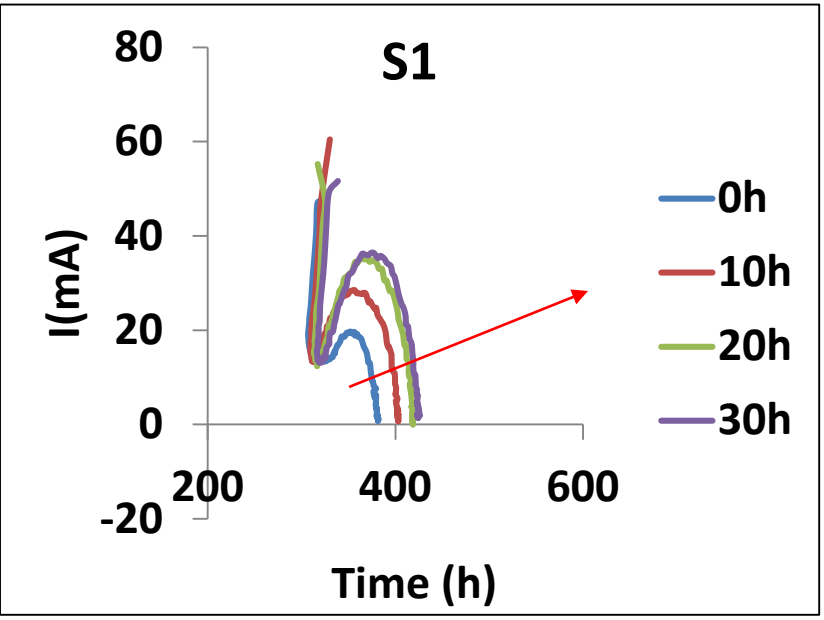
- Complete validation of 1 kg/ batch getter powder synthesis process
- Use the above getter powder for coating getter support (foam, honeycomb)
- Complete getter desgn
- Test coated getters under SOFC system conditions
- Test getters in the cell
- Provide powder and fabricated getters to SOFC industry under DOE guidelines
- Assist DOE in technology transfer

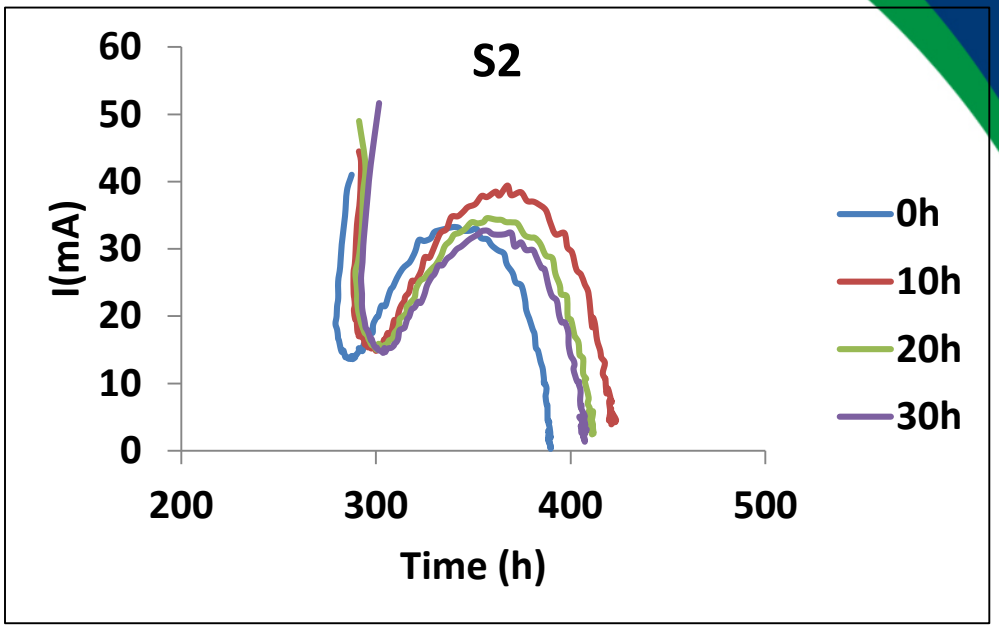
I-t performance

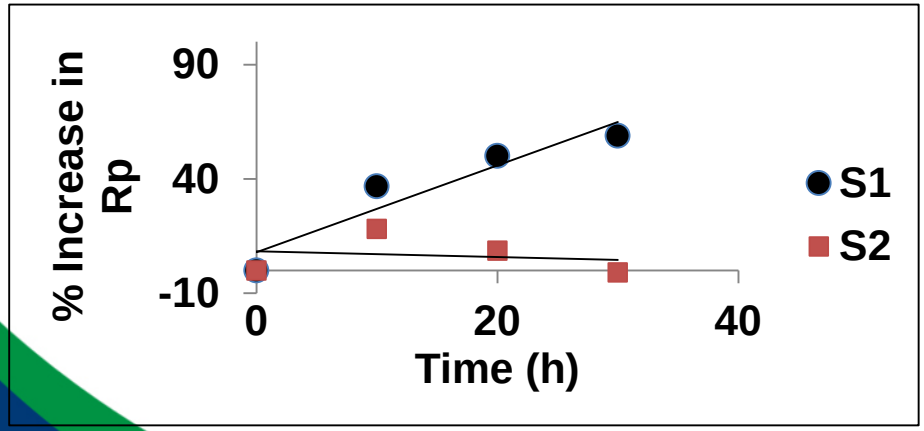


•Performance of S1 decreases continuously and S2 performance stabilizes after 5h

Changes in Rp and Rnp



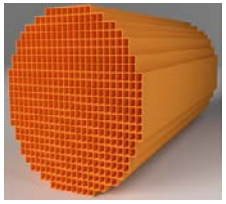


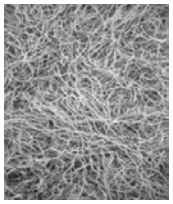


- Polarization resistance (Rp) of S1 continously increases and within 30h, it increased by more than 60%
- Increase in Rp of S2 is relatively stable over time.
- No significant changes in Rnp for both sensor.
- Continue to monitor the performance over longer time

Design and Optimization of Chromium Getter through Computational Modeling

Design and Optimization of Chromium Getter through Computational Modeling



Aman Uddin
Collaboration with PNNL

Objectives

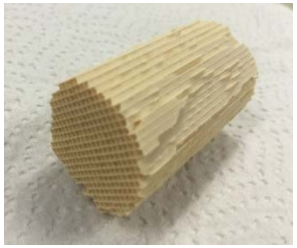
The overall objective is to design and optimize chromium getter to capture the chromium species originating from the metallic stack and BOP components. The objectives include:

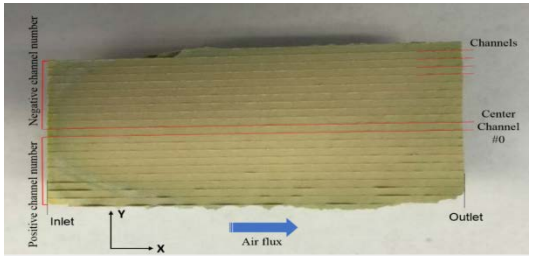
- *Parametric study of getter to predict the effects of the key parameters such as geometric surface area, porosity, thickness of coating materials, etc. when:*
  - *Surface reaction is rate limiting*
  - *Solid state diffusion is rate limiting*
  - *Diffusion through porous product la*yer is rate limiting
- Optimize design for higher utilization and low pressure drop requirement.
- Fabricate and test getter according to the proposed model and validate

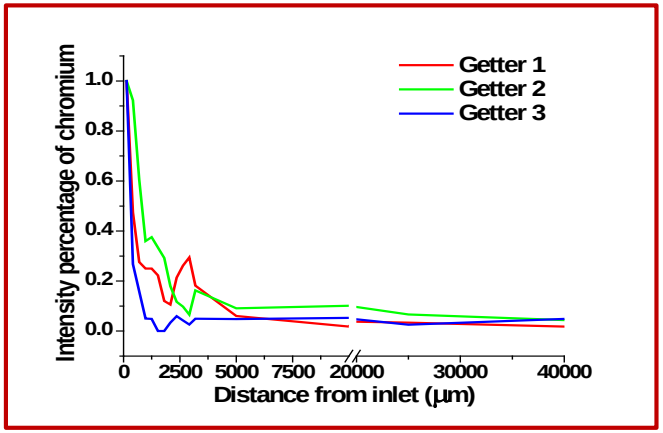
- **A transient, two dimensional model of chromium getter is developed to predict the utilization of getter with various rate limiting cases.**
- **In this model, cordierite substrate with 400 cpsi (cells per square inch) is considered as the getter support material for 1 kW SOFC system (4 SLPM flow rate), and the model is solved for high Cr partial pressure (1e-6 atm).**
- **In solid state diffusion case, Chromium front moves forward before reaching to maximum capacity because porosity of getter decreases due to product layer formation with time and diffusion is rate limiting.**
- **Chromium front moves faster in solid state diffusion case compared to reaction rate limited case.**
- **Current efforts are underway to optimize design for higher utilization and low pressure drop requirement.**

Background

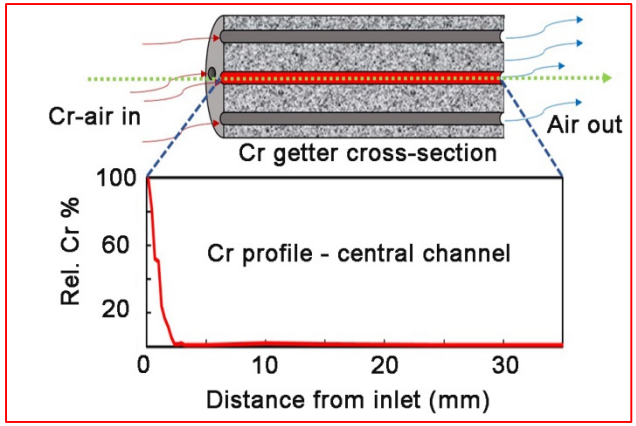
- Cr poisoning is one of the major causes of cathode degradation in high temperature electrochemical systems such as SOFC.
- A novel approach called Cr getter is developed to mitigate the Cr poisoning.
- Cr getter contains SrNiOx getter material supported by various structure.
- Support materials: cordierite, porous alumina.
- Successfully captured Cr within 2-3mm of getter.







air flow rate of 300 sccm for 500hr at 850˚C.



air flow rate of 50 sccm for 100hr at 850˚C

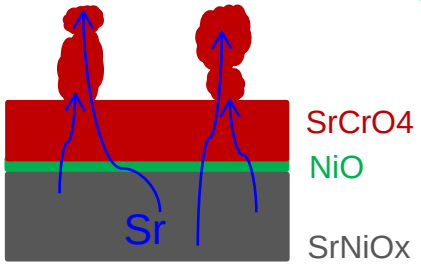
Hu *et al.* J. Power Source, 2016, submitted

Rate Limiting Step: Solid state diffusion

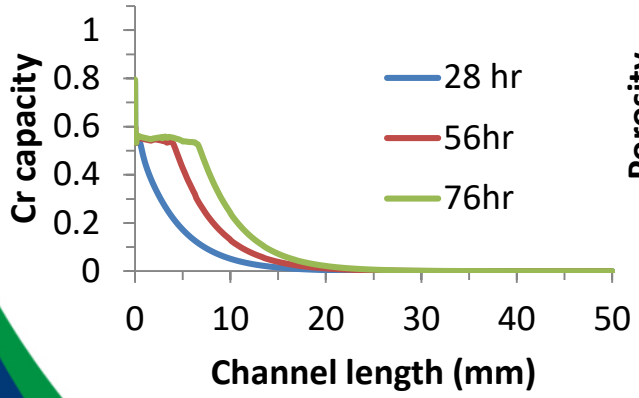
Assumption:

- 10μm thick coating with 50% porosity
- Product layer reduces porosity of getter
- Solid State Diffusion $S_{Cr} = D_e * \frac{C_{sr}}{\delta(t)} * \frac{A}{V}$

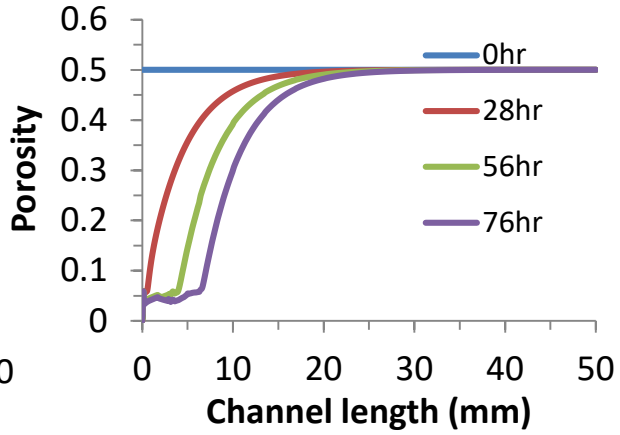
Where, C_{sr}=concentration of Strontium, D_e= Diffusion coefficient; δ(t)=thickness product layer, A/V= area to volume ratio



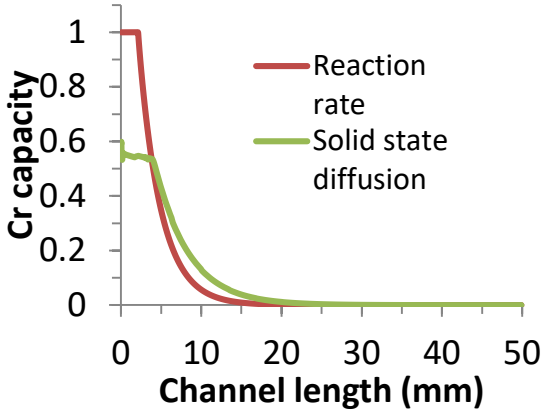
Chromium profile at 4 SLPM flow rate with 0.1 Pa Cr pressure



Porosity of getter

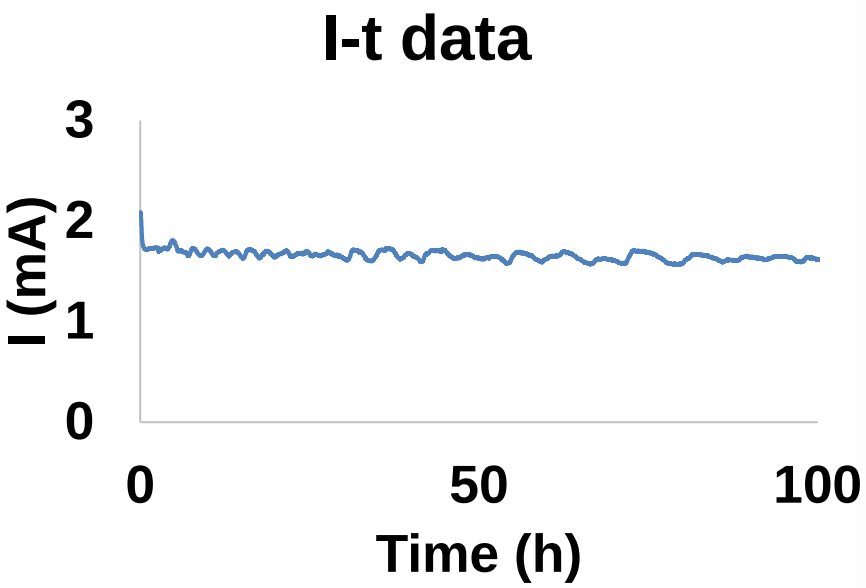


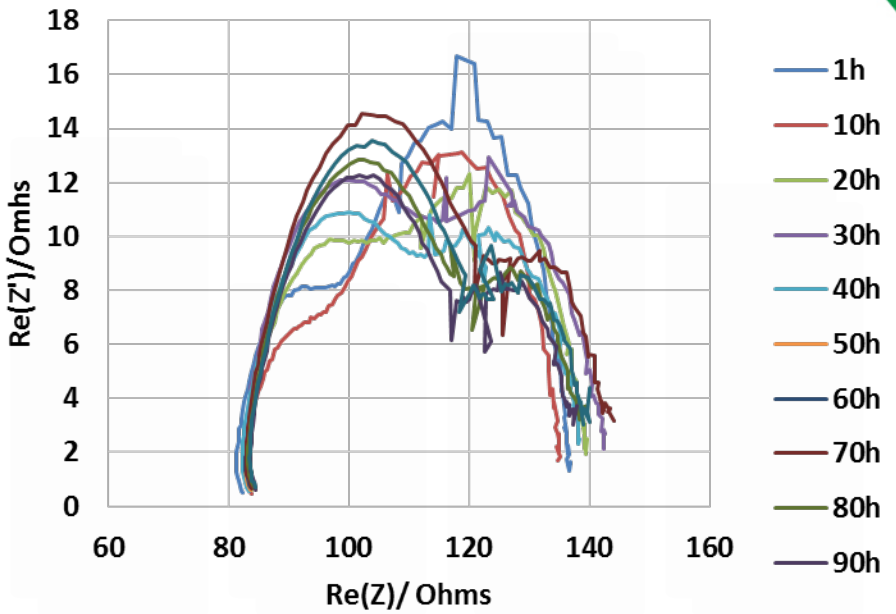
Comparison (after 56hr)



- Chromium front moves forward before reaching to maximum capacity because porosity of getter decreases and diffusion is rate limiting.
- Chromium front moves faster in solid state diffusion case compared to reaction rate limited case.

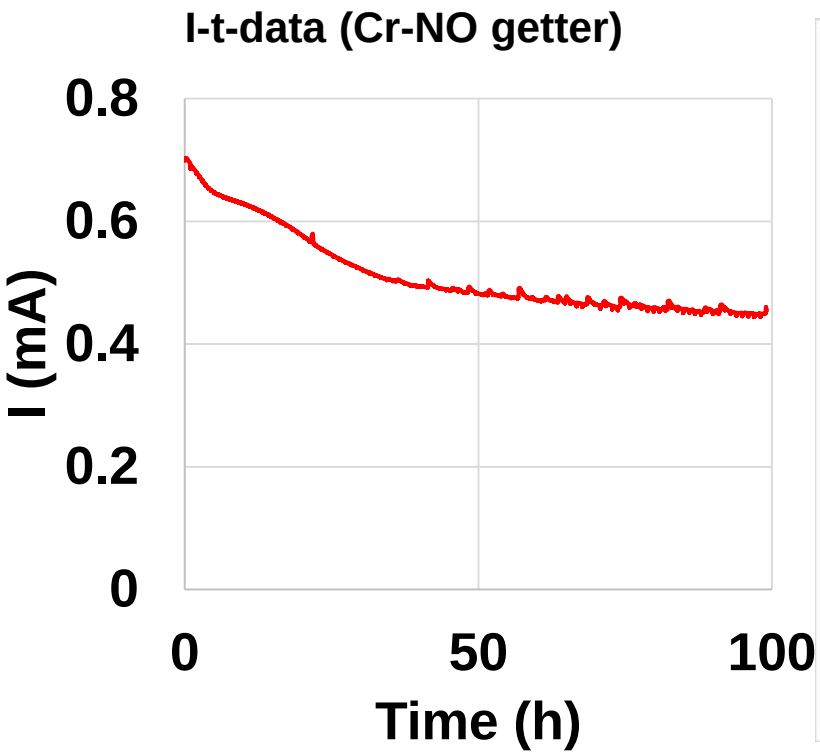
Electrochemical Performance (Baseline- No Cr-No Getter)

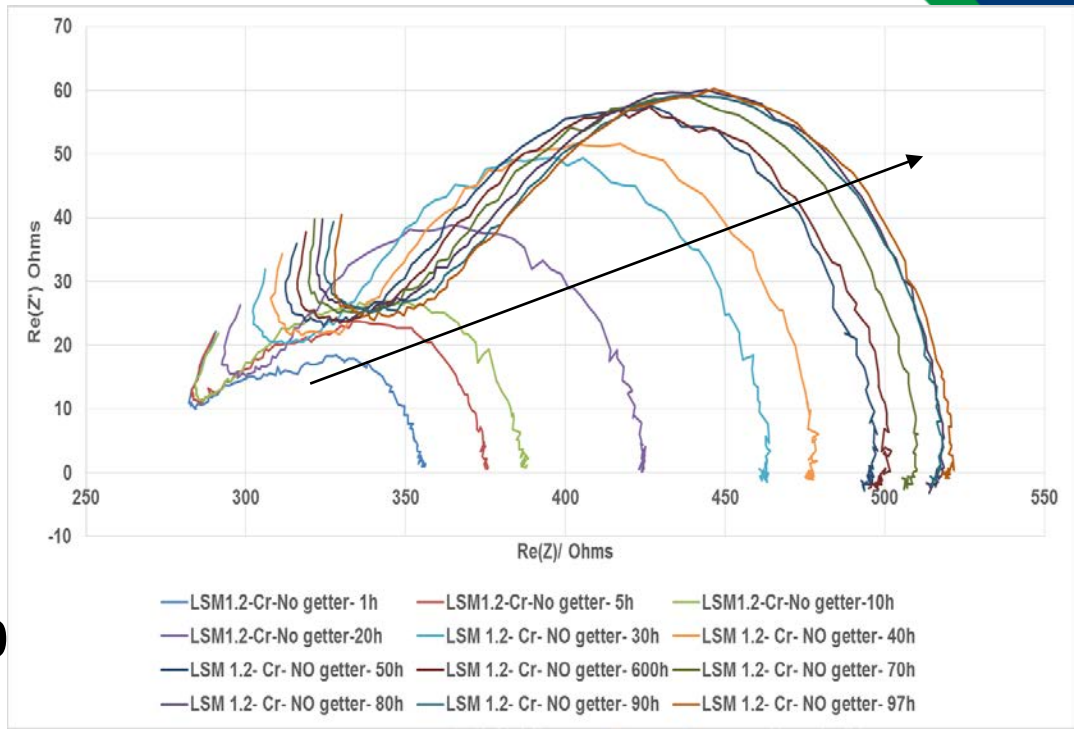




- Results from 100 h I-t data shows stable performance
- Polarization resistance remained stable at (Rp) ~60 Ω
- Ohmic resistance also remains constant at (Rnp) ~80 Ω

Electrochemical Performance (Cr- No Getter)





- LSM degrades rapidly after the exposure to Cr vapor
- Nyquist plot indicate continuous increase in the polarization resistance due to Cr degradation

Acknowledgements

- Helpful technical feasibility discussions with Dr. Rin Burke
- Systems and applications related discussion
  - Drs. Goettler, Ghezel-Ayagh, Aligner, Mukherjee
  - Provided experimental data to LGFC, FCE, GE, Ceres Power
  - Discussed scale-up issues
  - Discussed system constraints and experimental parameters
- Cell and stack related discussion with Dr. Stevenson
  - Provided getter materials and performance data
  - Discussed approaches for application in cells