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

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Technical Contributors

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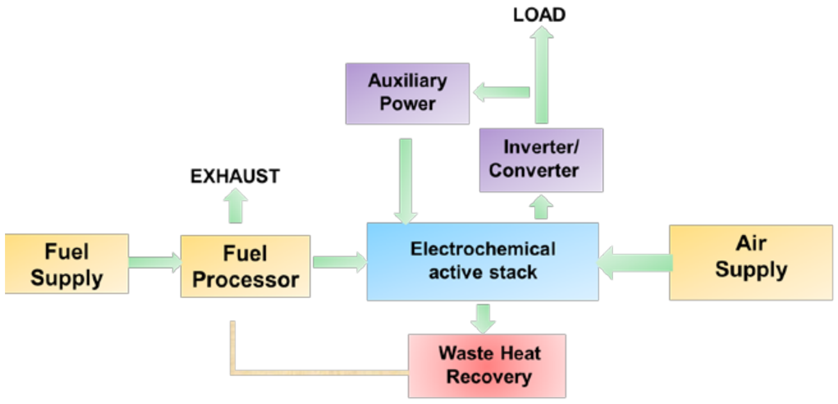
Problem statement

- **One of the largest contributor for electrochemical performance degradation in SOFC is assigned to cathode degradation – associated with increase in the cathode polarization (ohmic/non-ohmic) due to surface poisoning and interface compound formation.**
- **The long term degradation is mostly irreversible as the chemical and morphological changes in the electrode is largely permanent.**
- **Identification of cost effective solutions requires understanding of the degradation processes under the “ real world” or system operating conditions.**

Technical Innovation and impact

- **The research provides an understanding of the degradation mechanism and cost-effective approaches for implementation in SOFC system –**
  - **long-term solution is design agnostic**
  - **applicable under wide operating conditions.**
- **Use of low cost, non-noble, non-strategic materials and conventional ceramic processes to fabricate Cr getters.**



Existing laboratory capabilities can provide getters for up to 1-2 MWe SOFC’s for near term demonstration

Project Objectives

The overall objective of the proposed research program is to develop cost effective materials, modifications of the material chemistry and the exposure environments that inhibit long term solid-gas and solid-solid interactions to minimize/mitigate the degradation of SOFC cathode.

The objectives and approaches:

a. **Develop and demonstrate the viability of the application of cost effective ‘chromium getter’ to capture the chromium species originating from the metallic stack and BOP components,**
b. **Develop modified cathode compositions to control and prevent oxide segregation and compound formation at the surface and interfaces during exposure to “Real world” air exposure,**
c. **Develop cathode contact layer and modification to avoid chromium poisoning originating from metallic current collector/interconnect.**
d. **Develop alloy surface pretreatment conditions to minimize chromium evaporation.**

Outcomes

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

Benefits of Technology to the Program

Potential benefits of this project :

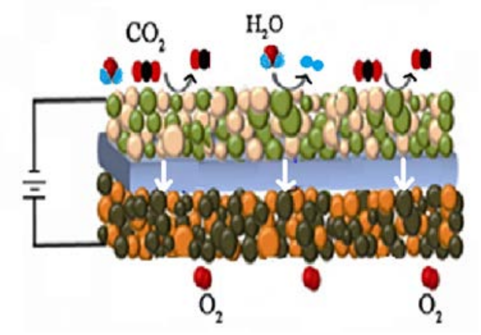
- **Mechanistic understanding of the degradation processes in LSM and LSCF (airborne contaminants)**
- **Development of mitigation process utilizing low cost getters**
- **Ease of getter synthesis and fabrication**
- **High Cr capture capacity through tailored high surface area powder and coatings**
- **Surface pretreatment for BOP application minimizes chromium evaporation**
- **Supports USDOE Office of Fossil Energy objectives for commercialization of SOFC systems.**

- **Innovation will support the development of getter platform to capture intrinsic and extrinsic impurities present in air.**
- **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.**

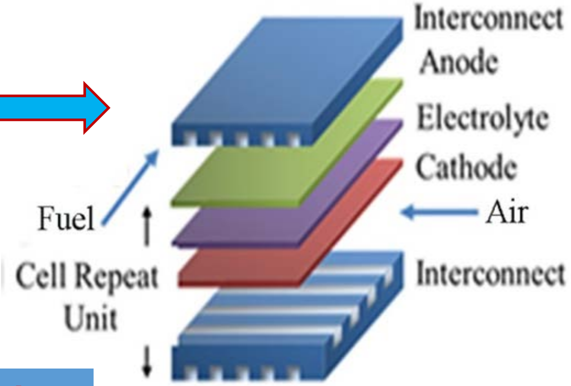
Use of conventional low cost materials
Application in 600-950C range
< 15-20 g of material needed for ~100kWe SOFC

SOFC Cathode Exposure to “Real World” Air

Single SOFC

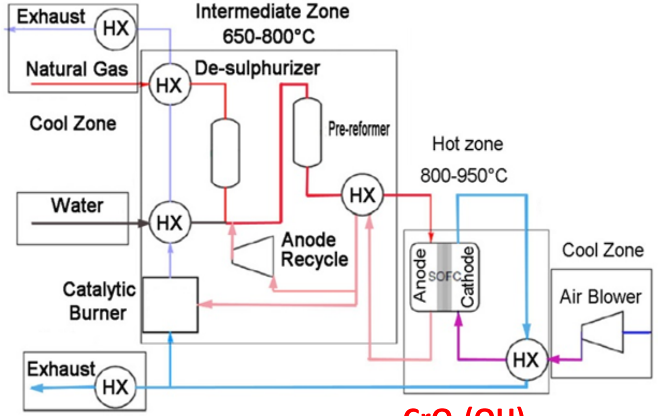


SOFC Stack



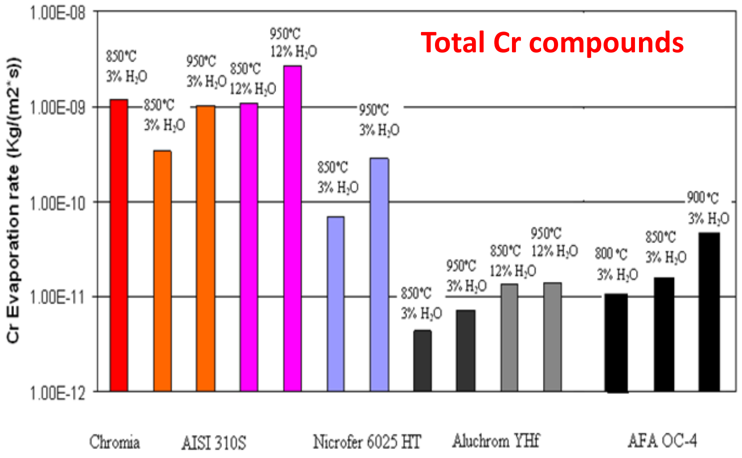
Cr vapor

SOFC Power System



$CrO_2(OH)_2$

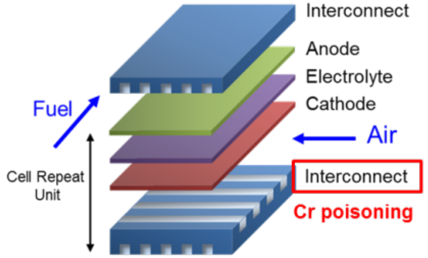
Composition in air	Concentration
Oxygen	20.9 v%
Nitrogen	78 v%
Water	1-3 v%
Carbon dioxide	350 ppm
Sulfur dioxide	~1 ppm
Noble gases	<1 v%
Particles	<50 µg/m^3

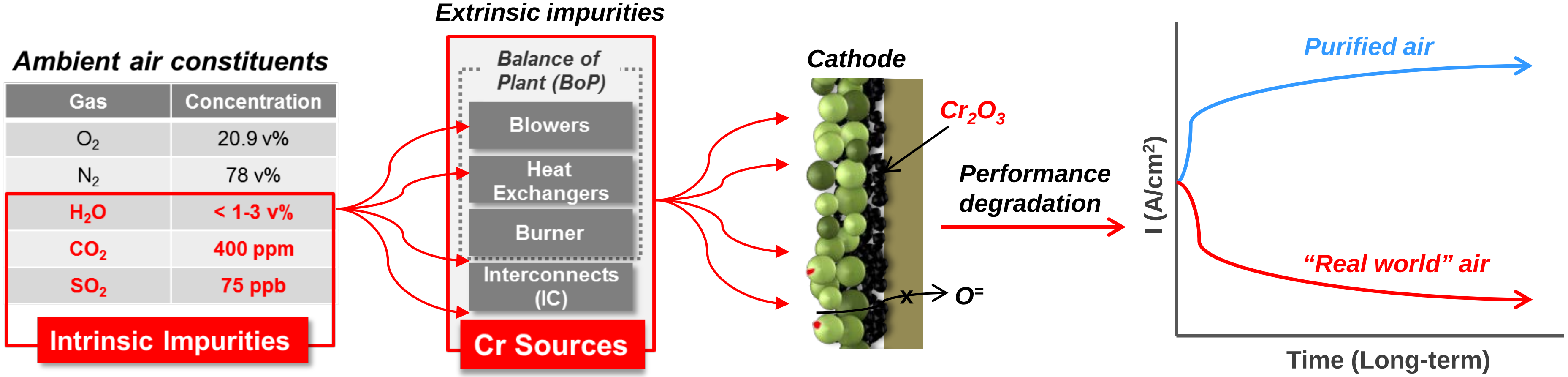


DOE Target of System Performance Degradation: 0.2%/1,000 hours

Sources of Cr-Vapor

- ➢ Chromia forming alloys
- ➢ Balance of plant materials
- ➢ Presence of H_2O aggravates Cr evaporation





Ambient air constituents

Gas	Concentration
O_2	20.9 v%
N_2	78 v%
H_2O	< 1-3 v%
CO_2	400 ppm
SO_2	75 ppb

Impurity capture:

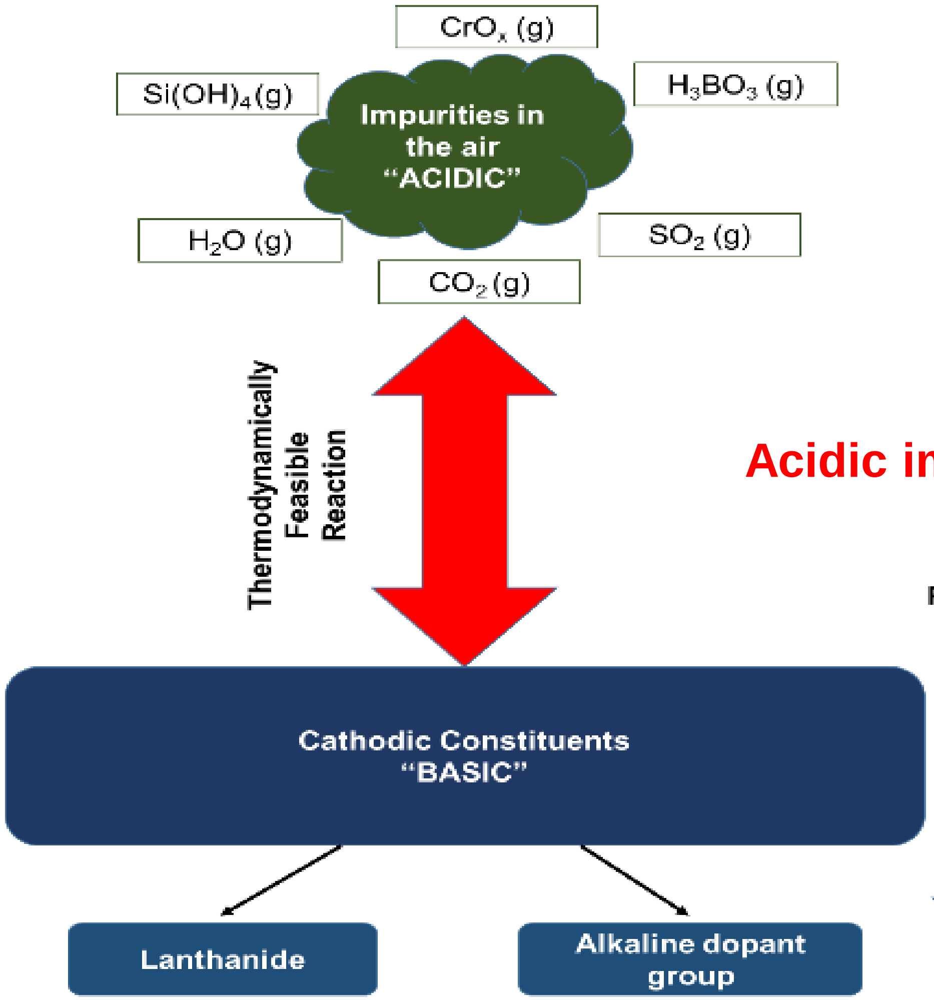
1. capture intrinsic impurities at the system inlet
2. Capture extrinsic impurities in BOP or in stack

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

Outline

- **Accomplishments**
- **Background**
- **Experimental**
    - **Getter synthesis, optimization and stability evaluation**
    - **Validation of getter performance**
    - **Fabrication and long term testing of Cr Getter**
    - **Electrochemical testing – BOP & In-Cell simulation**
    - **Characterization-SEM-EDX, XRD, and FIB-TEM**
    - **Alloy surface modification optimization**
- **Results and Discussion**
- **Future Work**
- **Acknowledgements**

Chemical Nature of Impurities



CrO_x (g)

$Si(OH)_4$ (g)

H_3BO_3 (g)

Impurities in the air "ACIDIC"

H_2O (g)

SO_2 (g)

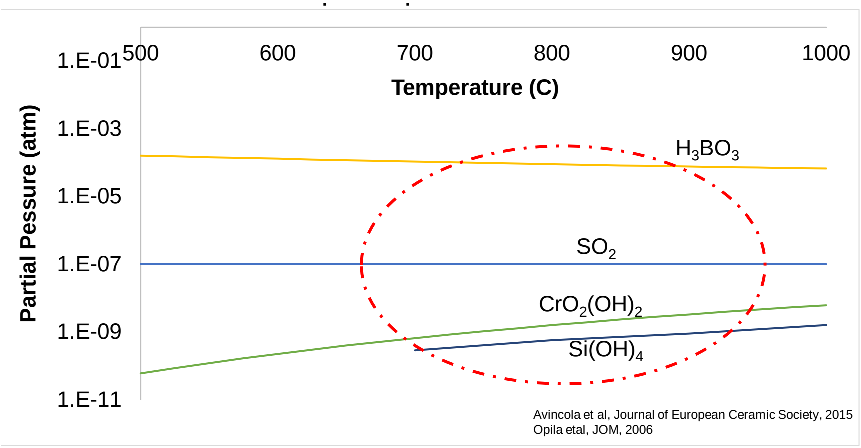
CO_2 (g)

Thermodynamically Feasible Reaction

Cathodic Constituents "BASIC"

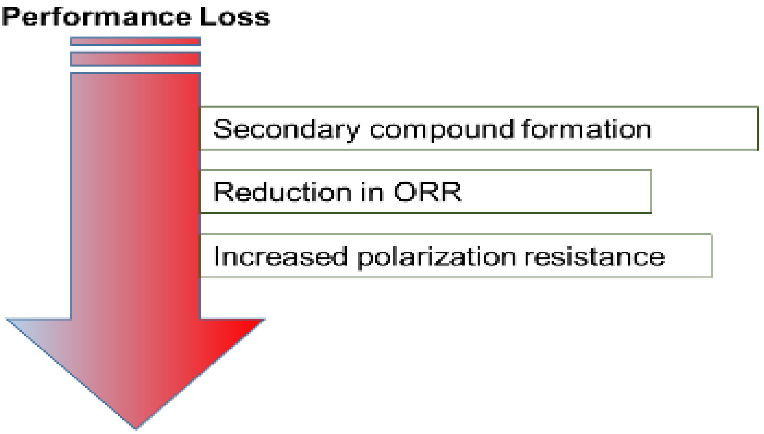
Lanthanide

Alkaline dopant group



Avincola et al, Journal of European Ceramic Society, 2015
Opila etal, JOM, 2006

Acidic impurities react with basic cathode (Host and dopant)



Performance Loss

Secondary compound formation

Reduction in ORR

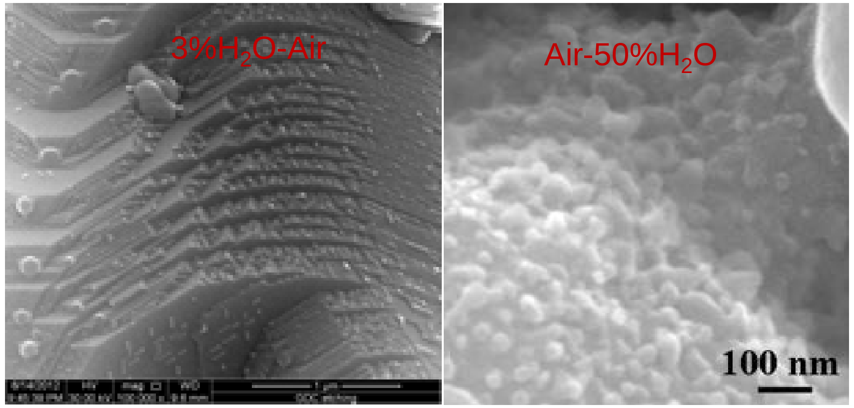
Increased polarization resistance

Prior Work

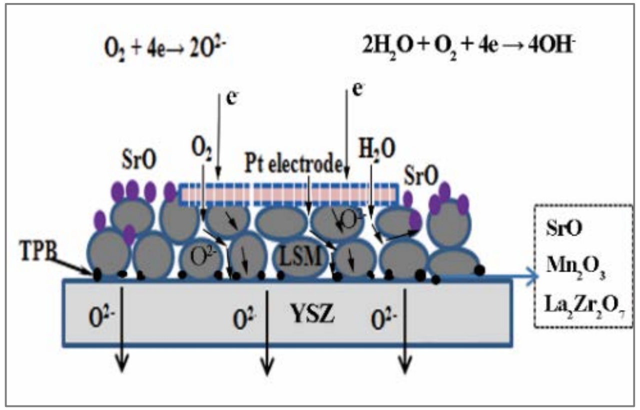
Cathode in “Real World” Air Exposure Atmospheres

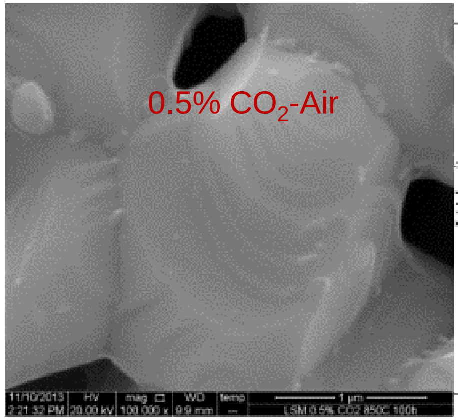
Presence of moisture in air:

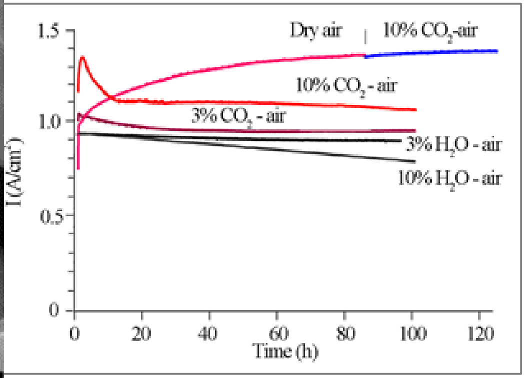
- **Presence of moisture in air degrades electrochemical performance and the degradation increases with moisture content, exposure temperature, and cathodic bias. Both ohmic and non-ohmic resistances increase with increase in moisture content**
- **Electrode surface shows SrO/Sr(OH)$_2$ segregation (nM particles) and formation of La$_2$Zr$_2$O$_7$ and MnO$_x$ at electrode–electrolyte interface**



H$_2$O-Air







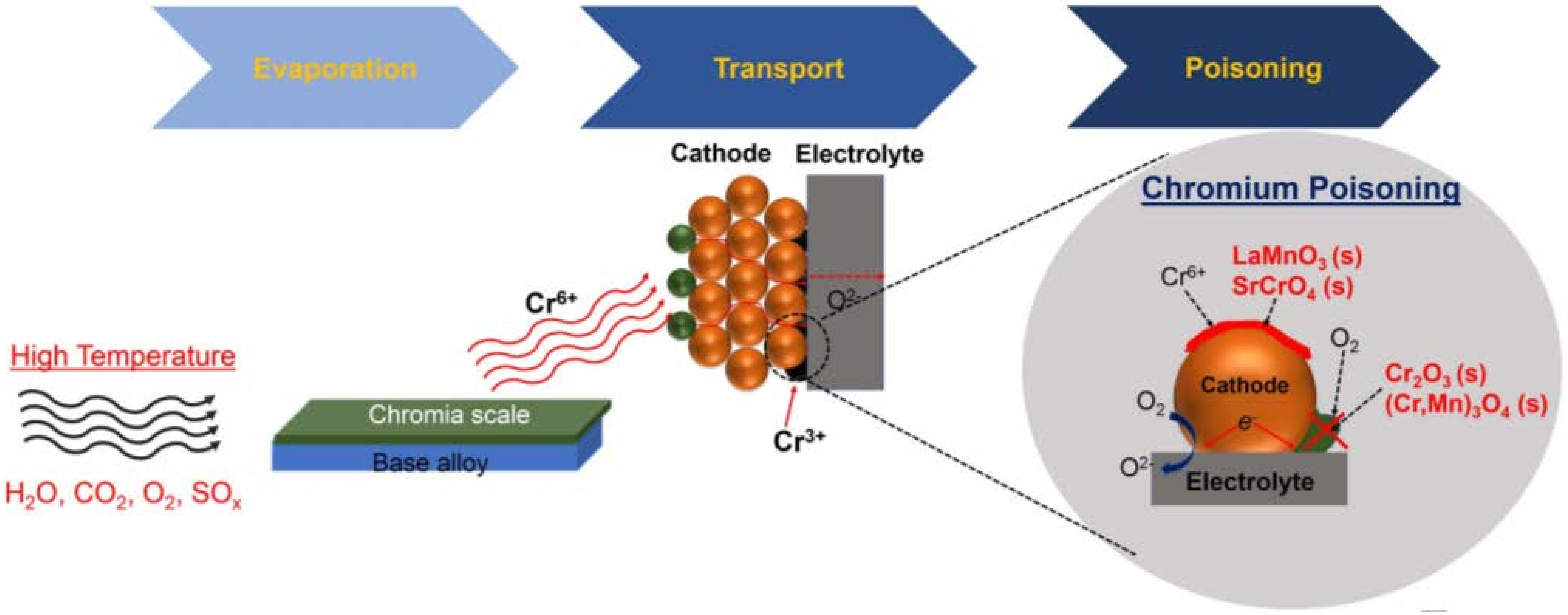
CO$_2$-Air

Presence of CO$_2$ in air:

- **Presence of CO2 (up to 3%) in air shows little to no influence on cathode performance degradation (100 hrs. tests).**
- **La$_2$O$_2$CO$_3$ and SrCO$_3$ form below 800°C but only SrCO$_3$ at 850°C and above.**
- **Pre-activated electrode shows insignificant degradation even at higher CO$_2$ (~10%CO$_2$) content.**

•Boxun Hu, Michael Keane, Manoj K. Mahapatra, Prabhakar, Journal of Power Sources 248, 196-204, 2014
• Boxun Hu, Manoj Mahapatra, Michael Keane, Heng Zhang and Prabhakar Singh, Journal of Power Sources, 268, 404-413, 2014

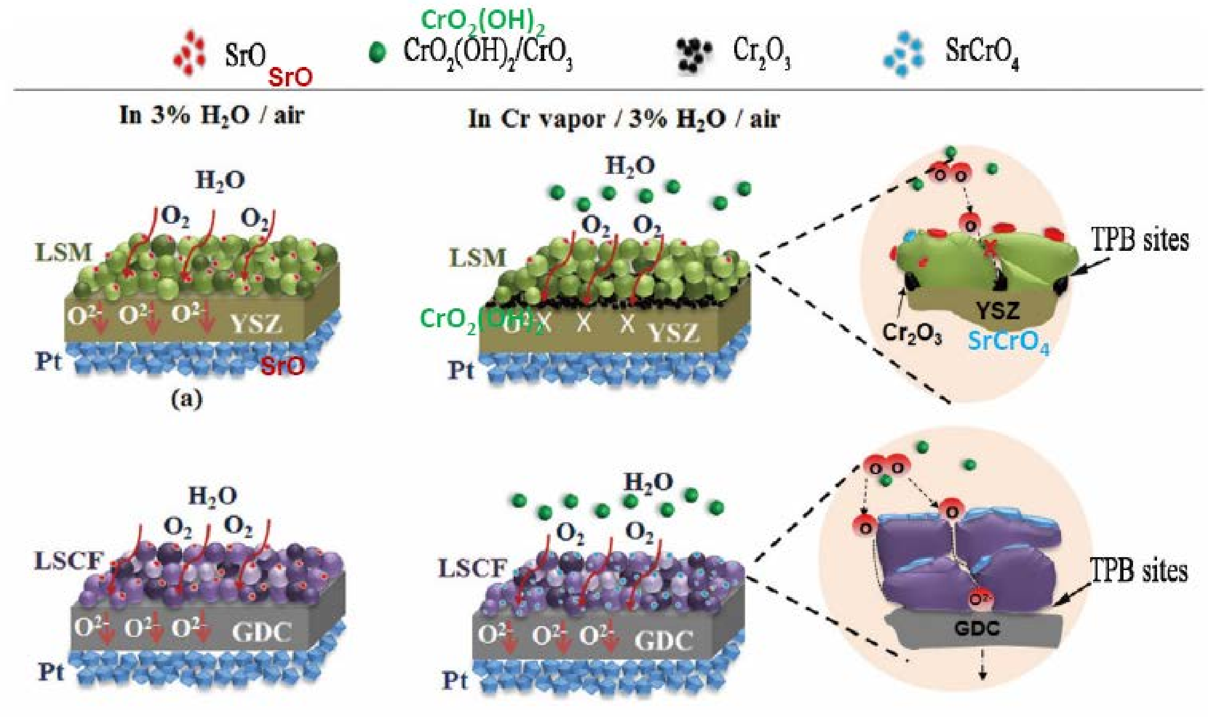
Chromium Poisoning



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

Chromium Poisoning of Cathodes

Different degradation mechanisms exists for LSM and LSCF type cathode materials

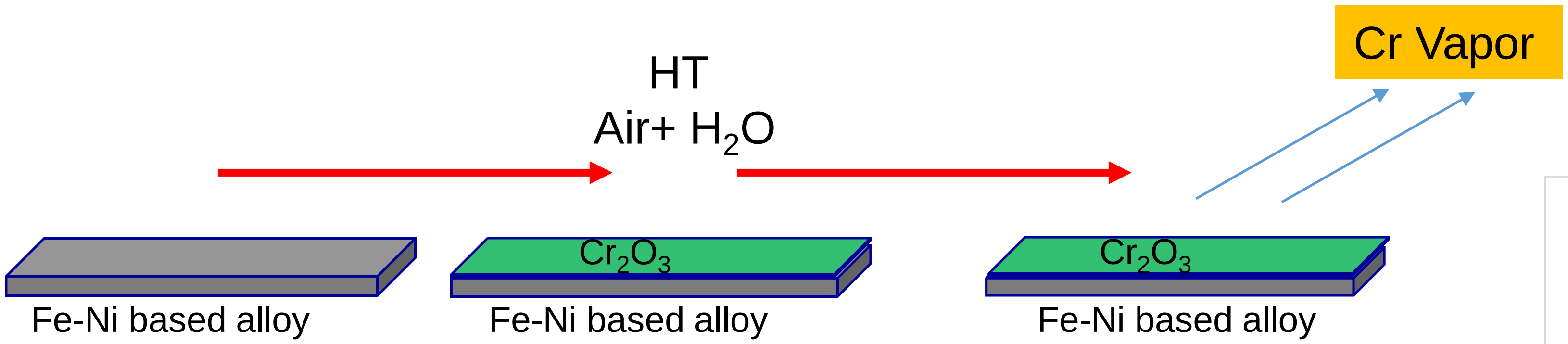


- Gas phase chromium species is largely reduced to Cr_2O_3 and deposited at the LSM/YSZ interface.
- For MEIC type cathodes, oxygen reduction reaction not only takes place at the TPB (as in the case of LSM) but also at the free exposed surfaces in contact with the gas phase.

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

Chromium Evaporation

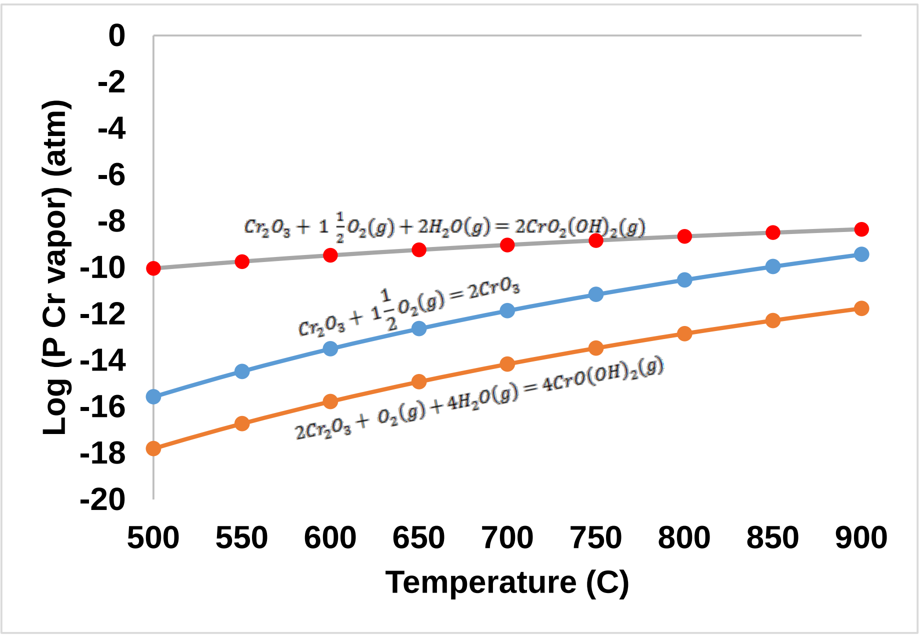
Interconnects and Balance of plant alloys lead to the formation of Cr vapor species during exposure to humidified air



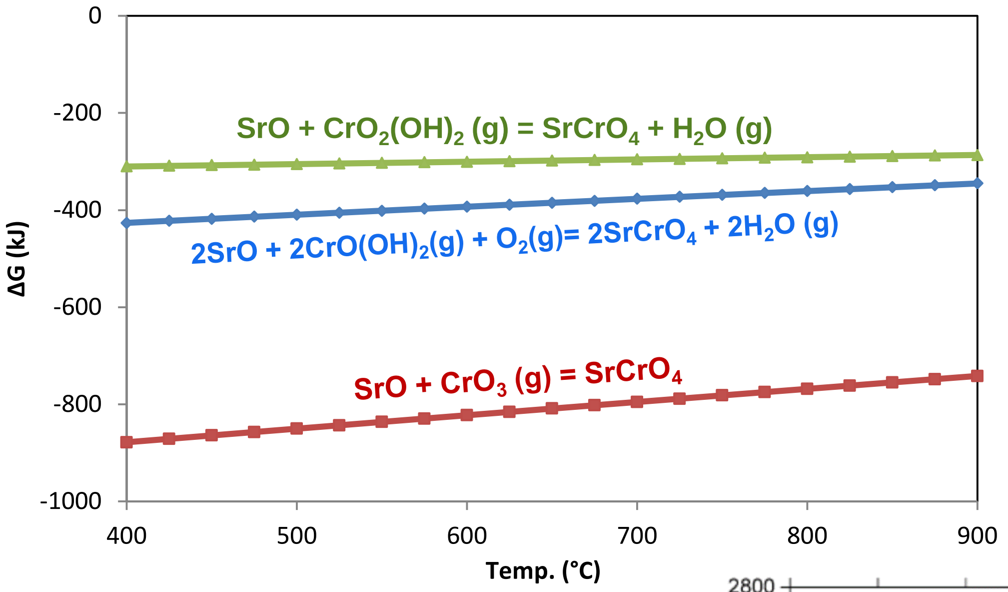
Vaporization reactions:½ Cr_2O_3(s) + H_2O (g) + ¾ O_2 (g) =$CrO_2(OH)_2$ (g)
½ Cr_2O_3(s)+ ½ H_2O(g)+ ½ O_2(g)=$CrO_2(OH)$ (g)
½ Cr_2O_3(s) + ¾ O_2(g)=CrO_3(g)

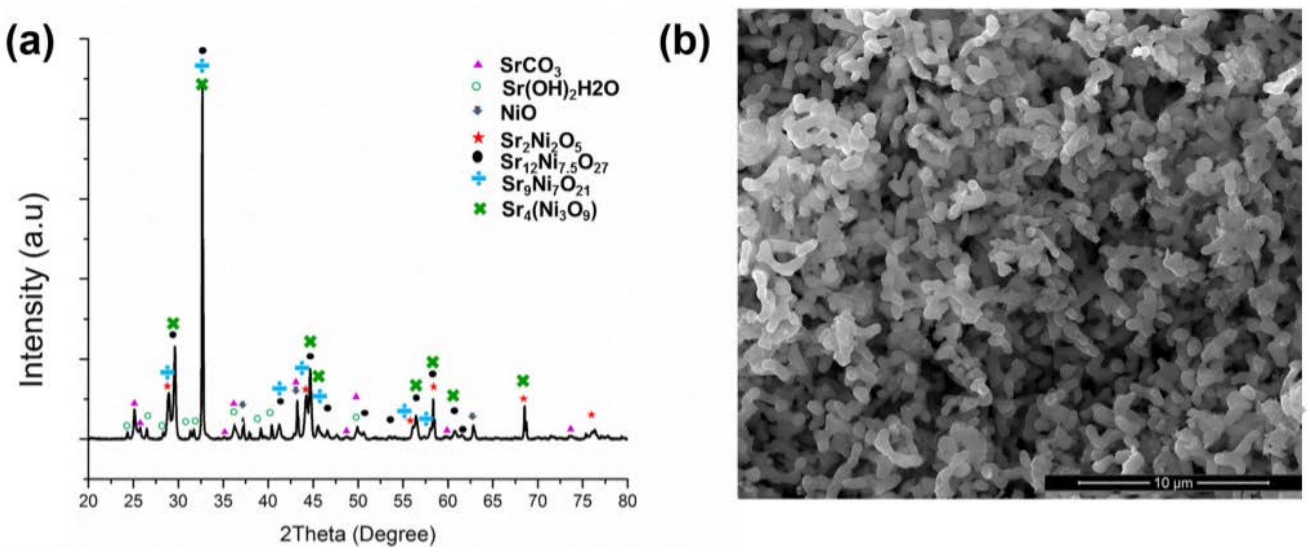
Cr vapor species have been found to react with cell air / fuel electrode leading to poisoning and performance degradation.

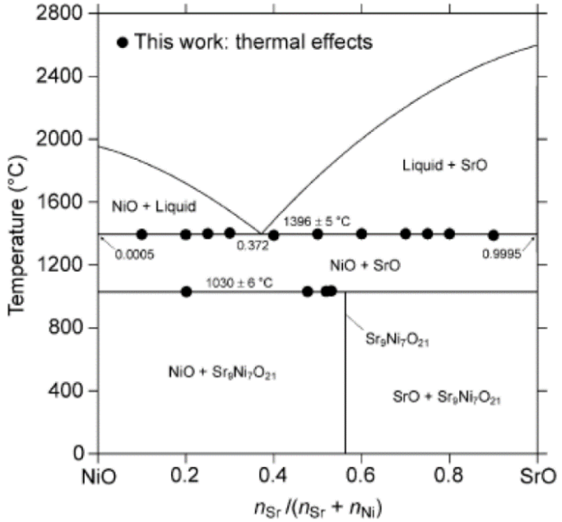
Thermodynamic calculations



Chromium Getter Development







Significant reduction in the Cr vapor pressure is observed using SrO based getters.

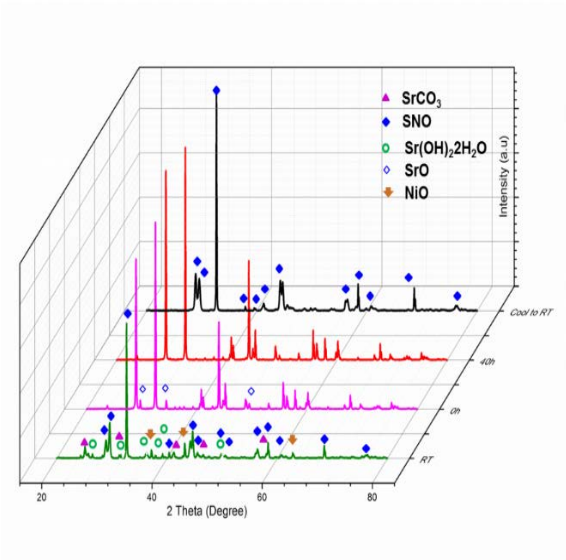
Getter Material	$Sr_xNi_yO_z$ compound
Materials synthesis	Dip-coating support in aqueous solution of $Sr(NO_3)_2$:$Ni(NO_3)_2$ (3:2 mole). Calcinaed at 600°C for 6 hours.
Substrate	Alumina fiber board
Substrate dimension	2” (length), 0.8-1” (dia.)

Use of Alkaline earth – Transition-metal elements for Getter

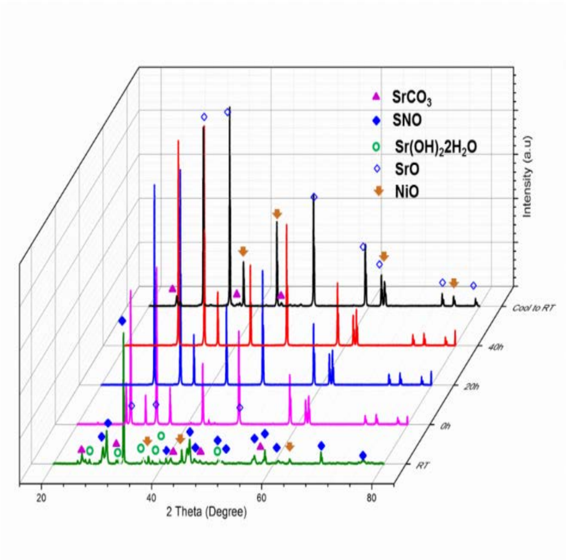
Ashish Aphale, Aman Uddin, Boxun Hu, Su Jeong Heo, Junsung Hong and Prabhakar Singh, Synthesis and Stability of SrxNiyOz Chromium Getter for Solid Oxide Fuel Cells”, ECS, 2018

Thermal Stability of Cr getters

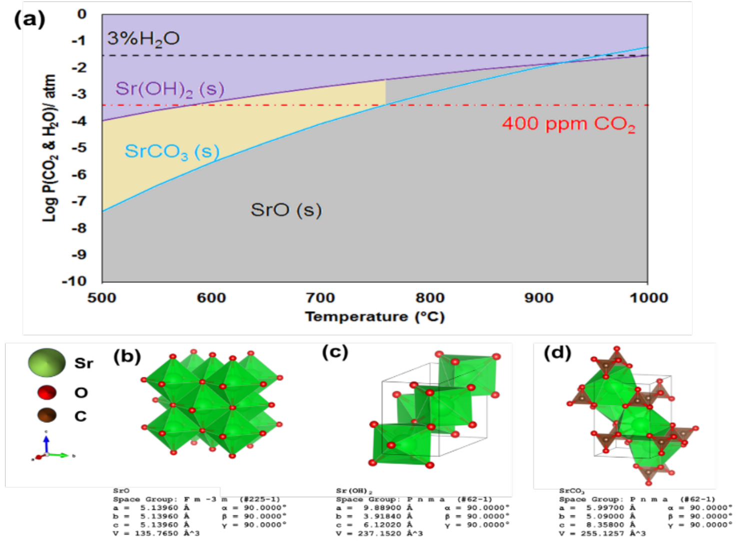
High temperature *in-situ* XRD performed on SrNiOx powder for 40h



850˚C

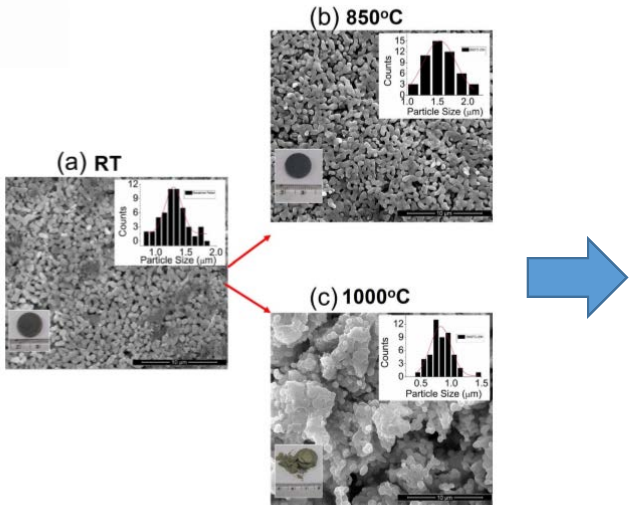


1000˚C

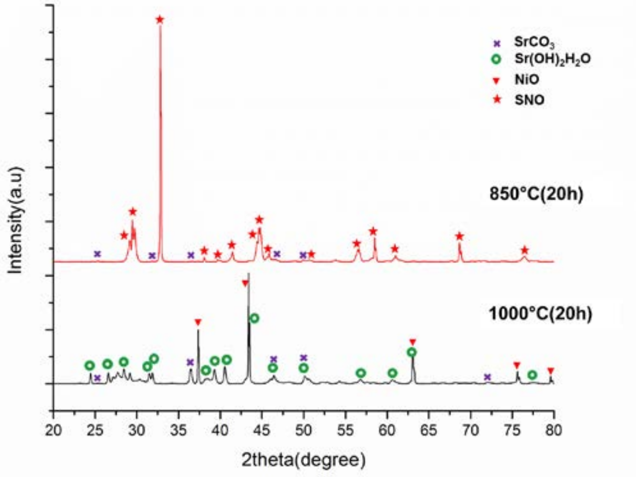


```
SrO
Space Group: F m -3 m  (#225-1)
a =   5.13960 Å        α = 90.0000°
b =   5.13960 Å        β = 90.0000°
c =   5.13960 Å        γ = 90.0000°
V = 135.7650 Å^3

Sr(OH)2
Space Group: P n m a  (#62-1)
a =   9.88900 Å        α = 90.0000°
b =   3.91840 Å        β = 90.0000°
c =   6.12020 Å        γ = 90.0000°
V = 237.1520 Å^3

SrCO3
Space Group: P n m a  (#62-1)
a =   5.99700 Å        α = 90.0000°
b =   5.09000 Å        β = 90.0000°
c =   8.35800 Å        γ = 90.0000°
V = 255.1257 Å^3
```

VESTA and COD utilized for crystallographic representation



XRD analysis after sintering



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

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

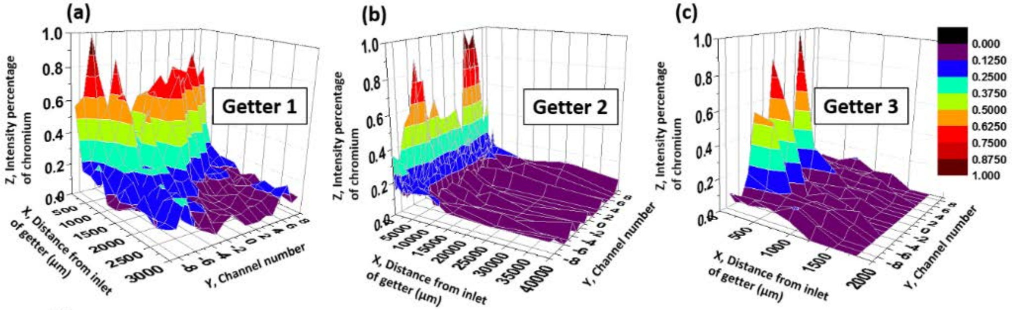
Getter Validation: BOP Simulation

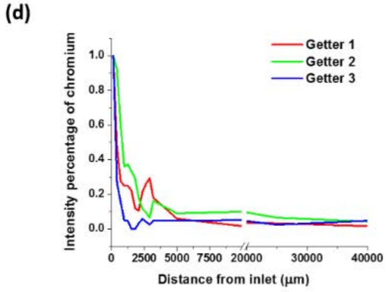
Transpiration

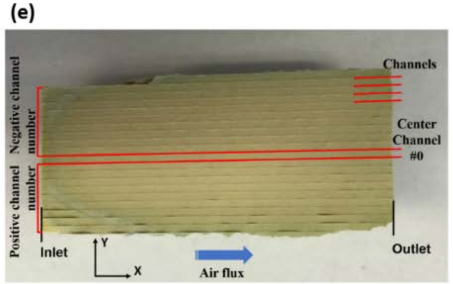
Getter Validation

Without getter

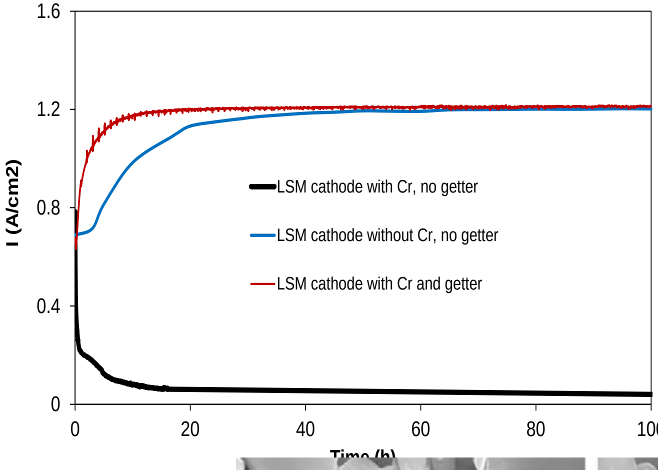
With getter

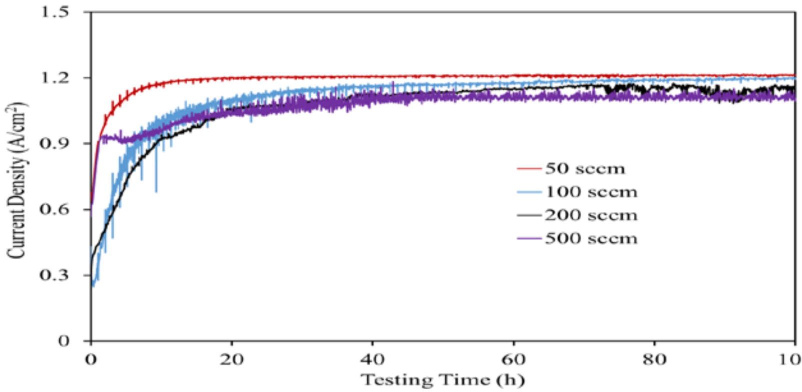






Electrochemical



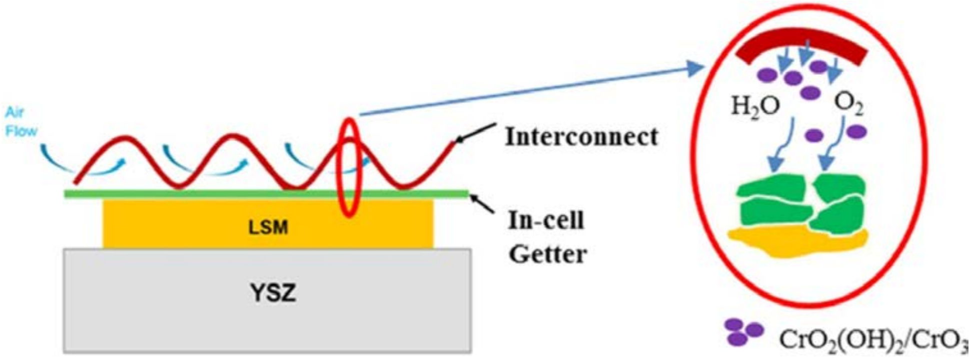


Air Flow Rate (SCCM) : 50, 100, 200, 500 completed

Tests completed/ In progress

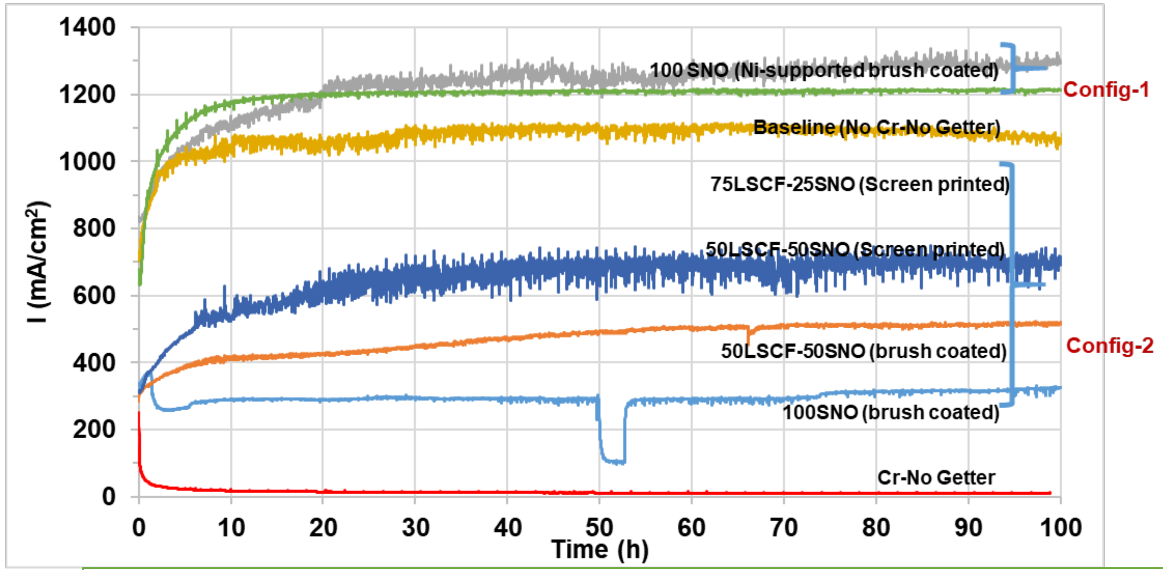
B. Hu, S. J. Heo, A. N. Aphale, P. Singh, Manuscript in preparation.

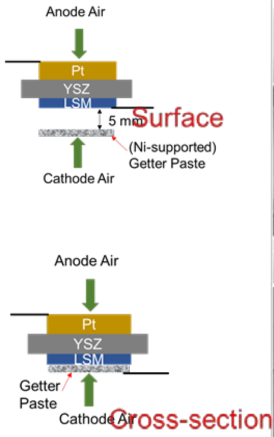
In-Cell Chromium Capture

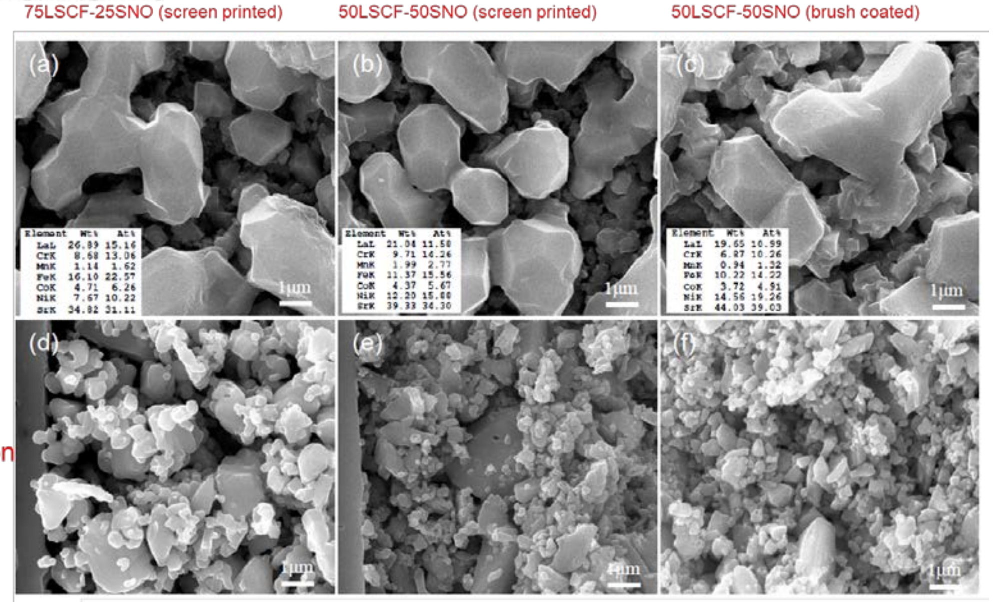


Concept also validated independently by industry

I-t data







(a)

Element	Wt%	At%
LaL	26.89	15.16
CrK	8.68	13.06
MnK	1.14	1.62
FeK	16.10	22.57
CoK	4.71	6.26
NiK	7.67	10.22
SrK	34.82	31.11

(b)

Element	Wt%	At%
LaL	21.04	11.50
CrK	9.71	14.26
MnK	1.99	2.77
FeK	11.37	15.56
CoK	4.37	5.67
NiK	12.20	15.88
SrK	39.33	34.30

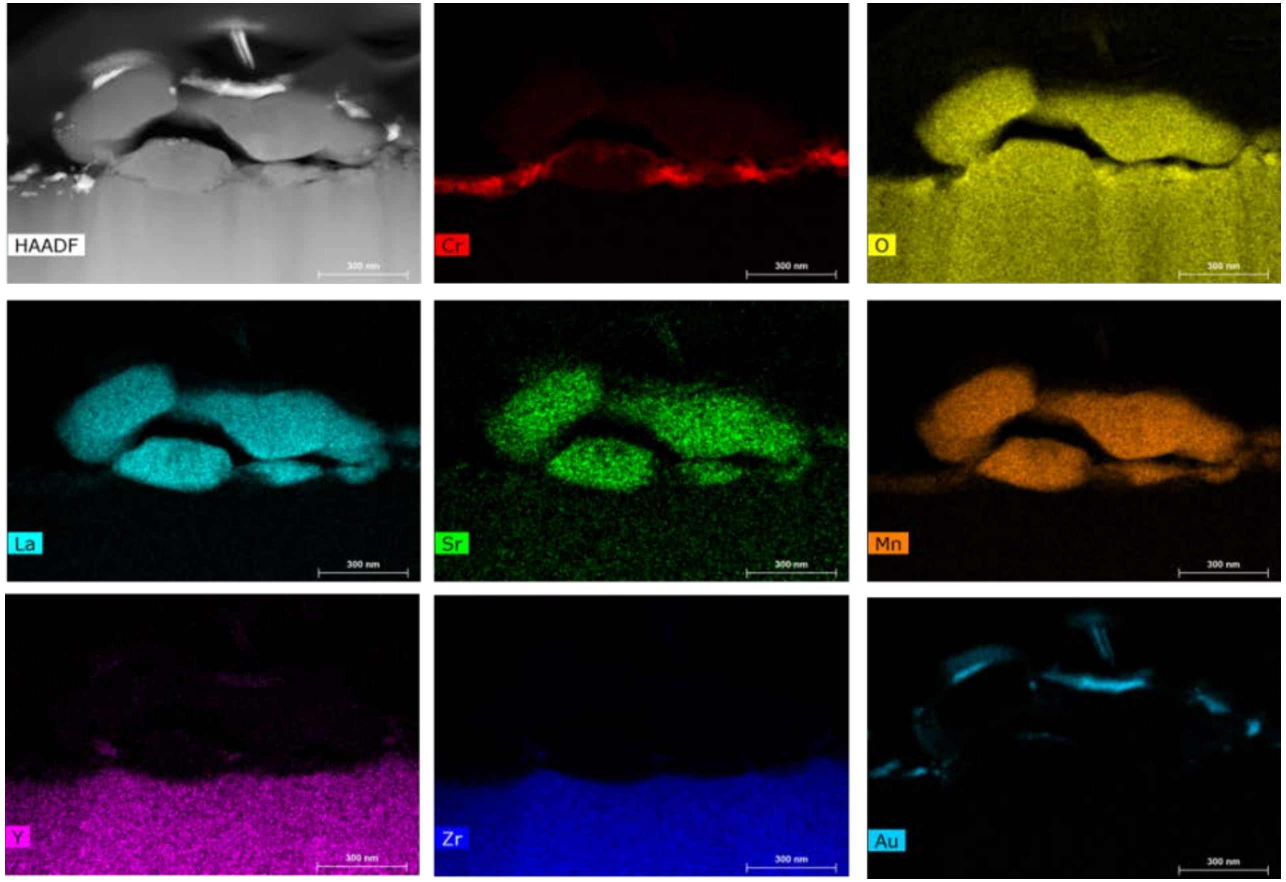
(c)

Element	Wt%	At%
LaL	19.65	10.99
CrK	6.87	10.26
MnK	0.94	1.32
FeK	10.22	14.22
CoK	3.72	4.91
NiK	14.56	19.26
SrK	44.03	39.03

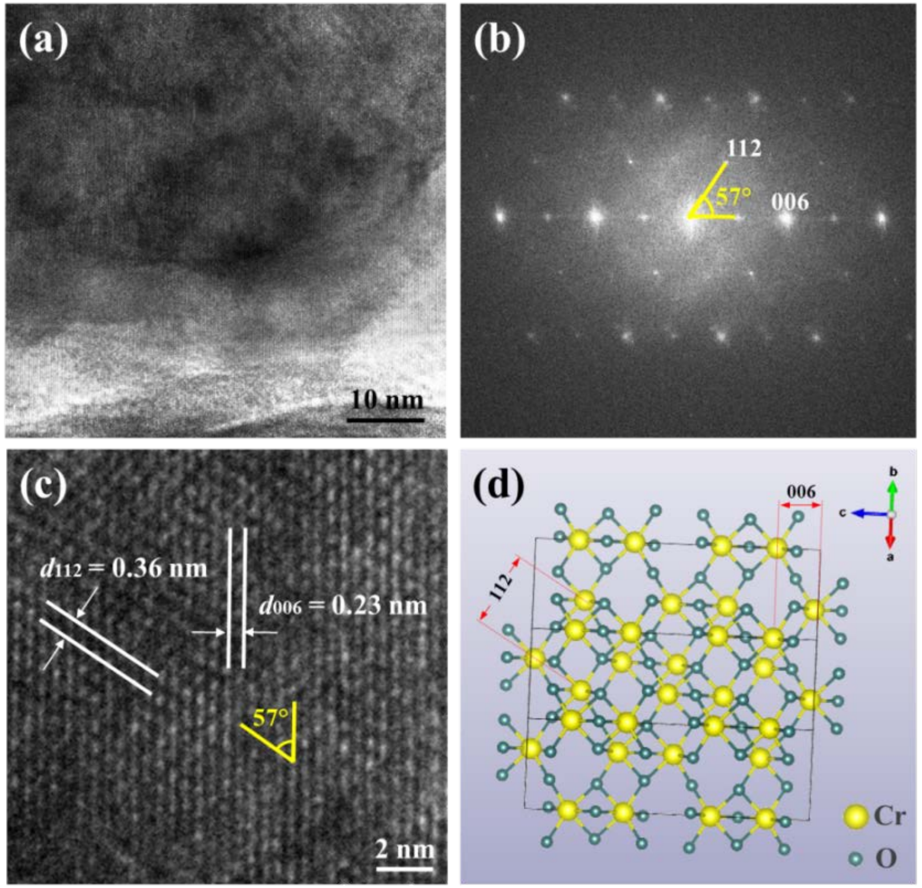
- Half-cell fabrication procedure was maintained for all the half-cell fabrication
- LSM was screen printed and sintered at 1200 ˚C for 1h
- SNO or LSCF/SNO getter was brush coated and sintered at 850 ˚C for 20h
- Config-1: Getter paste is 5 mm apart form LSM and Config-2: Getter paste is in direct contact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

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

Cr deposition: LSM/YSZ interface



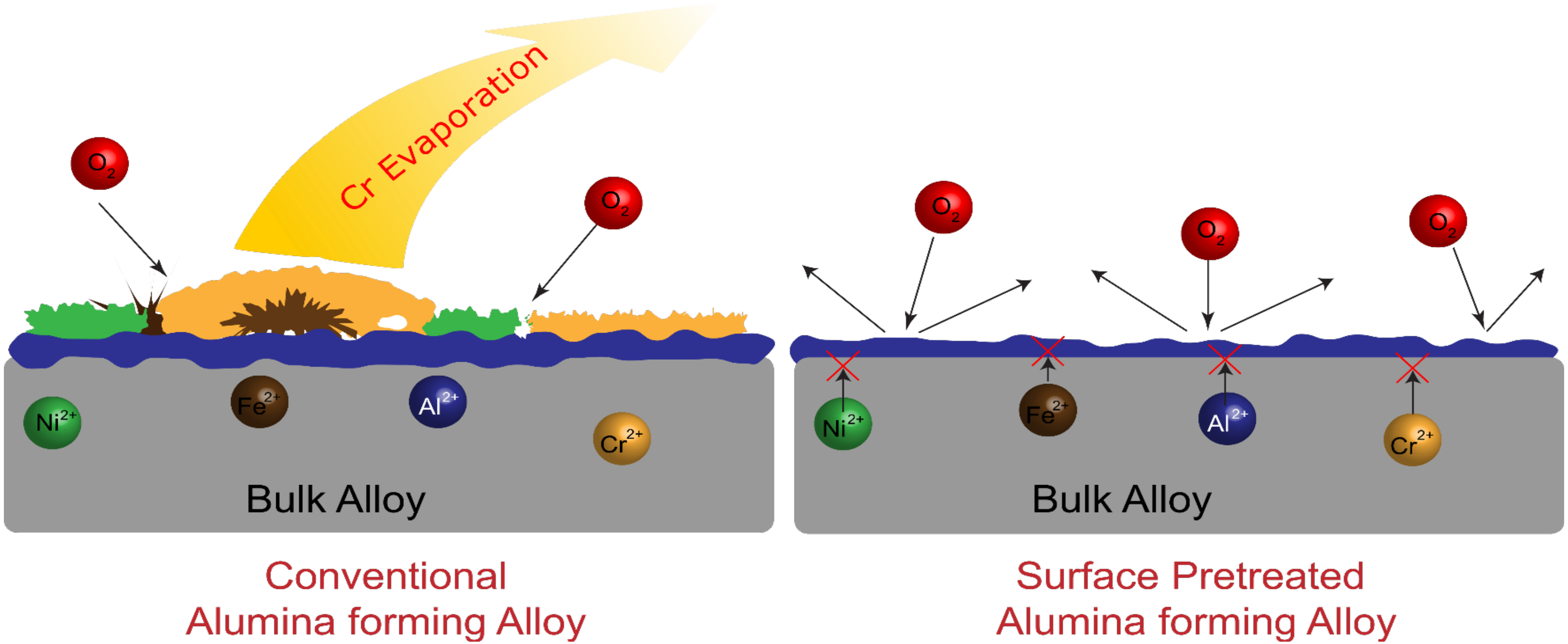
Cross sectional FIB-STEM micrograph and mapping of LSM/YSZ interface after Cr poisoning at 650C



(a) TEM image of region of the chromium deposition taken along [110], (b) The corresponding FFT pattern (c) HRTEM image of the crystalline and (d) the atomic model illustrated.

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

Surface Morphology: Pretreatment V/s of Conventional Alloy



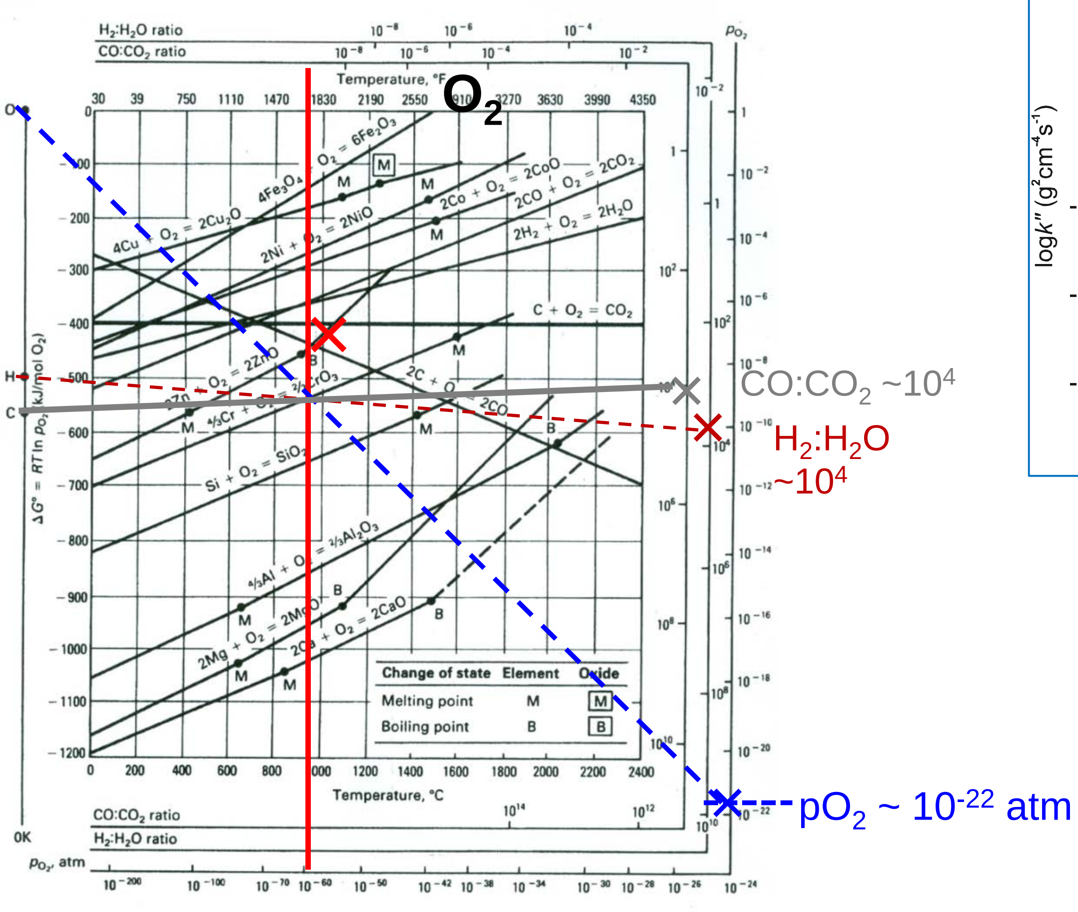
Conventional
Alumina forming Alloy

Surface Pretreated
Alumina forming Alloy

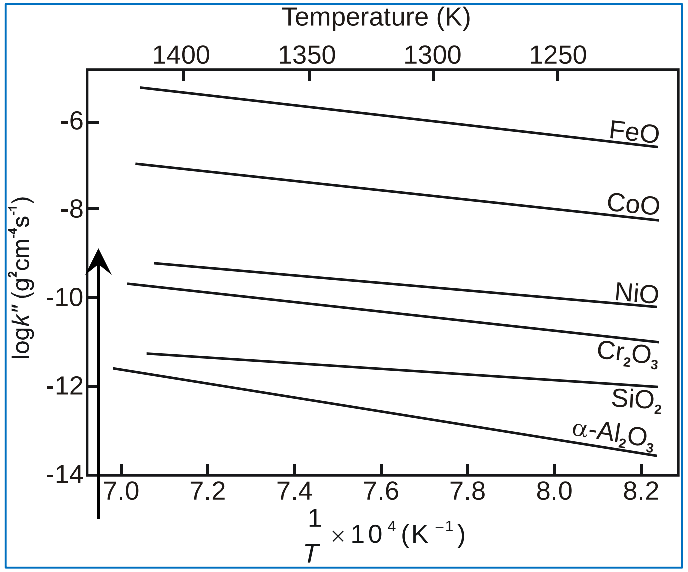
- Oxidation of alumina forming alloy leads to formation of mixed oxide scales and alumina subscale.
- Surface pretreatment leads to the formation of exclusive alumina scale only.

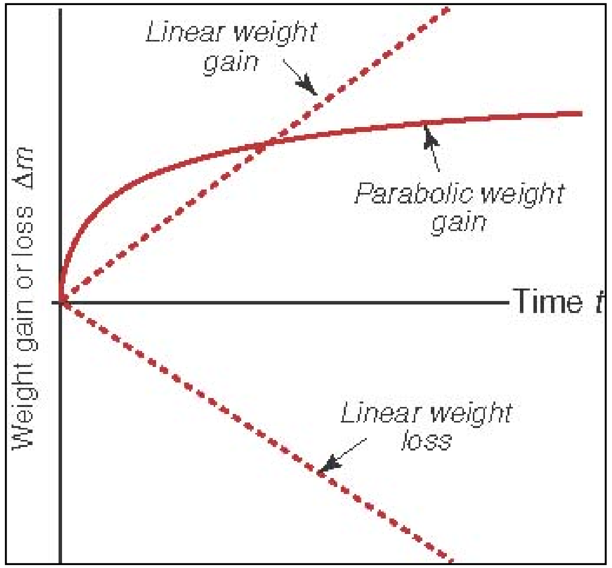
Ashish Aphale, Boxun Hu and Prabhakar Singh, " Surface pretreatment of alumina forming alloys" 2018 (Manuscript in preparation)

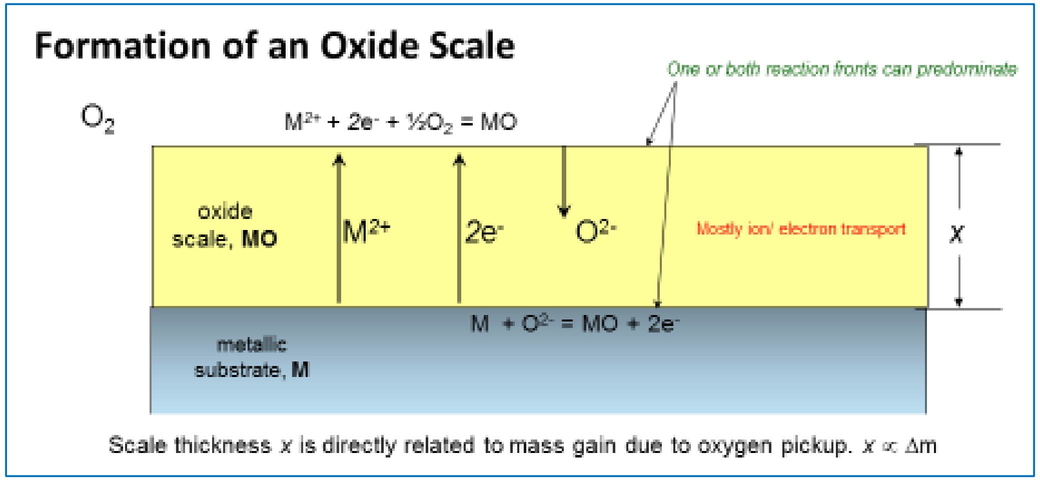
Oxidation: Thermodynamics and Scale Growth



Standard Gibbs free energy of formation of oxides as a function of temperature – Ellingham diagram







Scale thickness x is directly related to mass gain due to oxygen pickup. $x \propto \Delta m$

Initial Oxidation – Nucleation and Growth

Necessary and Sufficient Conditions for the formation and growth oc surface oxide:

- Surface oxide formation thermodynamically favorable : ΔG for the reaction is negative

  $M + n/2\ O_2 = MO_n,\qquad \Delta G = -\ RT\ln K$

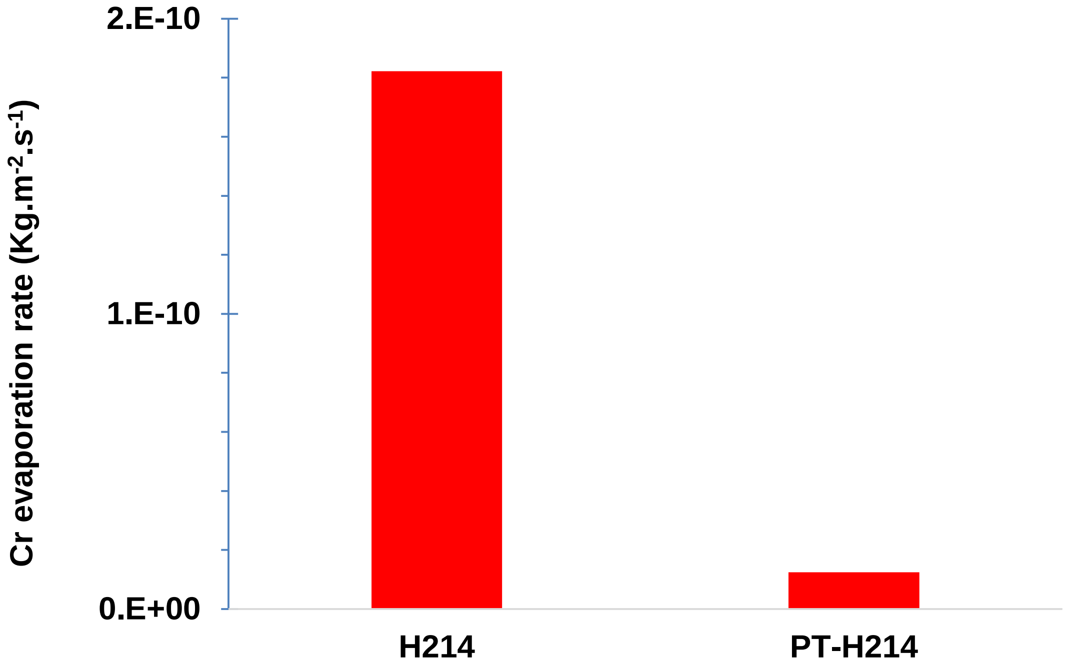
- Growth of oxide nuclei is determined by bulk anion or cation diffusion process. The oxide thickness is governed by Wagner's Law:

  $X^2 = k.t$

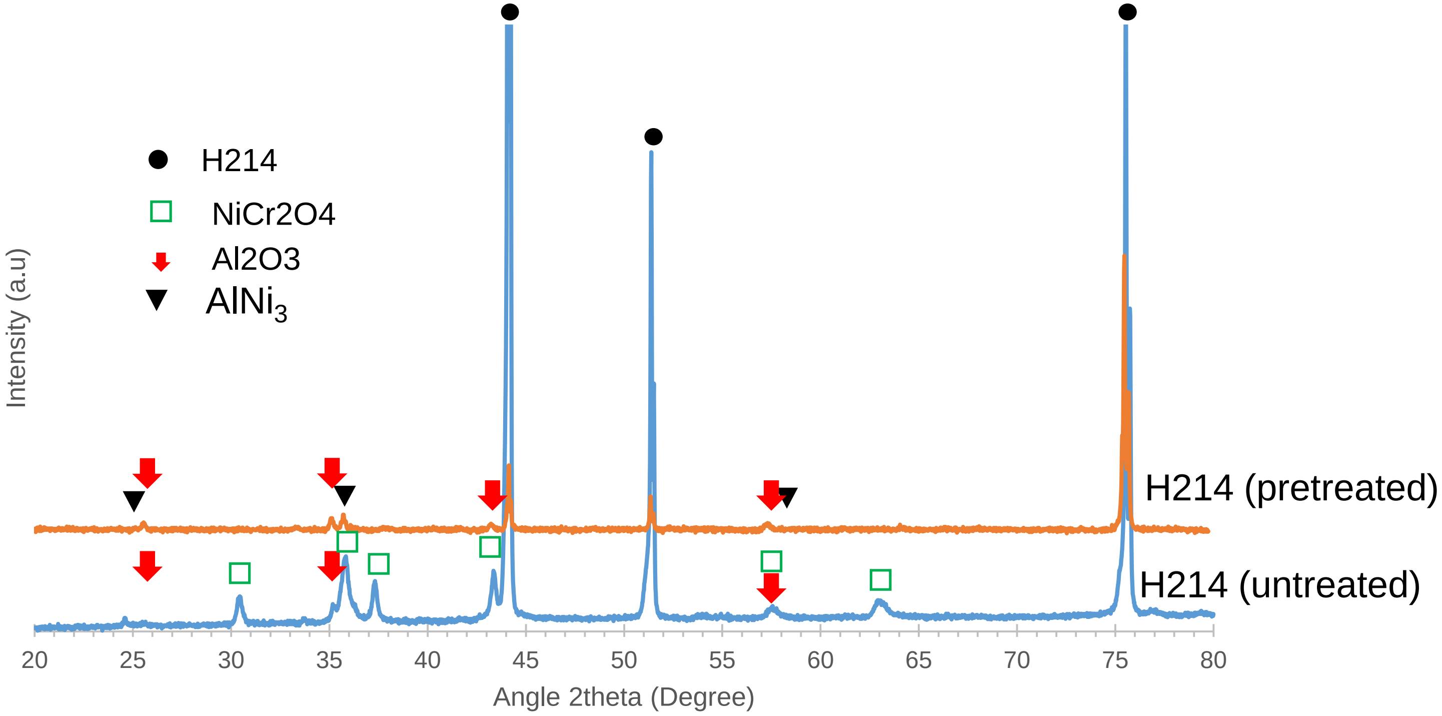
For initial oxidation, it is considered that alloy constituents are accessible to the gas atmosphere and able to react to form respective oxides. Most cations present in the Fe and Ni base alloys (Fe, Ni, Cr, Al, Si, Mn, Ti, RE and others) will oxidize to form their respective oxides.

$k_{Al2O3} < k_{Cr2O3} < k_{NiO} < k_{FeO}$……..

Cr Evaporation Rate Measurement: Alumina Former



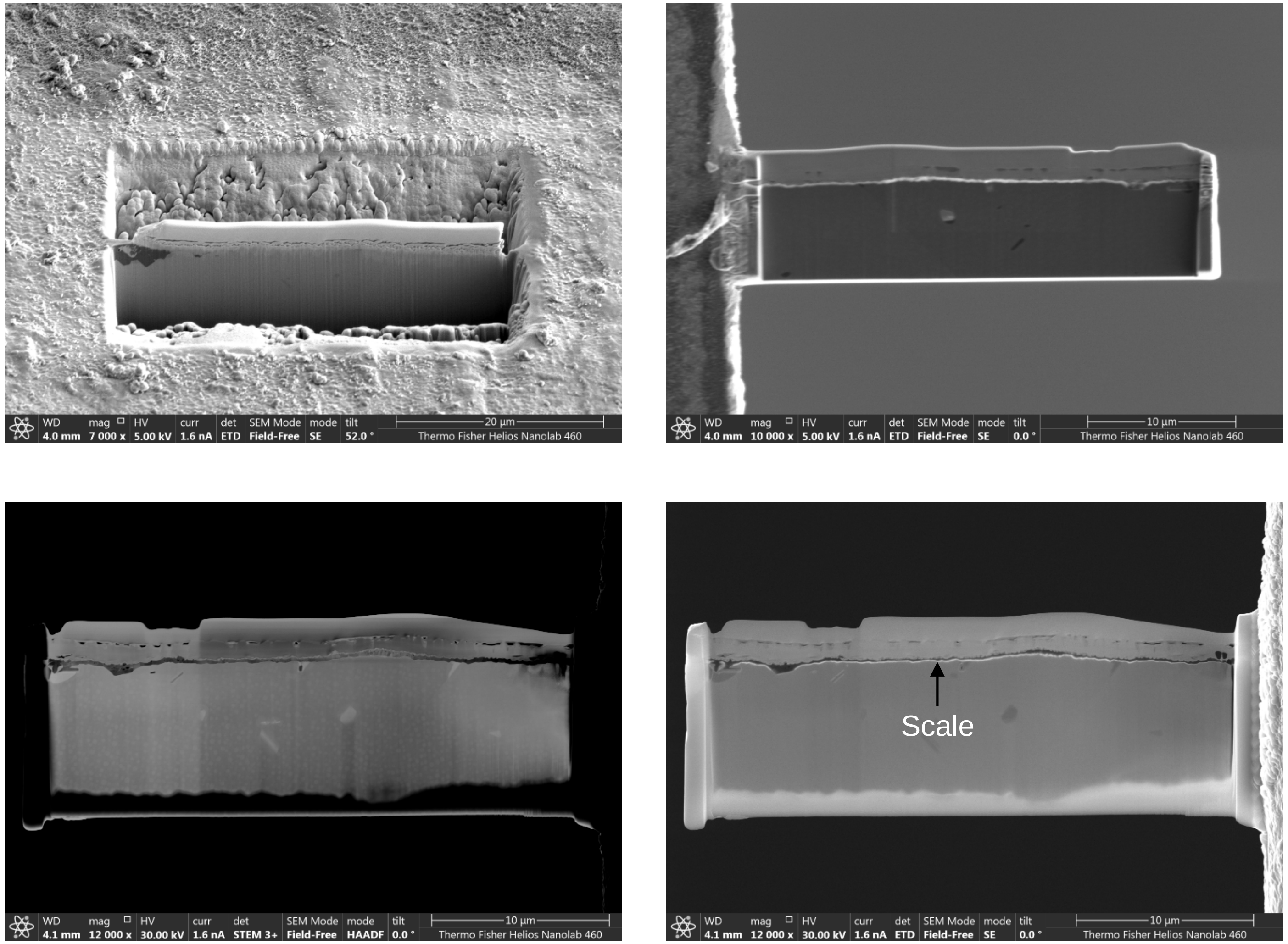
XRD after Cr Transpiration Test: 500 hrs – 850C -3%H2O- Air



Sample	Cr Evaporation Rate (Kgm²s⁻¹)	Cr Partial Pressure (atm)
H214	1.82E-10	2.06E-8
PreTreated-H214	1.24E-11	1.45E-9

- Significant reduction in the Cr evaporation rate is observed after pretreatment of H214 alloy.
- Morphology and chemistry changes - observed after 500 hrs of Cr transpiration from untreated and pretreated H 214 samples.

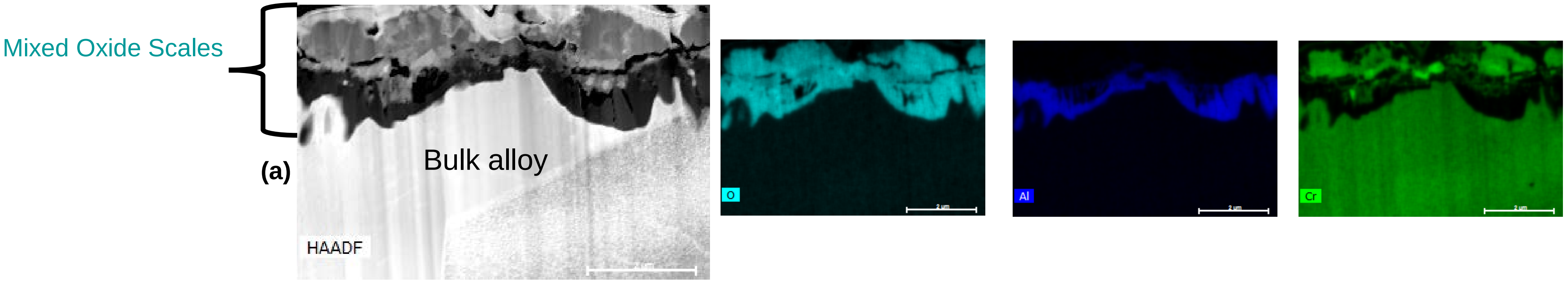
FIB Cross Section of Pretreated H214 post Cr Transpiration



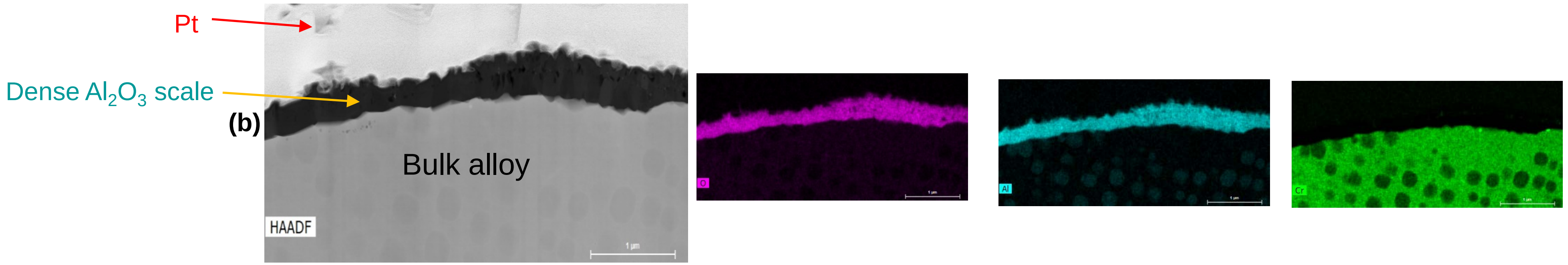
Scale chemistry and morphology studies were conducted on post tested alloy samples by FIB/TEM technique.

FIB/TEM Analyses

Posttest analysis- 500 hrs of Cr evaporation at 3%H_2O air



As received

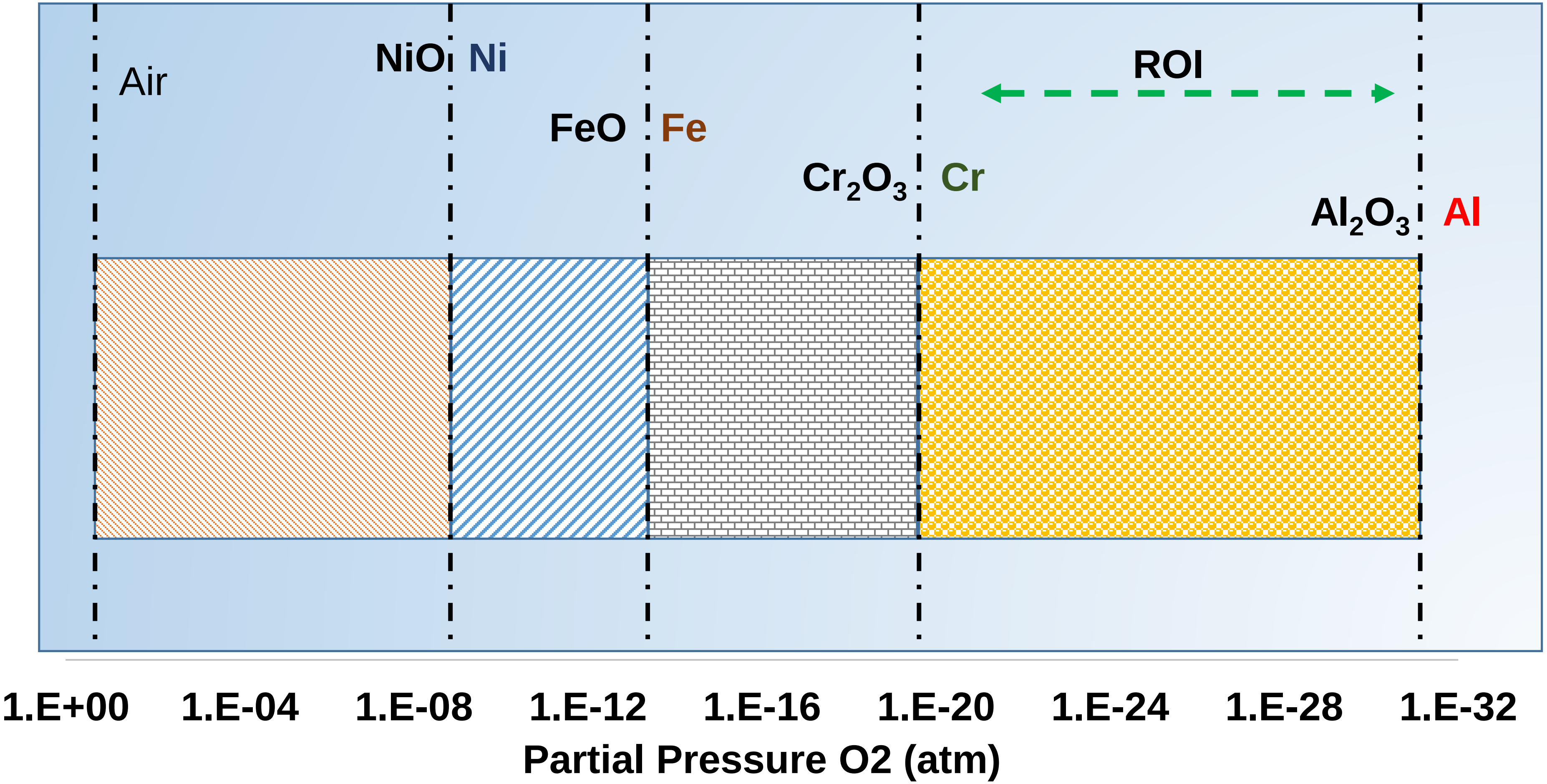


Pretreated

- Mixed oxide scale formation is observed in as received H214 alloy after 500 hrs of Cr transpiration test.
- Surface pretreatment of the alloy in reducing atmosphere leads to selective oxidation of Al in bulk alloy at the exclusion of the other alloy elements.

Pretreatment condition : oxide chemistry

Oxide phase stability at 850C in 3%H_2O air. M_a is unity.



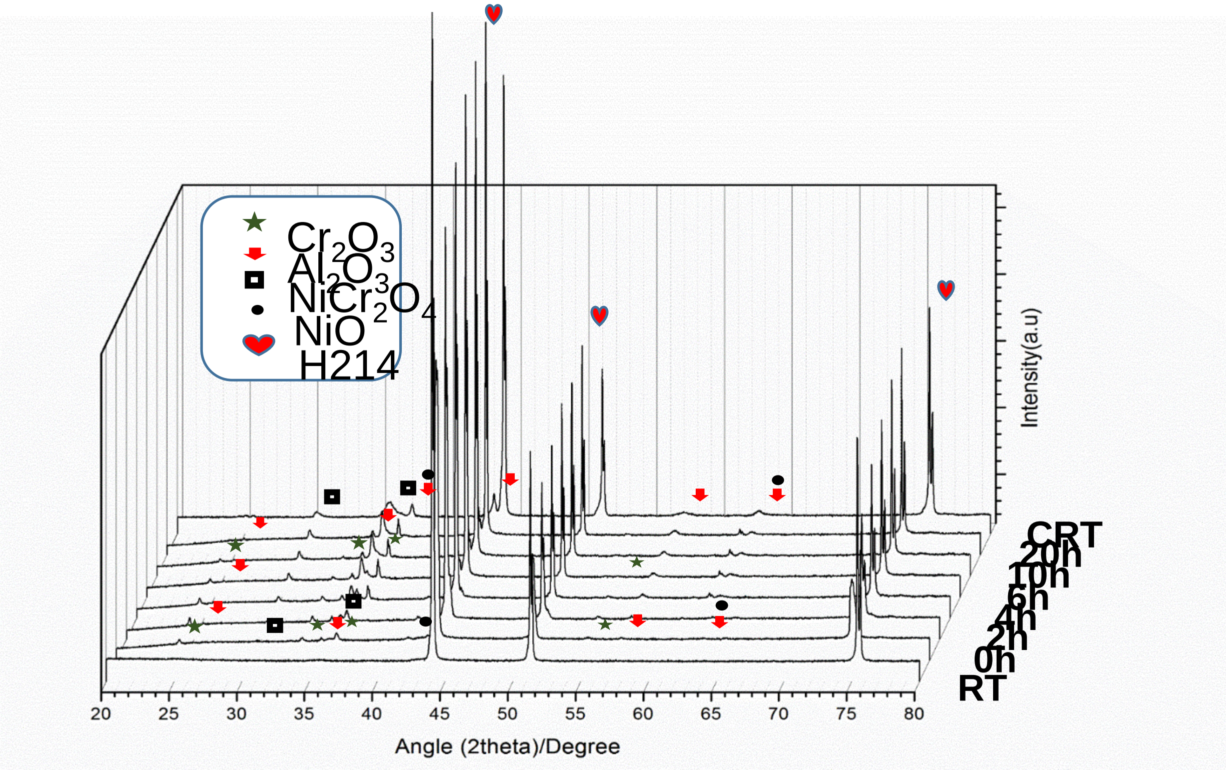
- In air atmosphere, all the elements undergo oxidation and form multi-constituent oxides.
- Surface pretreatment in reducing atmosphere leads to selective oxidation of Al

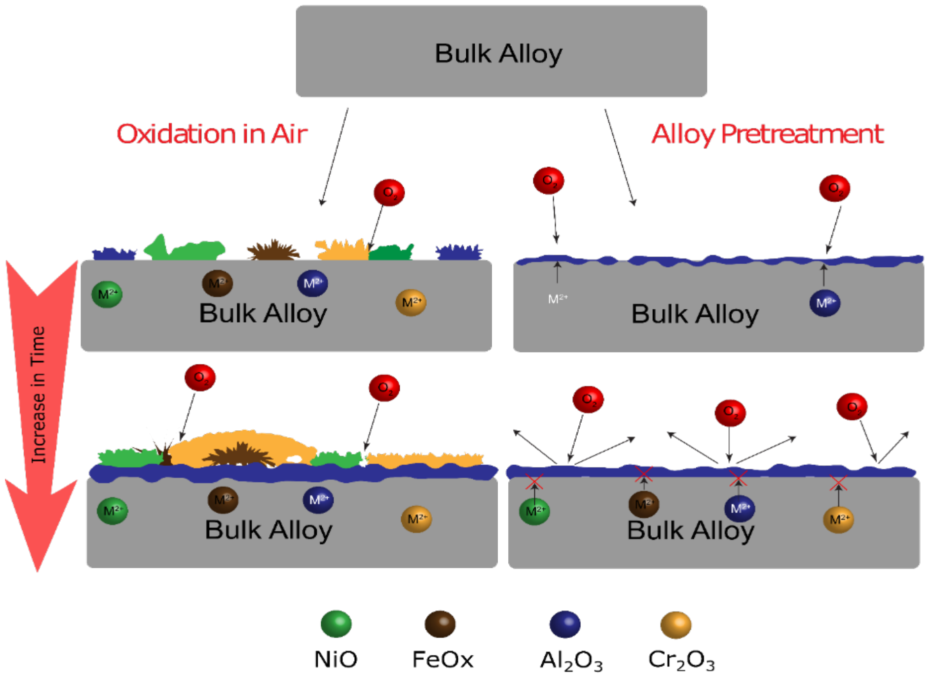
Experimental Results: Evolution of Oxide Scales

High temperature *in-situ* XRD performed on alumina forming alloy 20h at 900C in 3%H_2O air.

- Evolution of oxide scales with time at 900C.
- Early oxide nuclei for Cr, Ni, Al is observed at time (T=0)
- Predominantly alumina sub-scale is formed after 20 hrs of oxidation in air

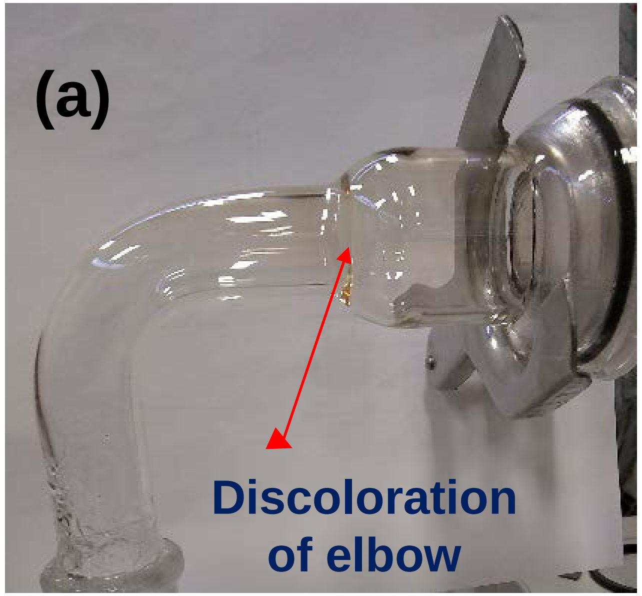
Transition from mixed oxide scale to passivating alumina scale

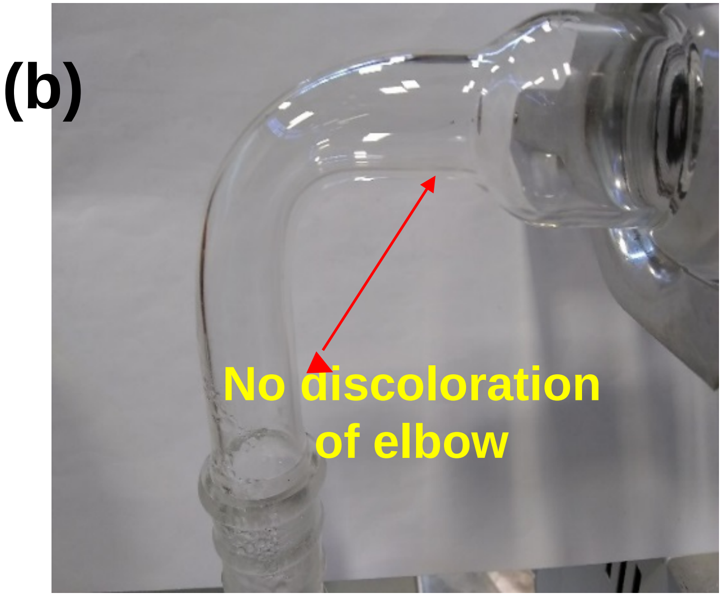


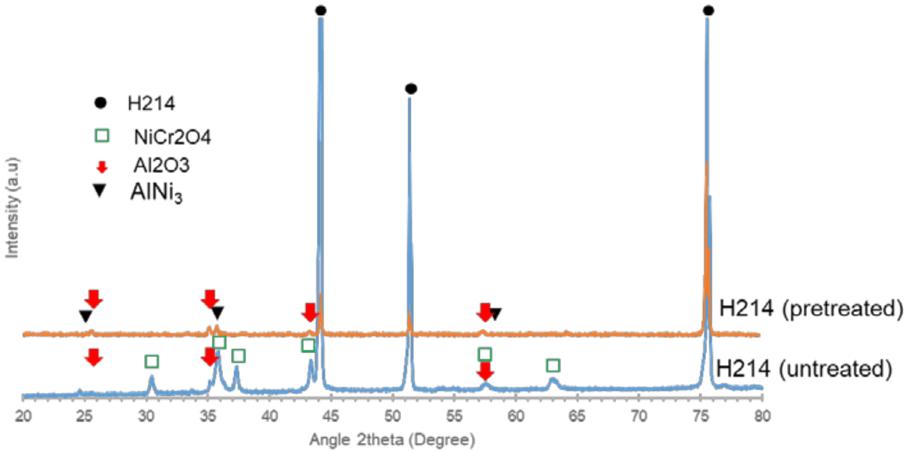


Performance comparison

Alloy performance compared in 3%H_2O air at 850C, duration 500hrs.







Sample	Duration (hrs)	Temperature (C)	Atmosphere	Flow rate (SCCM)
H214	500	850	3%H_2O-Air	300

Minimization of Cr evaporation from is evident from the visual images.
Significant minimization of Cr evaporation is observed after 500 hrs.
XRD confirms the presence of exclusive alumina scale post 500 hrs of Cr transpiration.

Conclusions

1. **Developed cost effective getters for the capture of gaseous Cr vapors.**
   - **Developed getters can capture gaseous Cr vapors in 600-900C temperature range**
2. **Demonstrated excellent blockage of Cr vapor for entering into cathode electrode by electrochemical and transpiration tests**
3. **Optimized getter coating process, thickness and coating morphologies for large scale testing.**
4. **Characterized pretest and posttest getters (including getters for our lab, PNNL, and LG Fuel Cell) and cathodes by XRD, SEM-EDS, FIB-STEM and XPS.**
5. **Investigated the stability of SrNiOx getter as a function of temperature.**
6. **Scaled up getter powder materials synthesis Laboratory process can meet ~1-2 MWe SOFC system needs.**

- Getter design can be tailored to meet various SOFC systems configurations and exposure conditions
- Getter materials can be used for capturing Cr originating from BOP and IC.
- Near term needs can be met by existing laboratory facilities.

Conclusions

- Gas phase acidic airborne impurities react with basic air electrode constituents to form stable reaction products at the free surface and TPB.
- Gr II Alkaline earth and transition metal oxides have been selected as potential getter materials as they offer oxide basicity and ability to capture acidic impurities.
- Thermodynamic calculations based on Gibbs free energy change indicates co-capture of sulfur and chromium impurity in wide temperature range.
- SrMnO based getter has been synthesized and fabricated.
- Getter has been validated electrochemically to demonstrate the successful capture of both Cr and S in gas phase at 850C.
- Posttest results from SEM indicates clean LSM/YSZ interface after 100 hrs of electrochemical test in presence of Cr and SO_2 vapor.
- SEM/EDS characterization of SMO getter reveals high concentration of S and Cr at the inlet of the getter and negligible concentrations at the center and the outlet of the getter, indicating complete capture.

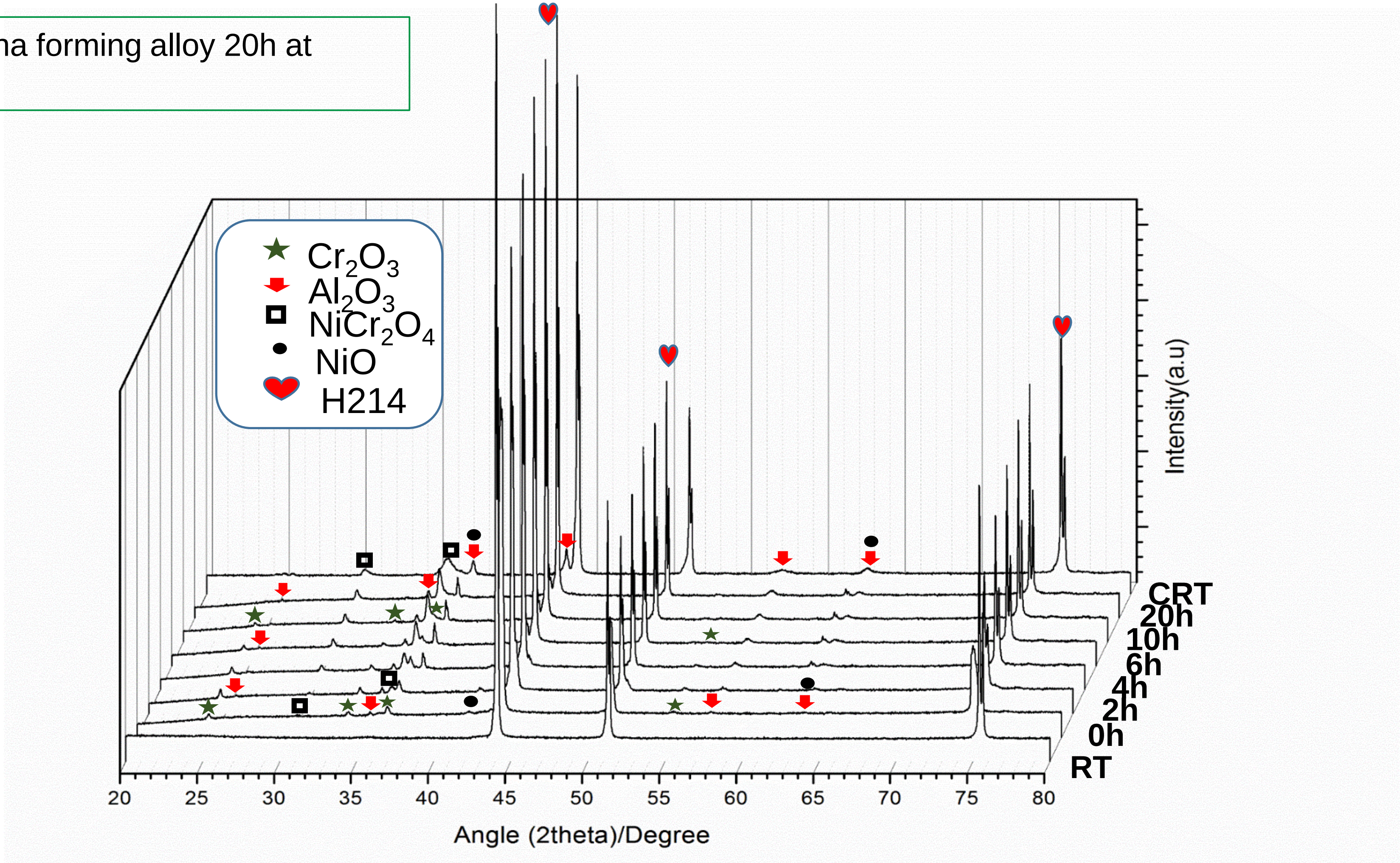
Acknowledgements

- **Financial support from the US DOE under federal grant DE-FE 0023385**
- **Dr. Rin Burke for guidance**
- **UConn for providing laboratory support**

Thank you

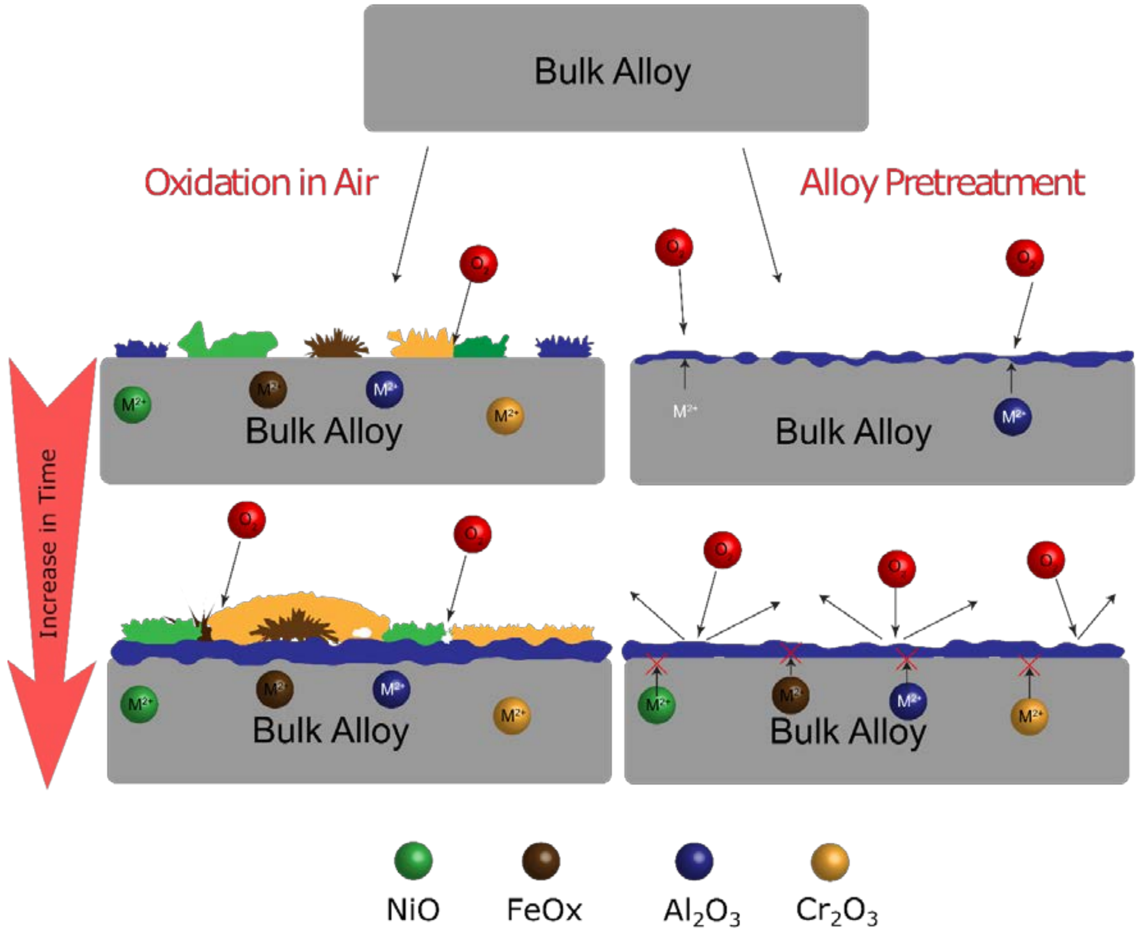
Evolution of Oxide Scales

High temperature *in-situ* XRD performed on alumina forming alloy 20h at 900C in 3%H_2O air.



- Evolution of oxide scales with time at 900C.
- Early oxide nuclei for Cr, Ni, Al is observed at time (T=0)
- Predominantly alumina sub-scale is formed after 20 hrs of oxidation in air

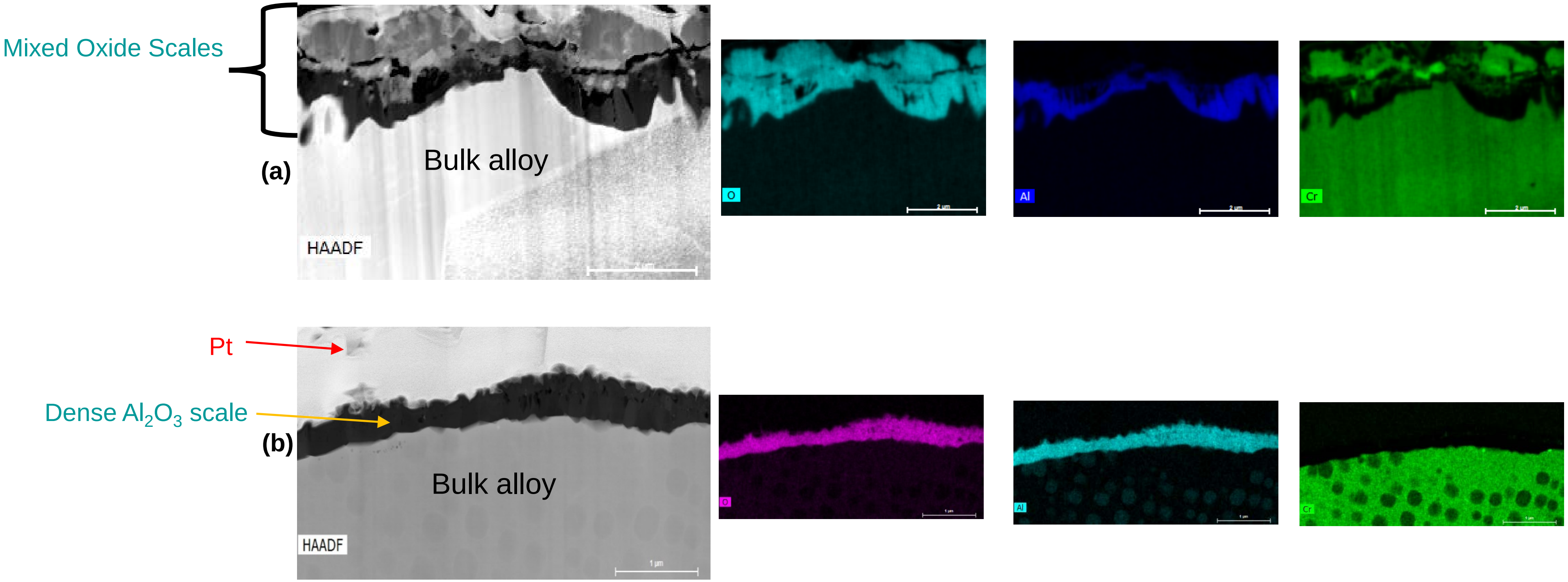
Time Dependent Oxidation



Oxidation of alumina forming alloy in air leads to formation of mixed oxides scales and predominant alumina sub-scale.

FIB/TEM Analyses

Posttest analysis- 500 hrs of Cr evaporation at 3%H_2O air



- Mixed oxide scale formation is observed in as received H214 alloy after 500 hrs of Cr transpiration test.
- Surface pretreatment of the alloy in reducing atmosphere leads to selective oxidation of Al in bulk alloy at the exclusion of the other alloy elements.