Electrochemical Validation of "In-cell Cr Getter" for the Mitigation of Cathode Poisoning in SOFC Power Systems

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Abstract: Non-noble, non-strategic and cost effective chromium getter has been synthesized using alkaline earth and transition metal nitrate precursors and chemical and structural stability of getter powder has been examined under both cell fabrication and operational conditions. A porous conductive cathode contact (CC) layer, consisting of mixtures of Cr getter and an electrically conducting perovskite phase, has been fabricated for incorporation in the electrochemically active cell area between the cell interconnect (IC) and cathode to capture gaseous Cr species. Contact layer configurations have been electrically tested in half-cell configuration in the presence of Cr vapor (Cr_2O_3/Air-3% H_2O) at 850°C for 100 hours. The electrical performance remains stable as evidenced by I-t and EIS data obtained during the test. The bulk electrode and electrode-electrolyte interface remain free of chromium. Results from post-tested half-cells for chromium concentration profile, reaction products chemistry and morphological changes will be presented. Phase stability of getter, studied by high temperature XRD technique, indicates that the synthesized powder remains stable up to 900°C. Our observations indicate that the conductive CC layer captures all the incoming Cr during 100 hours.

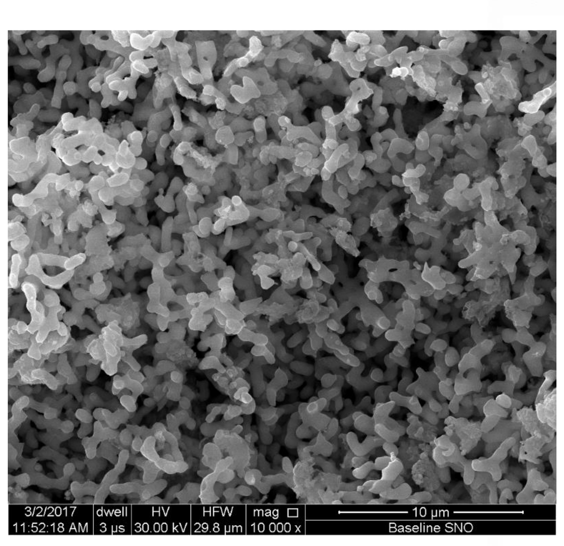
Background: Chromia forming metallic alloys are commonly used for BOP materials whereas ferritic iron based alloys are used for the IC components within the stack. Formation of protective chromia scale provides an excellent corrosion protection along with electronic conductivity. However, under humidified air atmosphere these chromia forming alloys can react with the oxygen and water vapor which leads to significant evaporation of Cr vapor species such as CrO_3, $CrO_2(OH)_2$ and $CrO(OH)_2$ form solid-gas interface. These evaporated Cr vapor are released into the air stream which poisons the cathode within the stack.

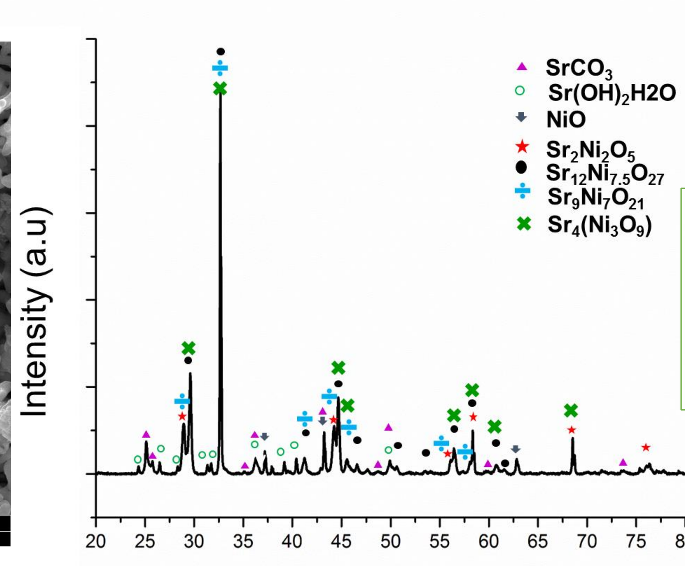
Objective: (a) Synthesis of cost effective Cr getter to mitigate cathode poisoning, (b) Investigate stability of SrNiOx getter as a function of temperature, (c) Electrochemical validation of "In-cell Cr getter" to capture Cr species evaporating from IC source.

Experimental

Synthesis

Procedure	Remarks
$Sr(NO_3)_2$ (9 mL of 2.4 M) and $Ni(NO_3)_2$-$6H_2O$ (9 mL of 1.6 M) stock solutions are mixed in a beaker.	Formation of transparent green solution
16 ml of 2.4 M EDTA in NH_4OH solution is added	The EDTA: metals was 1:1
Addition of 5 M ammonium hydroxide (30 mL) to increase pH to 8.75	Formation of sky blue to navy blue solution
Dry over a hot plate at ~100°C.	Blue waxy compound formation after ~1h
The blue wax is placed in oven at 200°C, followed by increase in the temperature to 260°C at 1°C/min (1h).	Formation of foamy dark color compound
Foam is crushed and calcined at 920°C to obtain SrNiOx powder	Black powder synthesized

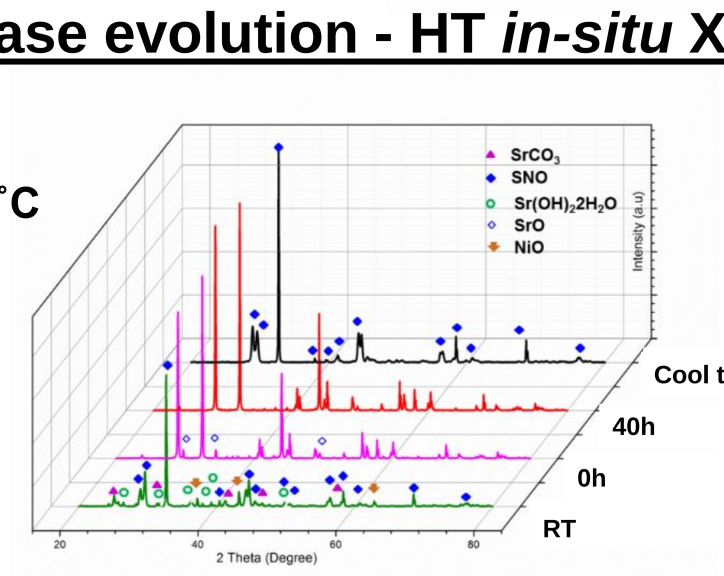




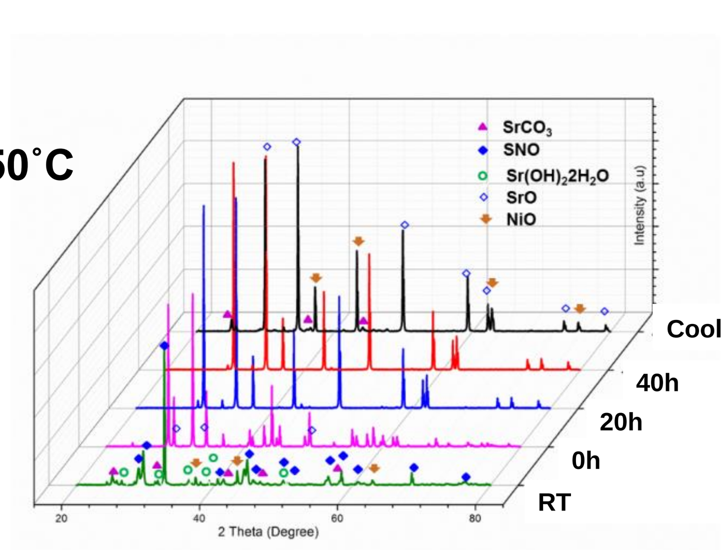
- Uniform powder morphology
- Consists of $Sr_2Ni_2O_5$, $Sr_{12}Ni_{7.5}O_{27}$, $Sr_9Ni_7O_{21}$ and $Sr_4(Ni_3O_9)$ phases.

Phase evolution - HT *in-situ* XRD

850˚C



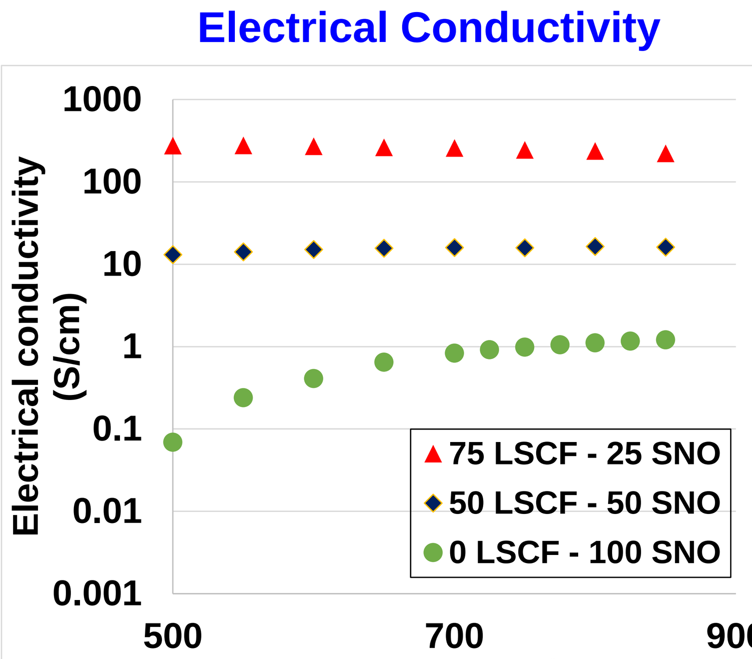
950˚C



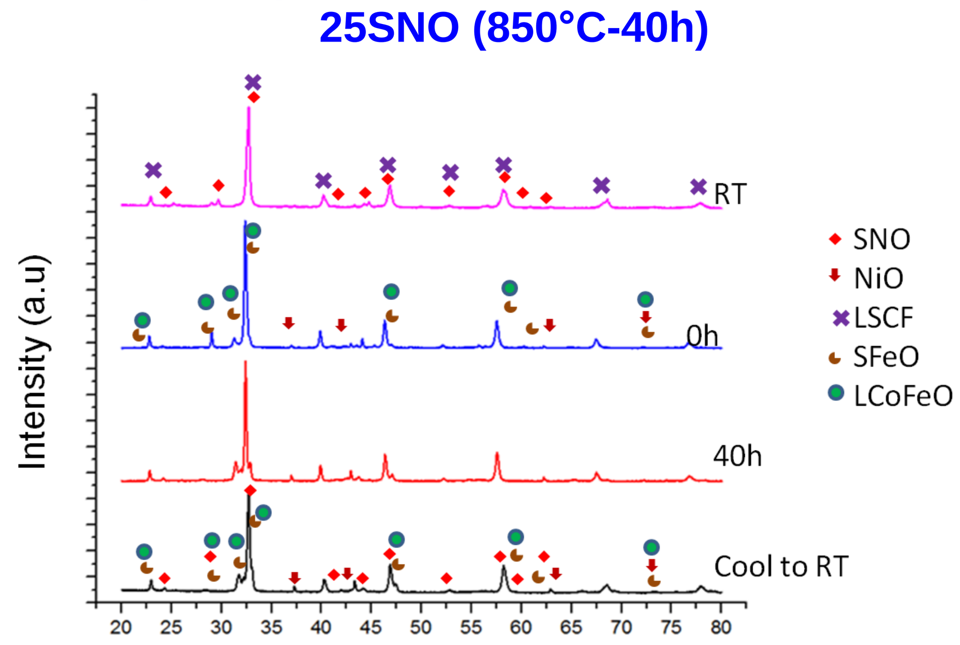
- $SrNiO_x$ maintains phase stability below sintering temperature of 900 °C.
- Sintering $SrNiO_x$ above 950 °C dissociates into separate SrO and NiO phases.

Conductive cathode contact paste

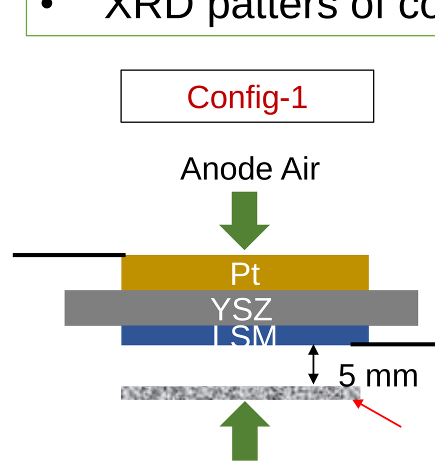
Electrical Conductivity

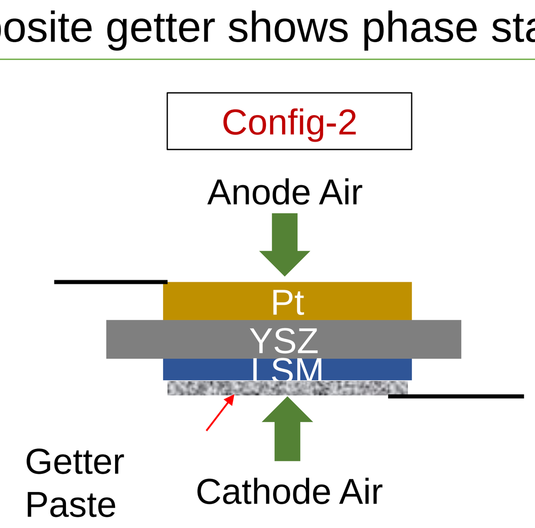


High temperature *in-situ* XRD on 75LSCF-25SNO (850°C-40h)



- $SrNiO_x$ getter materials is combined with a conductive phase of LSCF.
- LSCF-SNO composite getter shows higher conductivity compared to only SNO getter.
- XRD patters of composite getter shows phase stability at 850°C.

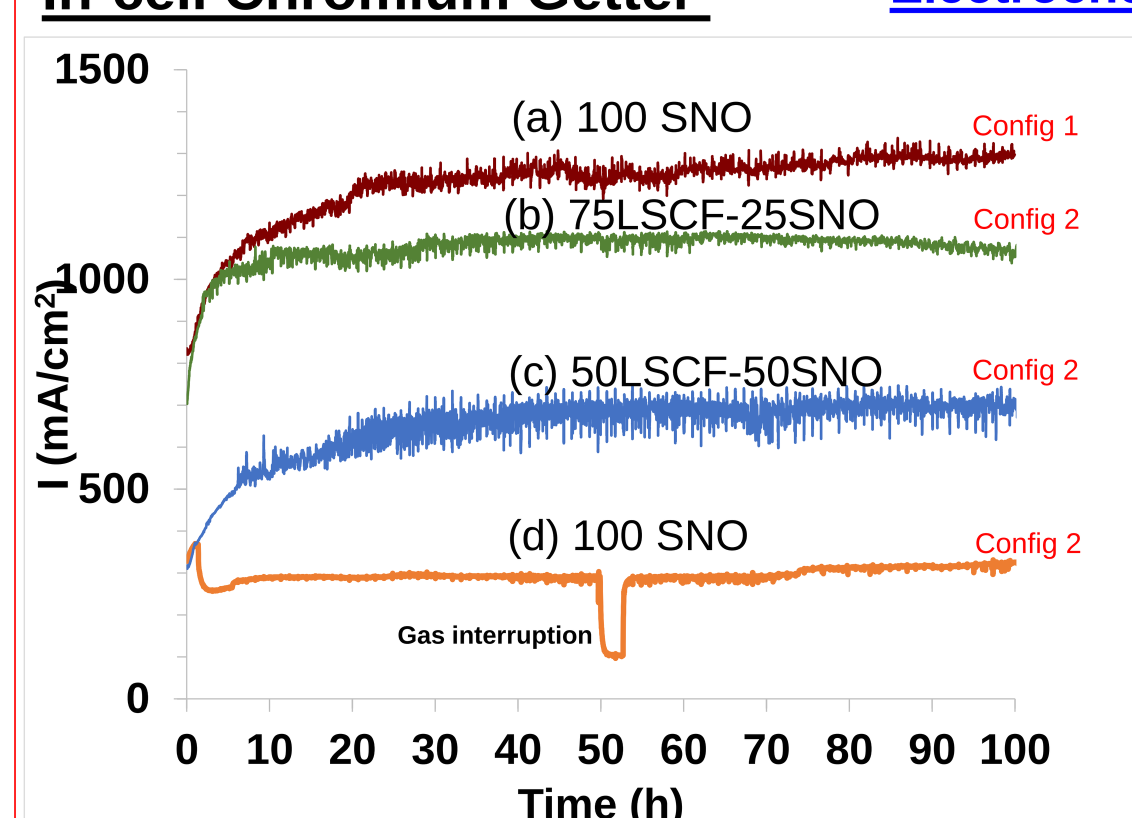


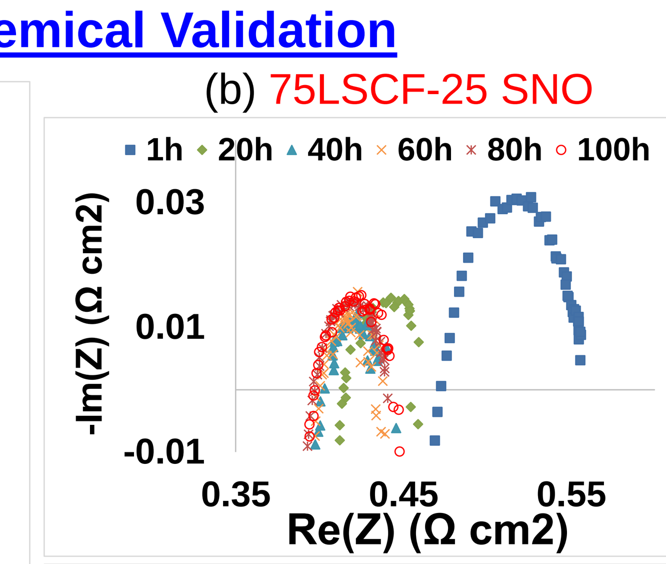


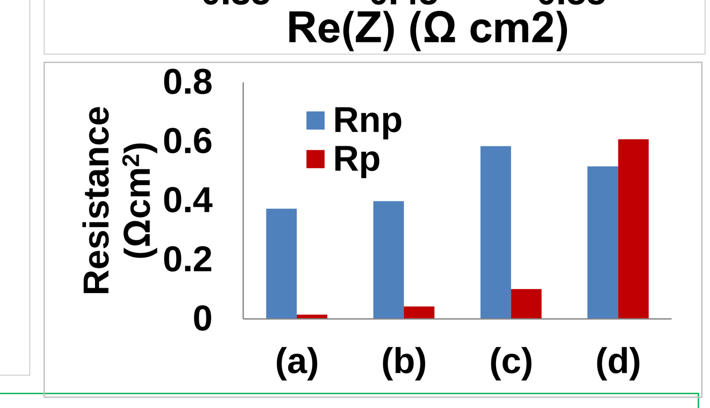
Conditions	
Temperature	850°C
Flow rate	150 sccm
Cr Source	Cr_2O_3
Cr Getter	LSCF-SNO
Bias	-500 mV

Electrochemical Validation

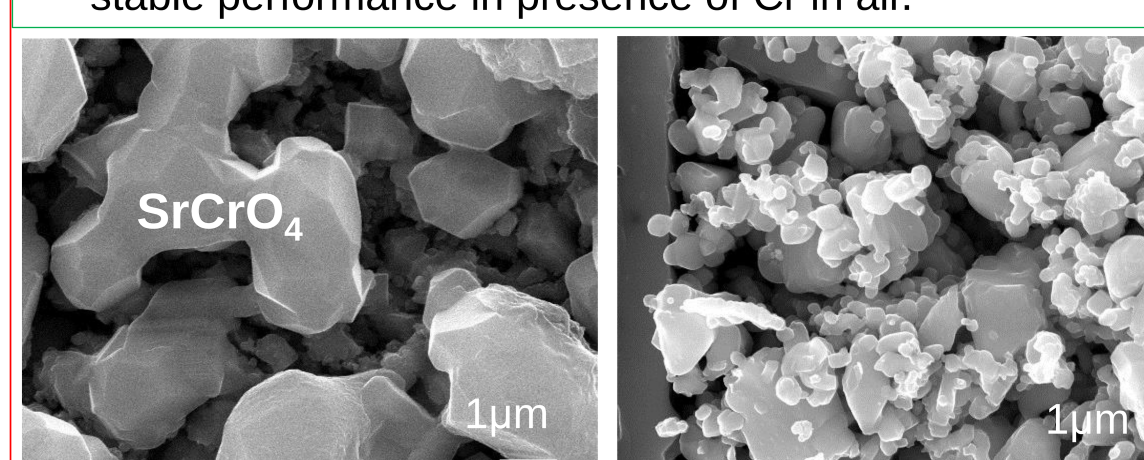
In-cell Chromium Getter





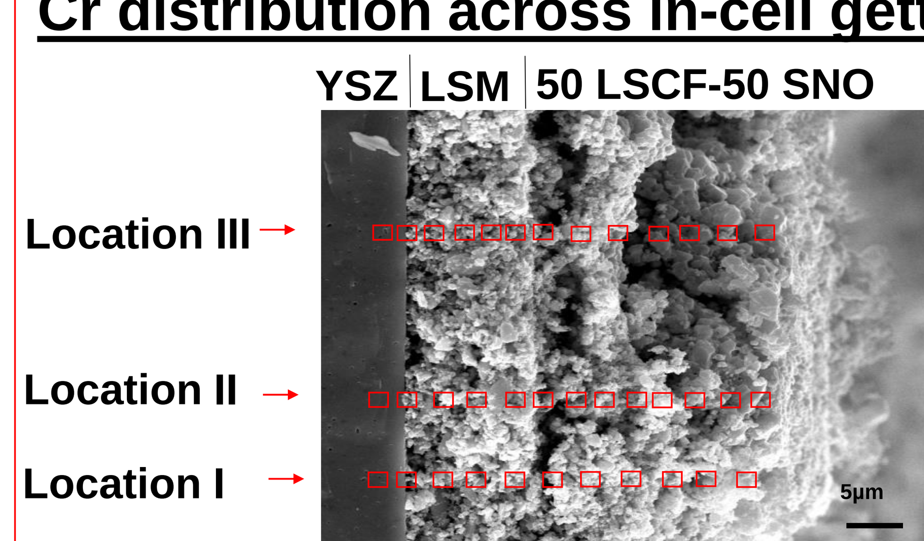


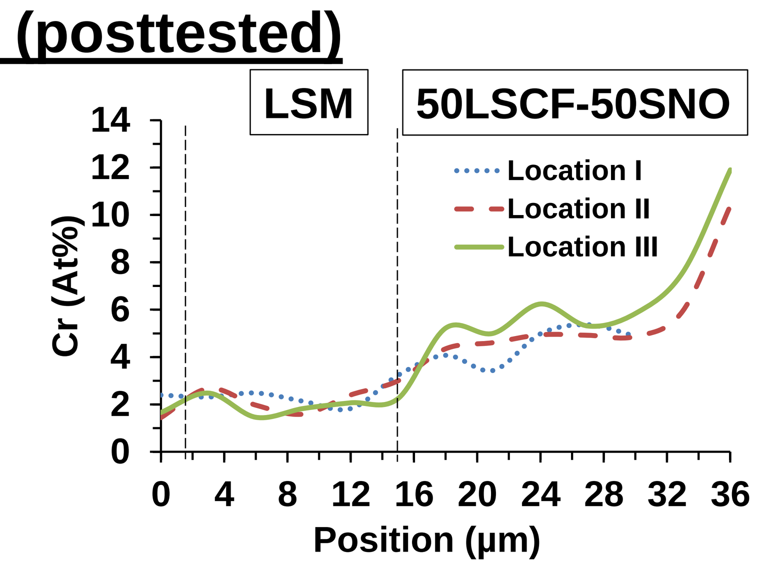
- Stable I-t performance of half-cells during 100h- demonstrating "In-cell" Cr capture.
- All the half-cells demonstrated a decrease in ohmic and polarization resistances indicating stable performance in presence of Cr in air.



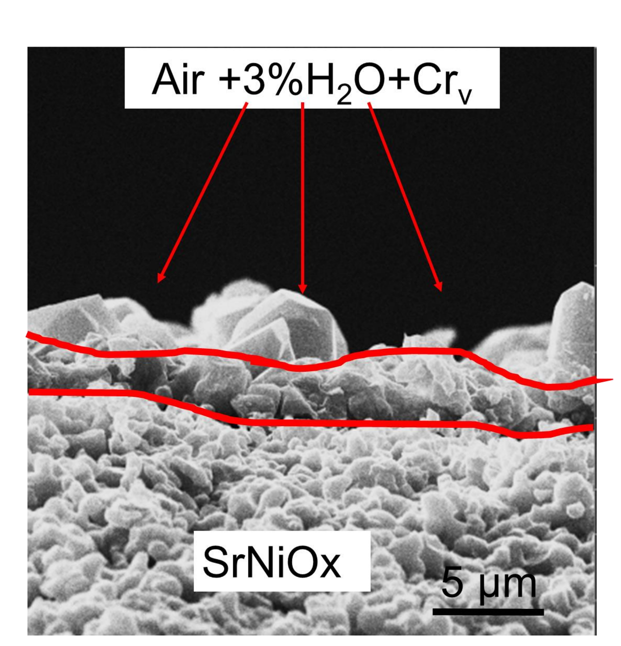
- Higher Cr concentration is observed at the surface of cathode contact layer.
- No Cr observed across LSM/YSZ interface.

Cr distribution across in-cell getter (posttested)

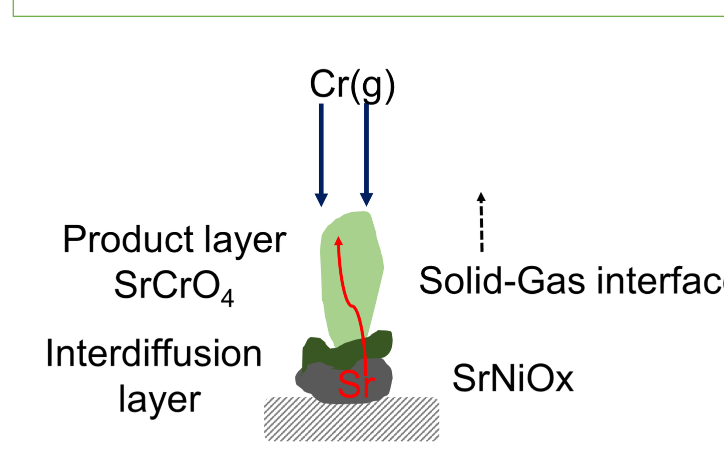




Discussion



- Solid state diffusion is rate limiting
- Dense surface product layer is observed



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

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

Summary

- Phase stability of SrNiOx getters have been investigated in air up to 1000°C.
- Conductive contact paste has been optimized for the application of "In-cell" Cr getter.
- Electrochemical testing of LSM/YSZ/Pt symmetric cells validated the effectiveness of "In-cell getter" in capturing chromium vapor species from IC source.

Acknowledgements

Financial support from USDOE Office of Fossil Energy under grant DE-FE–0023385 is gratefully acknowledged. The authors thank Dr. Jeffery Stevenson (PNNL) and Dr. Rin Burke (NETL) for helpful technical discussion.

Presented at the 18th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting, Pittsburgh, 2017