

# **Novel Composite Materials for SOFC Cathode-Interconnect Contact**

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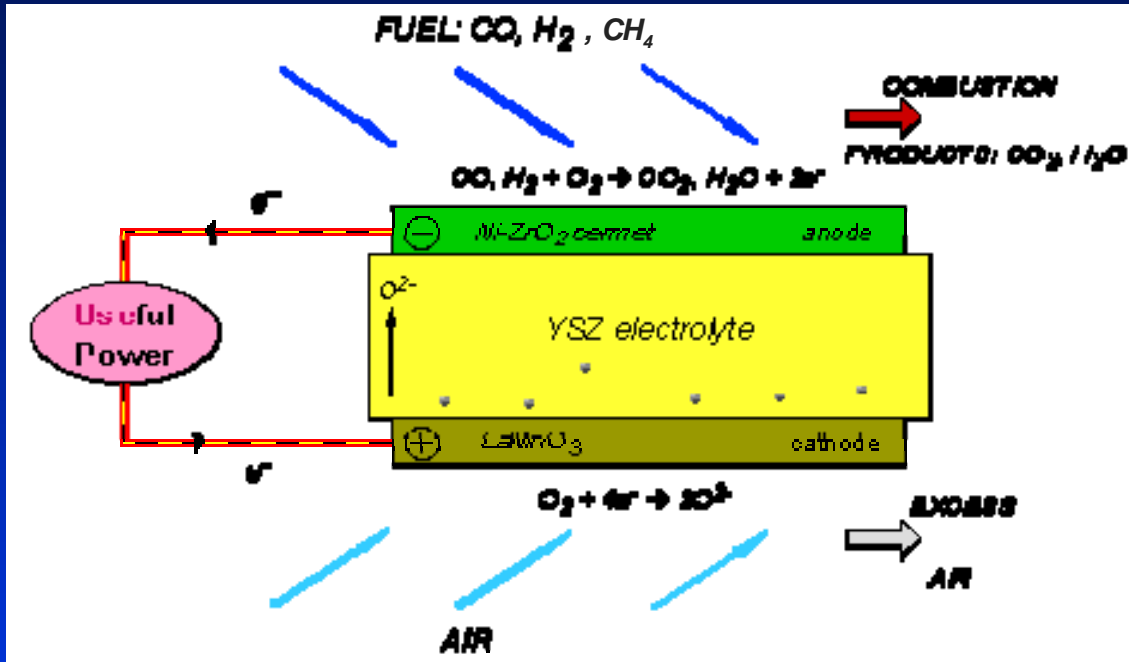
**Presented at UCR Contractors Review Conference, Pittsburgh, PA**  
**June 5-6, 2007**

# Outline

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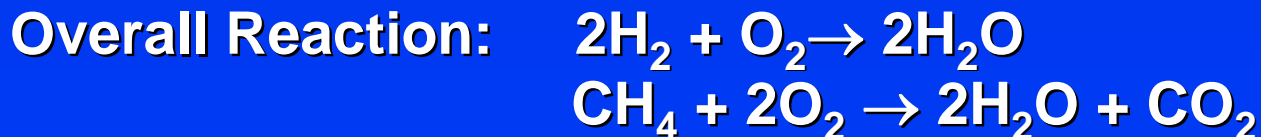
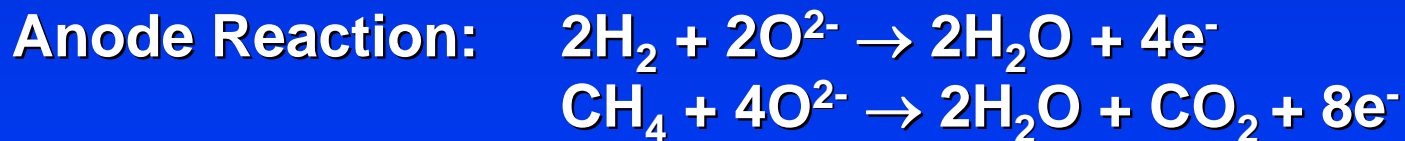
- **Introduction: Electrical Contacts for Solid Oxide Fuel Cell (SOFC) Stacking**
- **Study on the Ag-perovskite Contact Materials**
  - Fundamental study of Ag evaporation
  - Alloy design to mitigate Ag evaporation
  - Evaluation of Ag-perovskite composite materials
- **Concluding Remarks**
- **Acknowledgements**

# Introduction to SOFC

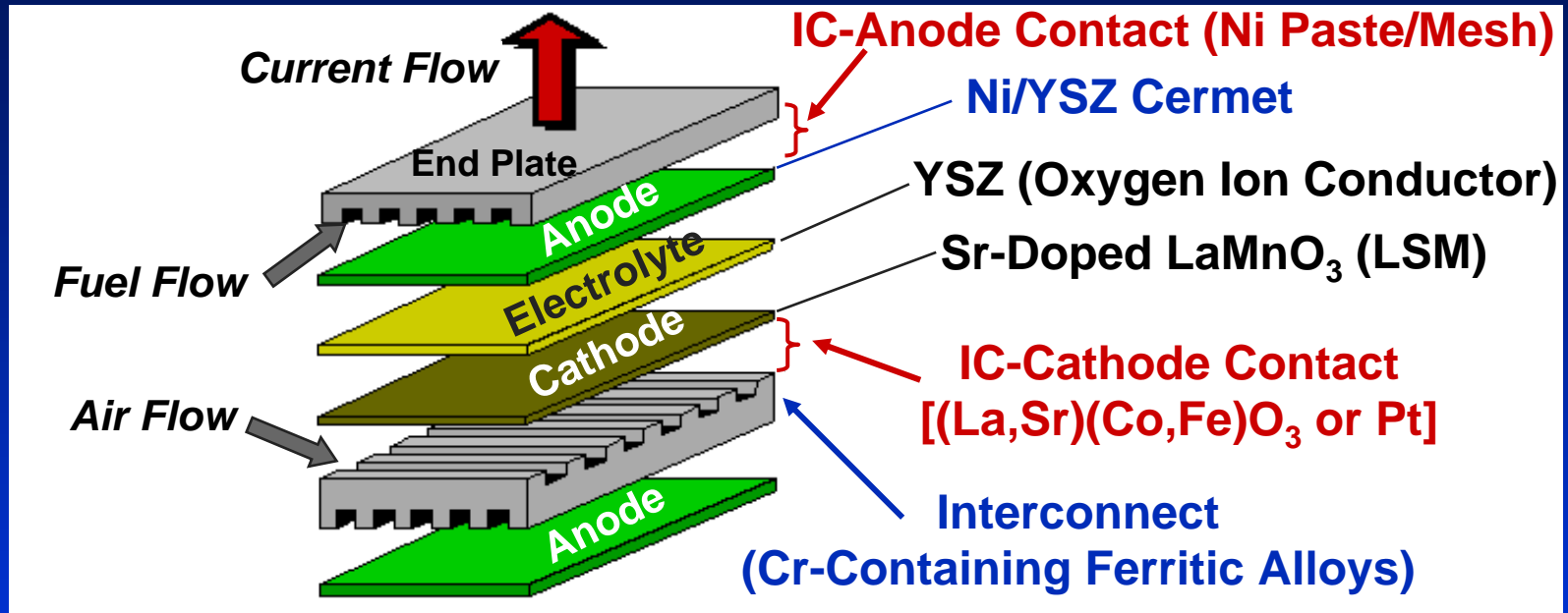


## • Why intermediate-temperature SOFCs?

- Higher efficiency
- Environment-friendliness
- Modular construction
- Fuel flexibility
- Reduced cost and improved durability



# Electrical Contacts in SOFC stacks



- Electrical contact layers are used to reduce the electrode/interconnect interfacial resistance by compensating for the corrugations present on their respective surfaces
- Ni-paste in combination with Ni-mesh is widely used to establish electrical contact between interconnect and Ni+YSZ anode.
- Finding a suitable material for electrical contact between the cathode and interconnect is challenging

# Criteria for Cathode/Interconnect Contact Materials

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- Sufficiently high electrical conductivity over SOFC lifetime
- Reasonable match in coefficient of thermal expansion (CTE) with other cell components
- Chemical stability under high current condition
- Stability with both the interconnect and cathode under oxidizing environment, especially negligible effects on the formation of protective oxides on interconnect alloy
- High sinterability at the SOFC operating temperatures
- Ability to buffer the interactions between interconnect oxide (usually Cr-containing) and electrode oxide
- Tolerance to thermal cycle-induced damage (possible self-healing if thermal cycle-induced cracking occurs in the contact layer)

# State-of-the-Art Contact Materials

- Noble Metals
  - Pt, Pd, and Au (high cost)
  - Ag (relatively low cost)
- Low Melting-Point Ceramics
  - Perovskites based on  $(\text{La,Sr})(\text{Mn,Ni,Co,Fe})\text{O}_3$
- Noble Metal-Ceramic Composite
  - Ag-ceramic composite

One major drawback of Ag is its tendency to evaporate at SOFC operating temperatures

The goal of this project is to develop Ag-perovskite composites with reduced Ag evaporation, ability to absorb Cr from the interconnect, and damage-tolerance for interconnect-cathode contact application.

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# **Ag Evaporation and Ag-Base Alloy Design**

# Ag Evaporation and Striation Formation

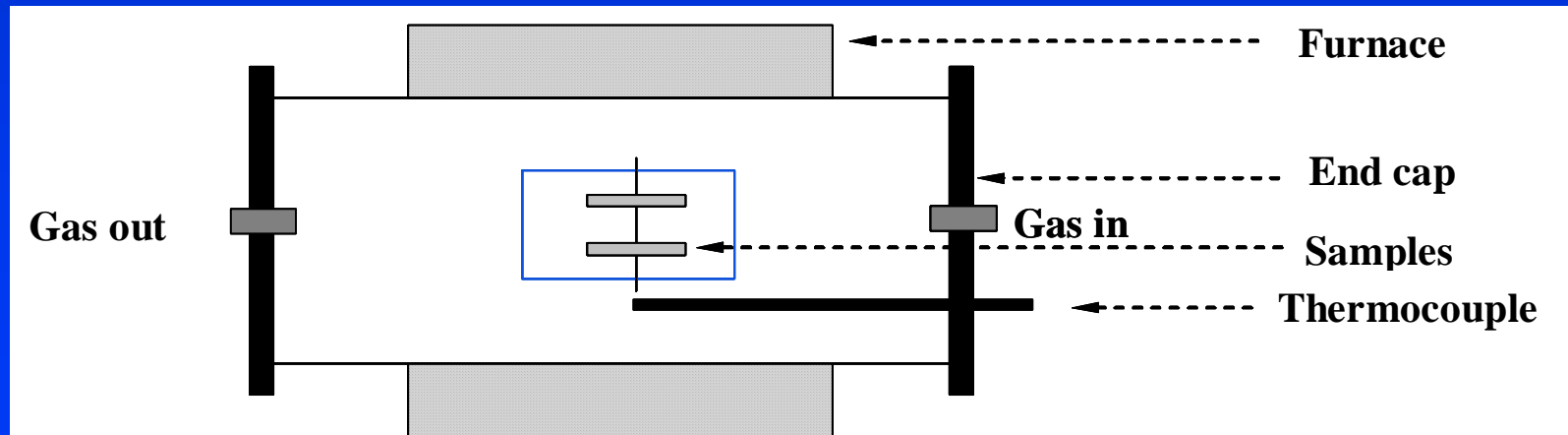
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- The phenomenon has been known since the turn of the century.
- Numerous studies have been carried out on the change of both topography and weight after thermal exposure.
- No solid conclusions have been reached on the mechanism of Ag evaporation
- No systematic data on Ag evaporation under the SOFC working conditions are available.

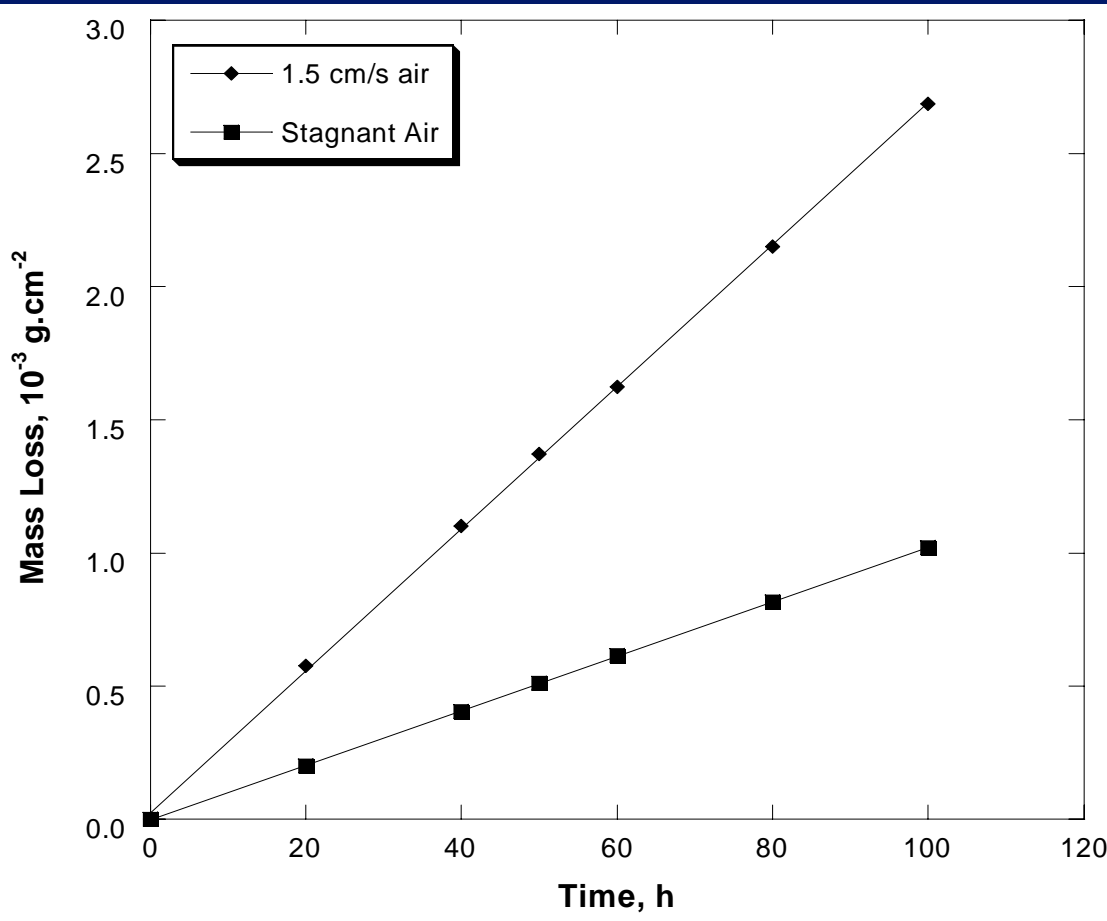


# Sample Preparation & Testing Conditions

- Preparation of Ag samples
  - Commercial 99.95% Ag plate, 1200-grit finish, ultrasonic cleaning
  - Ag-base alloys were prepared by powder or ingot metallurgy
- Testing conditions
  - Evaporation temperature/time
  - Exposure environment (air, Ar+5%H<sub>2</sub> w or w/o 3%H<sub>2</sub>O)
  - Gas flow rate
- The sample weight before and after exposure was measured with a high-accuracy balance; surface morphologies were observed with SEM



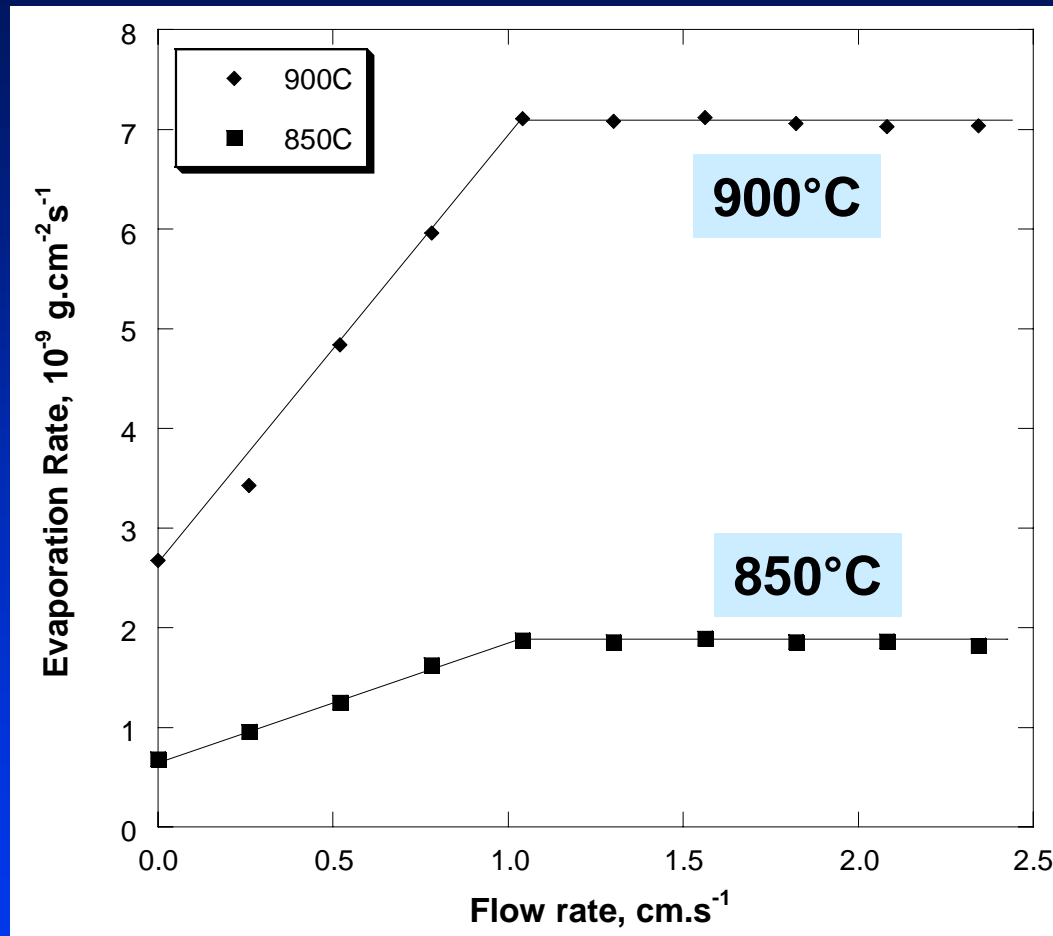
# Effect of Exposure Time on Evaporation



- A linear relationship was found between the mass loss of Ag and the exposure time in air.
  - Can be extrapolated to obtain the amount of Ag evaporation after long-term exposure
- The flowing air increased the evaporation rate of Ag.

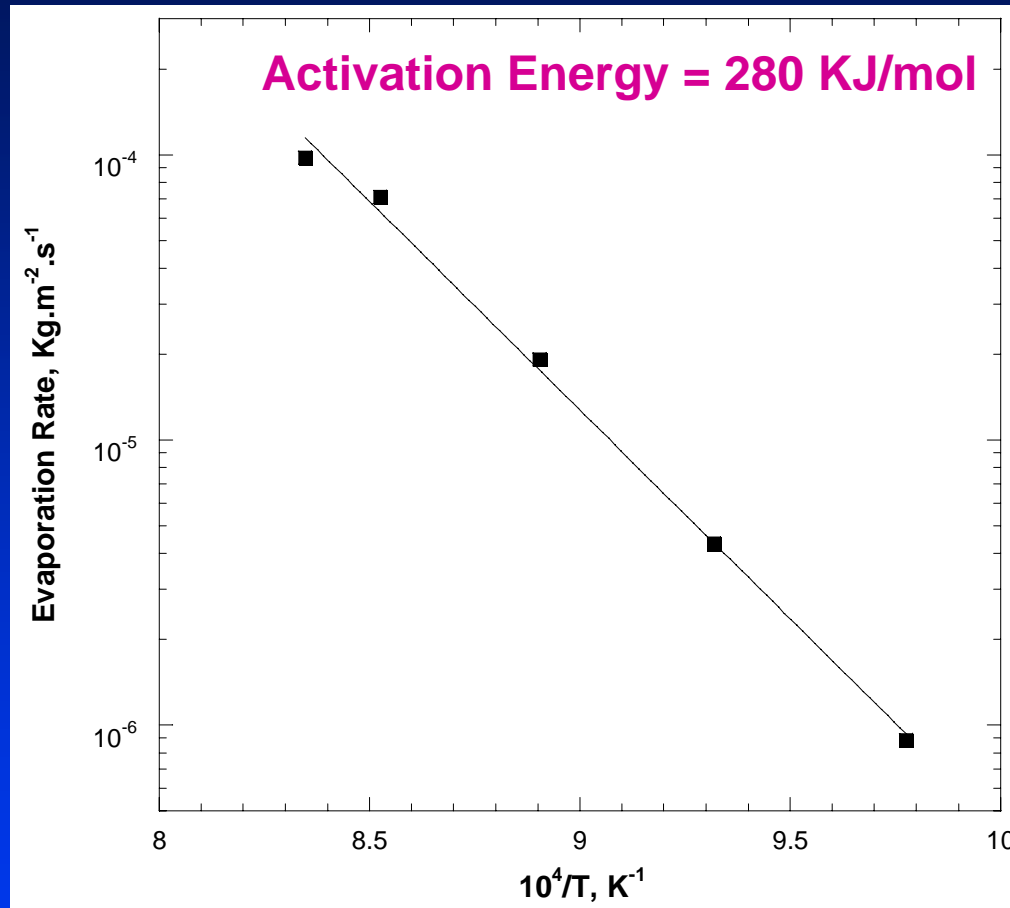
Mass loss of Ag at 900°C in both stagnant air and flowing air with a flow rate of  $1.5 \text{ cm.s}^{-1}$

# Evaporation of Ag: Effect of Air Flow Rate



- With low air flow, Ag evaporation rate increased linearly with the flow rate
- The air flow rate did not affect the Ag evaporation at  $> 1.0 \text{ cm/s}$

# Effect of Temperature on Ag Evaporation



- Activation energy is close to the heat of atomization for pure Ag
- The bonding between the Ag atoms mainly determines the evaporation rate of Ag

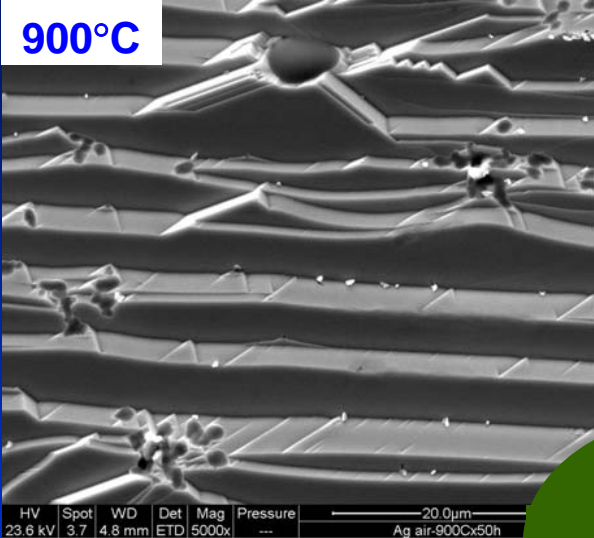
# Effect of Atmosphere on Ag Evaporation

Atmosphere	Flow Rate (cm.s <sup>-1</sup> )	Temperature (°C)	Evaporation Rate (x10 <sup>-9</sup> g.cm <sup>-2</sup> .s <sup>-1</sup> )
Ar+5%H <sub>2</sub> +3%H <sub>2</sub> O	1.5	900	7.12
Ar+5%H <sub>2</sub>	1.5	900	7.06
Air+3%H <sub>2</sub> O	1.5	900	7.22
Air	1.5	900	7.11

- The exposure atmospheres showed no measurable influence on the evaporation rate of Ag at 900°C.
- The essentially same evaporation rate in different environments indicates that the exposure atmosphere is not involved in the critical step that controls the Ag evaporation kinetics.
- The effect of atmosphere on Ag evaporation at lower temperatures are currently being evaluated.

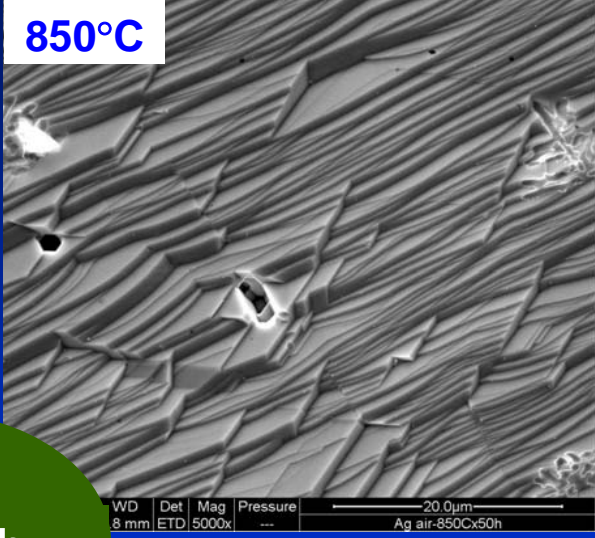
# Different surface morphologies were observed after evaporation test in oxidizing and reducing environments

900°C



HV 23.6 kV Spot 3.7 WD 4.8 mm Det ETD Mag 5000x Pressure --- 20.0µm Ag air-900Cx50h

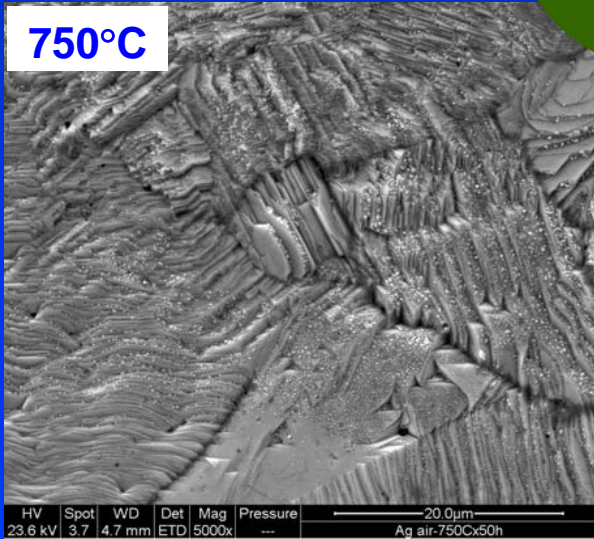
850°C



WD 8 mm Det ETD Mag 5000x Pressure --- 20.0µm Ag air-850Cx50h

Air, 50 h

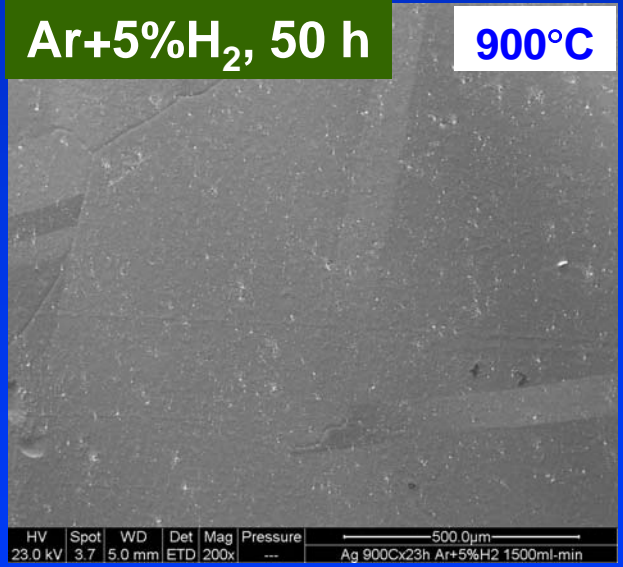
750°C



HV 23.6 kV Spot 3.7 WD 4.7 mm Det ETD Mag 5000x Pressure --- 20.0µm Ag air-750Cx50h

Ar+5%H<sub>2</sub>, 50 h

900°C



HV 23.0 kV Spot 3.7 WD 5.0 mm Det ETD Mag 200x Pressure --- 500.0µm Ag 900Cx23h Ar+5%H2 1500ml-min

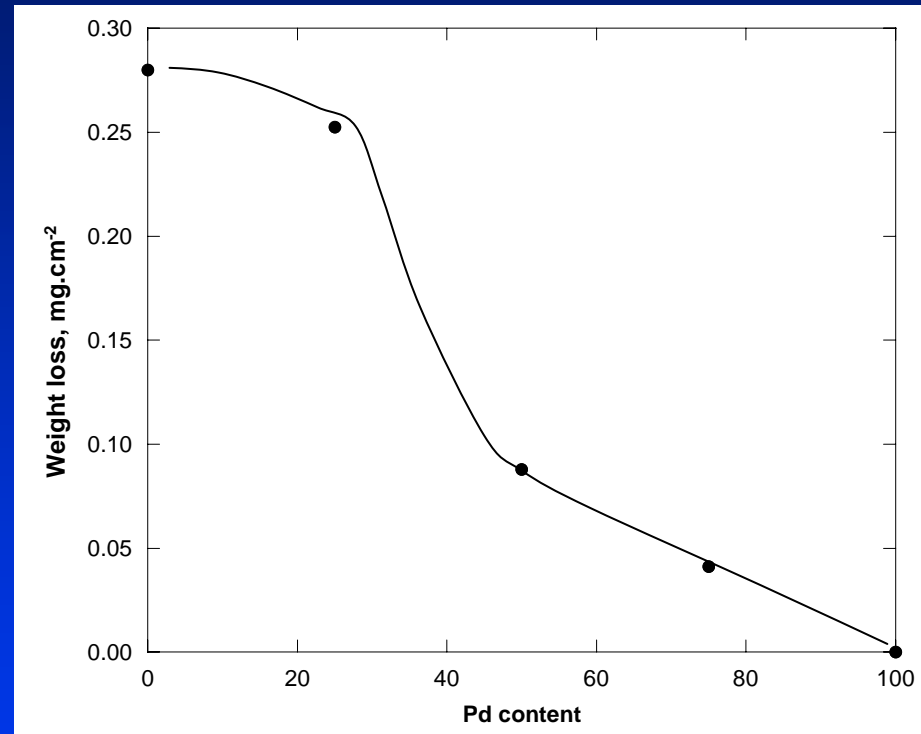
# Plausibility of Ag as Cathode-Interconnect Contact

- At 800°C and air flow rate of 1.1 cm/s, the evaporation rate of pure Ag is  $4 \times 10^{-10} \text{ g.cm}^{-2}.\text{s}^{-1}$
- Considering the SOFC target lifetime of 40,000 h, this value is too high (0.06  $\text{g.cm}^{-2}$  or 60  $\mu\text{m}$ )
- Since Ag evaporation is determined by the bonding of Ag atoms, alloy design should focus on identifying:
  - Alloying elements that drastically affect the bonding in Ag
  - Surface-active elements that block the surface Ag sites

While binary alloys with large difference in melting point between the two elements are made by powder metallurgy, other alloys are made by arc-melting and drop-casting.

# Effect of Noble Metal Additions on Ag Evaporation

- With the addition of 25%Pt, Au, and Pd, some reduction in Ag evaporation rate in the range of 10-30% was observed for all the alloying elements.
- As the Pd content increased in the alloys, the Ag evaporation rate dropped consistently.
- Additions of the noble metals (Pt, Au, and Pd) were not practical due to high cost of the raw materials



Weight losses of various Ag-Pd alloys after thermal exposure at 850°C for 40 hours in air with a flow rate of 1.5 cm.s<sup>-1</sup>

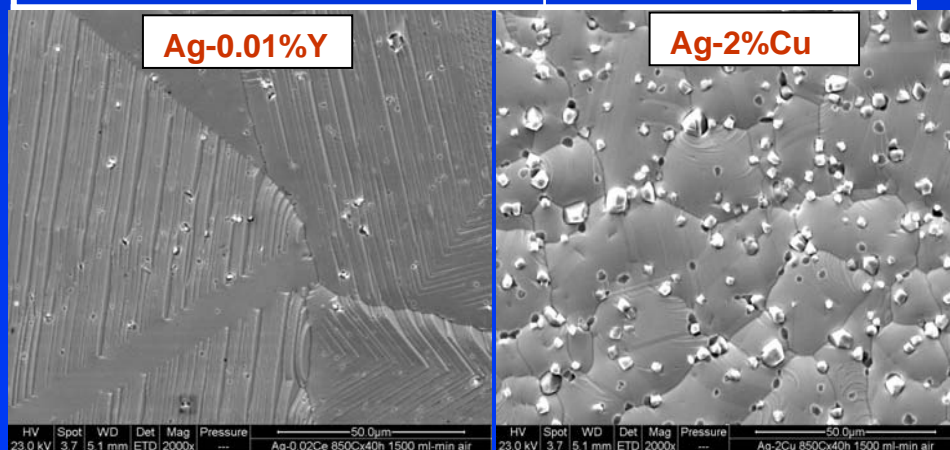


# Effect of Other Metal Additions on Ag Evaporation

- Micro-alloying with non-noble elements Cu, Ce, and Y turned out to have very little effect on the evaporation of Ag.
- All these Ag alloys exhibited a very similar weight loss, which was close to that of pure Ag. The Ag alloys with Ce and Y additions even showed a slightly larger weight loss than pure Ag.
- With the additions of Y and Ce, very fine metal oxide particles were formed on the surface of the Ag alloys, while the  $\text{Cu}_2\text{O}$  particles formed on the Ag-Cu alloys were much larger in size.
- About 20 new alloys have been prepared and are being studied.

Weight losses of Ag-base alloys after thermal exposure at 850°C for 40 hours in air with a flow rate of 1.5 cm.s<sup>-1</sup>

Alloy Composition (wt.%)	Weight Loss (mg.cm <sup>-2</sup> )
Ag	0.28
Ag-0.5%Cu	0.30
Ag-2%Cu	0.30
Ag-0.02%Ce	0.29
Ag-0.05%Ce	0.35
Ag-0.1%Y	0.33



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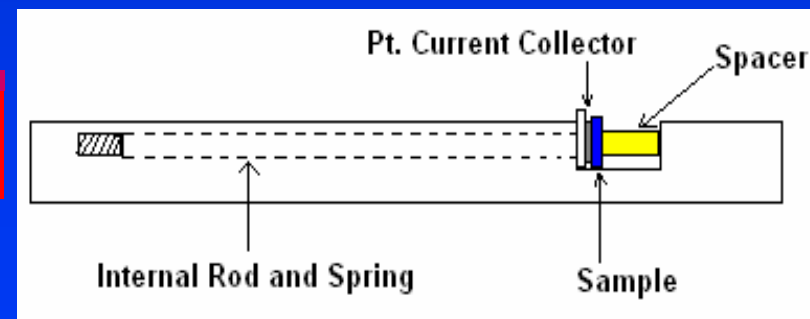
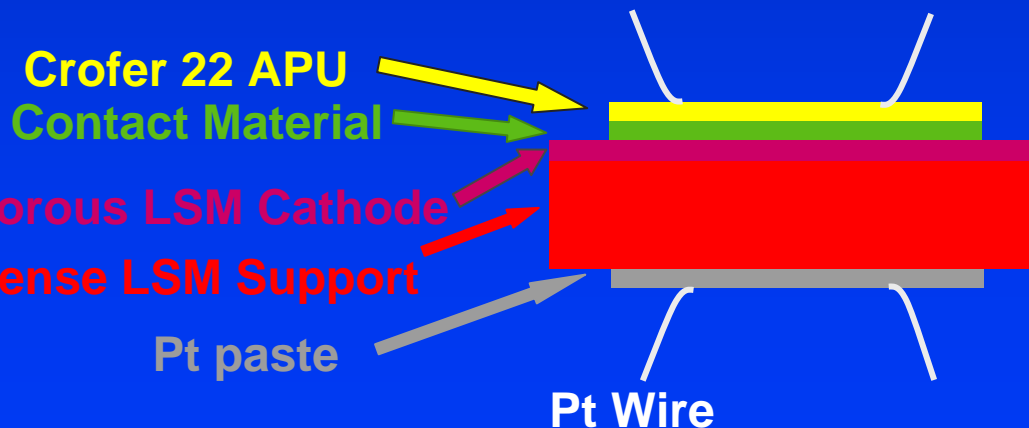
# **Ag-Perovskite Composites as SOFC Contact Materials**

# Why Ag-Perovskite Composite as Contact Material?

- Ag-perovskite composites might combine the attributes of the perovskite phases (e.g. the Cr-absorbing characteristics particularly for the Co-containing perovskites) and Ag (e.g. the excellent electrical and mechanical properties, and relatively low cost). For this initial evaluation,
  - Ag will be used as the noble metal component of the composite material. Ag does have a tendency to migrate through the cell at operating temperatures, but with alloying additions this evaporation might be mitigated. In addition, this effect may be less pronounced when used in a composite.
  - The perovskite chosen for use in the composite is  $(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_3$  (LSCF). This material is chosen for its good sintering characteristics at low temperature, good conductivity at low temperatures, etc.

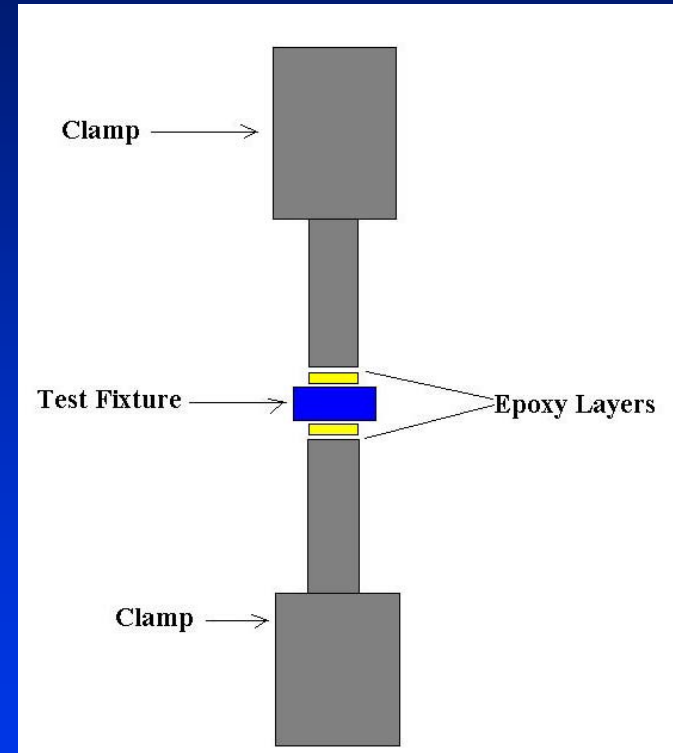
# Experimental Details

- A number of Ag-LSCF composites with the Ag contents of 0, 25, 50, 75, and 100% (in volume) in the composite have been processed and interconnect/contact/cathode test cells with the Ag-perovskite composites as contact material have been constructed.
- The test cells were placed in the spring-loaded alumina rig to apply a small compressive load throughout testing, of  $\sim 0.2 \text{ kg/cm}^2$ .
- The change in area-specific resistance (ASR) was recorded as a function of exposure time and thermal cycling. Data collection was achieved using the four-point method with the four Pt leads.



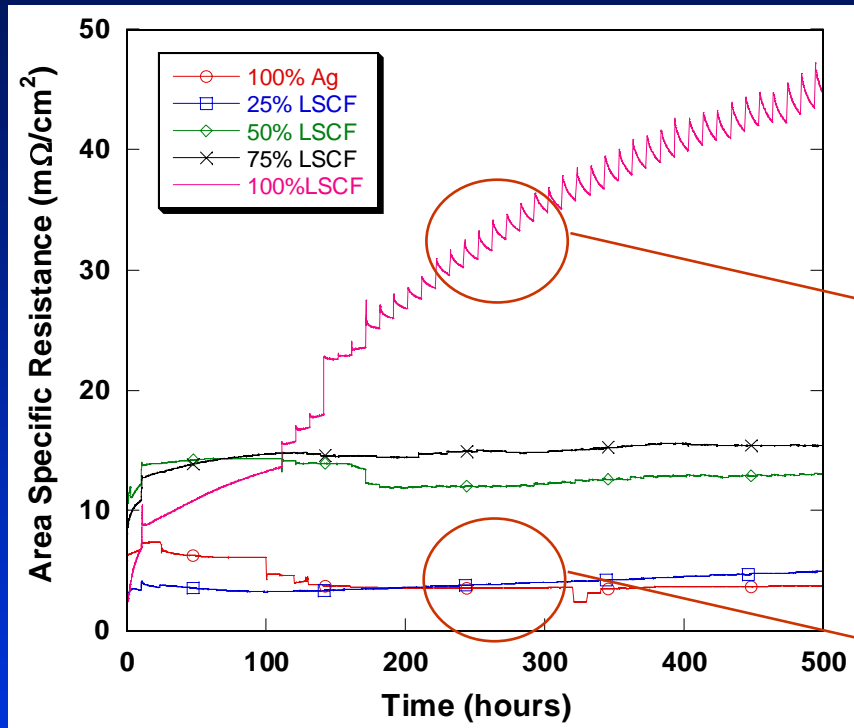
# Experimental Details (Cont'd)

- Using another set of cells, the adhesive strength of the contact layer was determined. After a 10 hour sintering treatment at 850°C and a 100 break-in period at 800°C, the cells are thermally cycled 10 times between 800° (with a holding time of 10 hours) and 250°C.
- The cells were carefully bonded to custom-built mounts and then pulled apart.
- The force required to accomplish this was recorded and the adhesion strength was calculated.



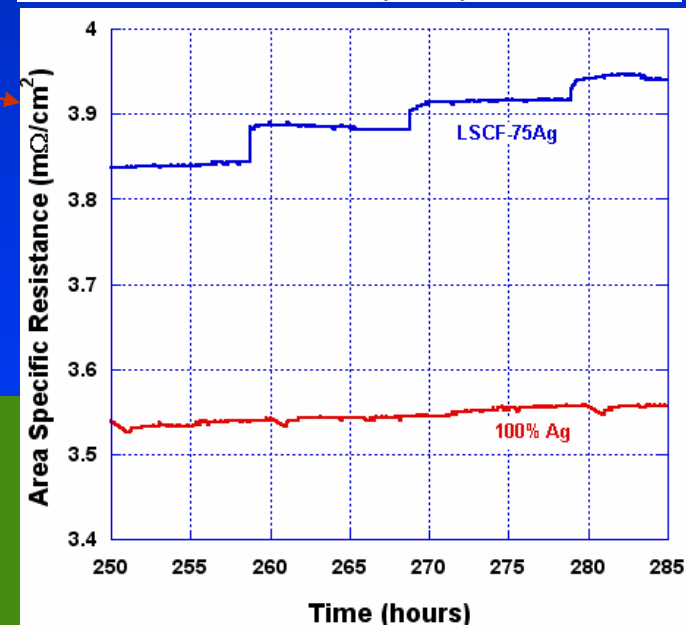
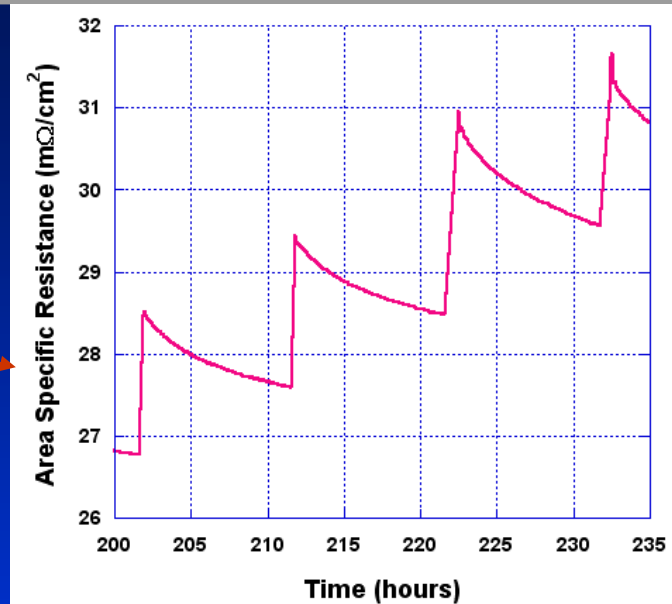
**Pull Test Fixture**

# As Ag content increased in the composite, the ASR decreased correspondingly

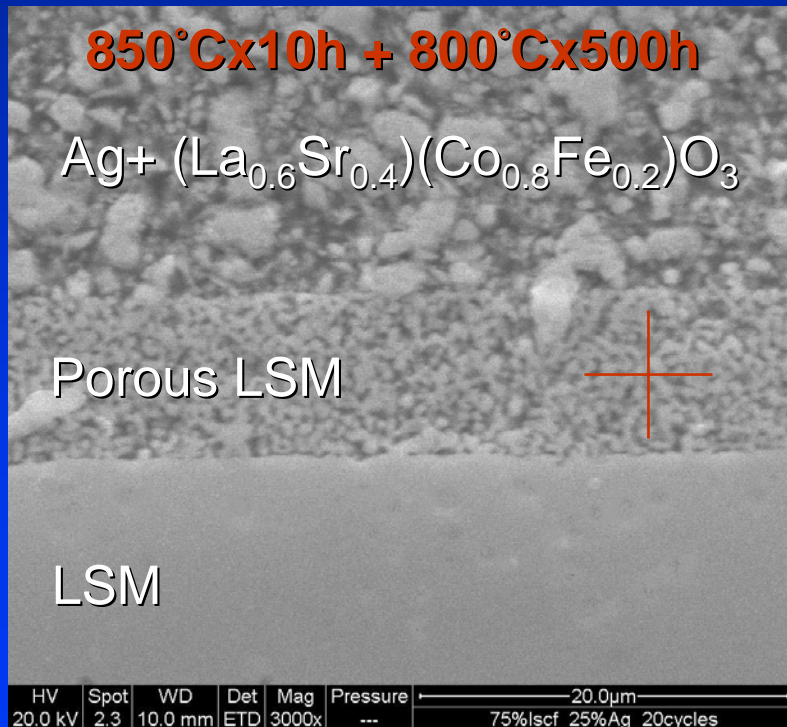
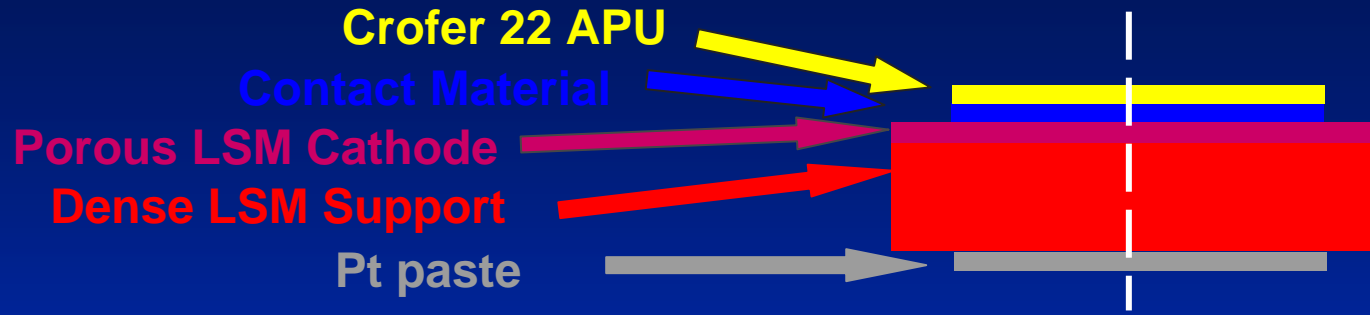


ASR change during thermal cycling (initial firing of  $850^\circ\text{C}\times 10\text{h}$ ; “break-in” of  $800^\circ\text{C}\times 100\text{h}$ ; 40 cycles with  $800^\circ\text{C}\times 10\text{h}$  holding plus furnace cooling to  $250^\circ\text{C}$ )

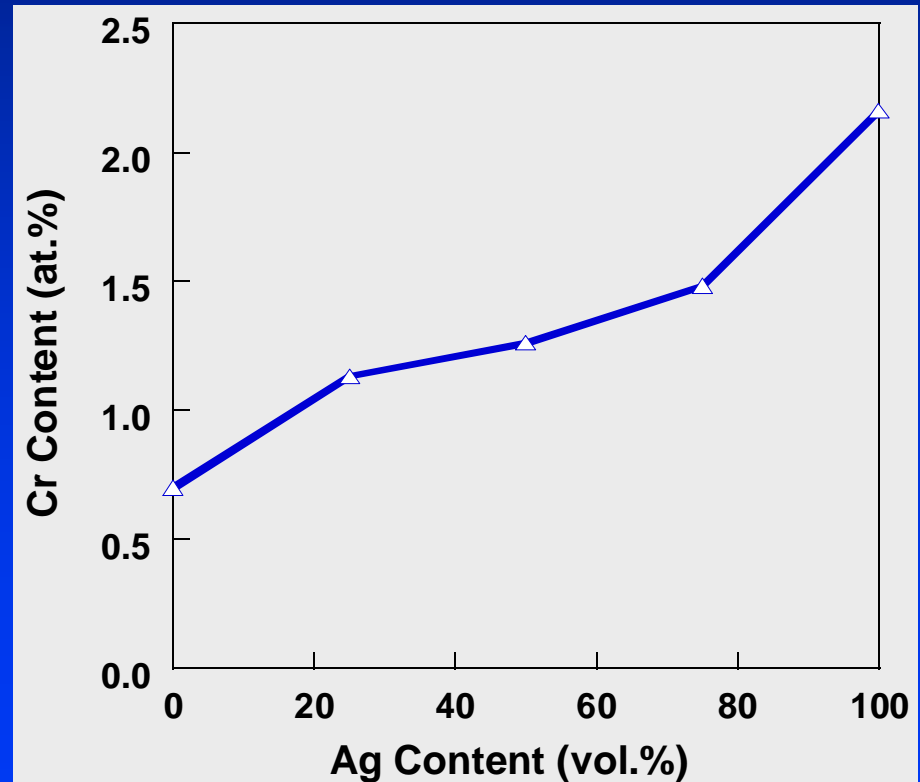
- Less damage was observed during thermal cycling for Ag-containing contact materials
- Some “self-healing” was observed for LSCF



# With the increase of LSCF in the contact layer, Cr migration to the cathode was reduced



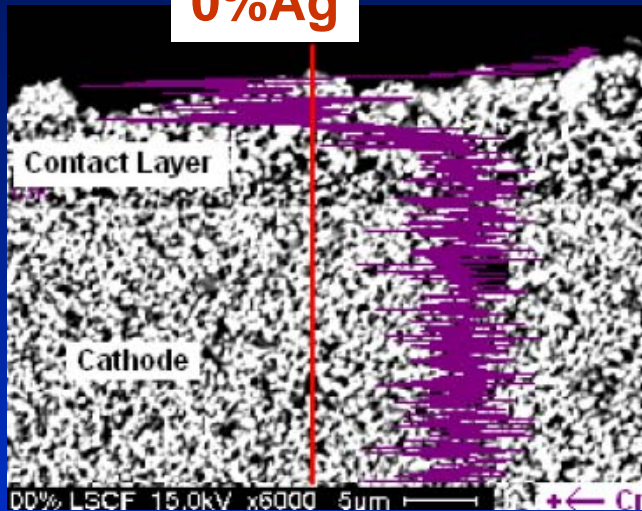
Cross-Sectional View



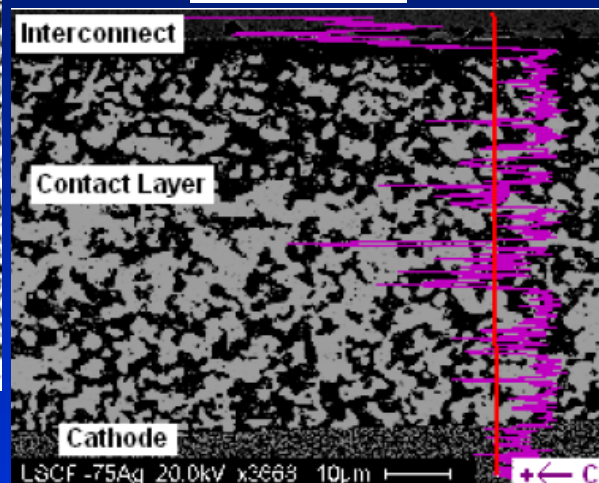
Cr Content in the Porous LSM Layer

# The perovskite phase in the contact layer acted as a “sponge” to absorb the migrating Cr species

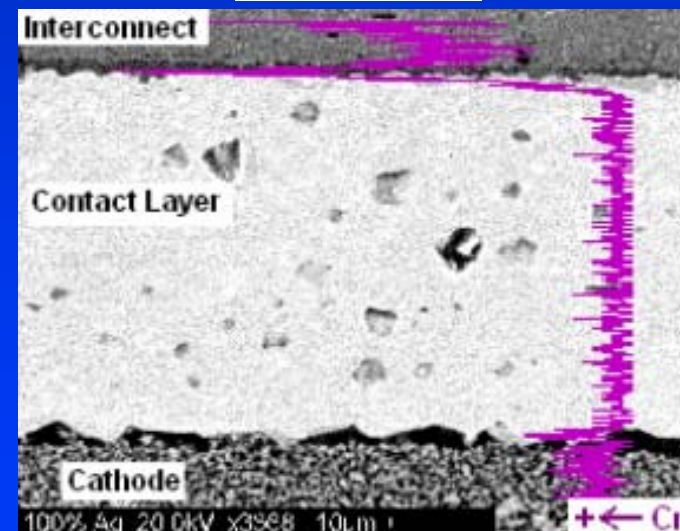
0%Ag



75%Ag



100%Ag



Cross-Sectional View and EDS Line Scanning of Cr Content



# Pull Test Results

## Adhesion Strengths of Different Contact Materials

Contact Material	Adhesion Strength (MPa)	Failure Location
100%Ag-0%LSCF	3.1	Cathode/contact interface
75%Ag-25%LSCF	2.01	Cathode/contact interface
50%Ag-50%LSCF	0.2	Both interfaces
25%Ag-75%LSCF	Fractured during mounting	Interconnect/contact interface
0%Ag-100%LSCF	Fractured after cycling	Interconnect/contact interface

- As the Ag content increased in the contact layer, the adhesion strength increased correspondingly due to the high ductility of Ag and its ability to accommodate thermal stresses.

# Concluding Remarks

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- The effects of various experiment conditions such as exposure temperature/time, air flow rate, and exposure atmospheres were investigated. Based on the experimental results, the evaporation of Ag was mainly determined by the bond strength between the Ag atoms.
- Pure Ag is not suitable for SOFC contact application because of its excessive evaporation. However, alloying with other elements might reduce its evaporation rate.
- The Ag-LSCF composite materials offer the potential to combine the attributes of Ag and the perovskite phase, therefore deserving further evaluation.

# Acknowledgements

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- This research was sponsored by Department of Energy (DOE) UCR Program under Grant # DE-FG26-05NT42533, Dr. Ayyakkanna Manivannan, Project Manager, DOE/NETL.
- Part of this work was also supported by The National Science Foundation under Grant # DMR-0238113 as well as the Center for Manufacturing Research, Tennessee Technological University.
- Contributions to experimental work from the following at TTU: Shujiang Geng, Brian Bates, Wayne Hawkins, and Jacky Shoulders