# 1. Electrode Studies at High Pressure
# 2. LSM Sintering at Low Temperature

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# Objectives and Approach –Electrode Studies at High Pressure

- Objectives: Determine how activation and concentration polarization losses for SOFC electrodes are affected by operation at elevated pressures – pressure effects identified as priority (*Surdoval*, *7th Annual SECA Workshop, 2006*).
- Approach:
  - Pressure vessel: 130 bar maximum pressure, internal furnace maximum temperature ~950°C, flowing gas maintained across electrode surfaces, shielded leads
  - Cathode compositions evaluated: LSM, LSM/ceria, LSF, Au
  - Electrochemical evaluation: electrochemical impedance spectroscopy (EIS) and DC methods
- Conclusion: All cathodes studied improved with increased pressure, ranging from a $P^{1/4}$ to $P^{1/2}$ dependence

# Background – High Pressure Electrode Studies

- Efficiency advantages have been projected for an SOFC/gas turbine hybrid fueled by coal gas at elevated pressures (~3-15 bar) (*e.g. Strakey, 7th Annual SECA Workshop, 2006*)
- Elevated pressure operation leads to enhanced SOFC stack performance – more than can be accounted by Nernst effects alone (*e.g. Minh, 7th Annual SECA Workshop, 2006*)
- Relatively few studies address electrode performance at elevated pressures (many at P≤1 atm, however). On the cathode side:
  - For cathode-supported cells, Virkar et al. (*DOE/FETC/C-98/7303, CONF-9704176, 1997)* concluded that increased pressure led to a lowering of cathodic concentration polarization following a 1/P dependence
  - LSM electrodes improved with $P(O_2)$ up to ~20 bar at 750$^oC$, with no further improvement at higher pressures (*Drevet et al. Solid State Ionics 2000;136:807*), using EIS to study symmetric cells at open circuit.
- On the anode side:
  - A minimum anodic concentration polarization at 5 bar in coal gas was projected by Gemmen and Trembly (*J Power Sources 2006; 161:1084*). The $H_2$ concentration is expected to reach a maximum at 8 bar.
  - Kikuchi et al. determined experimentally that concentration polarization <u>rose</u> with $P(H_2+H_2O)$ to at least 10 bar for a Ni/YSZ anode on YSZ (*Solid State Ionics 2004;174:111*). Activation polarization was independent of pressure.

# Models for Cathodic Pressure Dependence

- Electrode parameters determined from Butler-Volmer equation:

$$I/I_o = \exp(\alpha_a F\eta / RT) - \exp(-\alpha_c F\eta / RT)$$

where $\alpha_a$, $\alpha_c$ are anodic and cathodic charge transfer coefficients, $I_o$ is the exchange current, and η is the polarization loss

- Activation polarization trends depend on ability of electrode to continue to adsorb oxygen. If surface sites are nearly or completely filled with oxygen adatams at high pressure (Pt is an example), performance should decrease with pressure:

$$R_{CT} \approx 1/I_o \approx (P_{O_2})^{\alpha_c/2(\alpha_a+\alpha_c)}$$ (dissociative model)

If $\alpha_a \approx \alpha_c$, charge transfer resistance shows a +1/4 dependence.

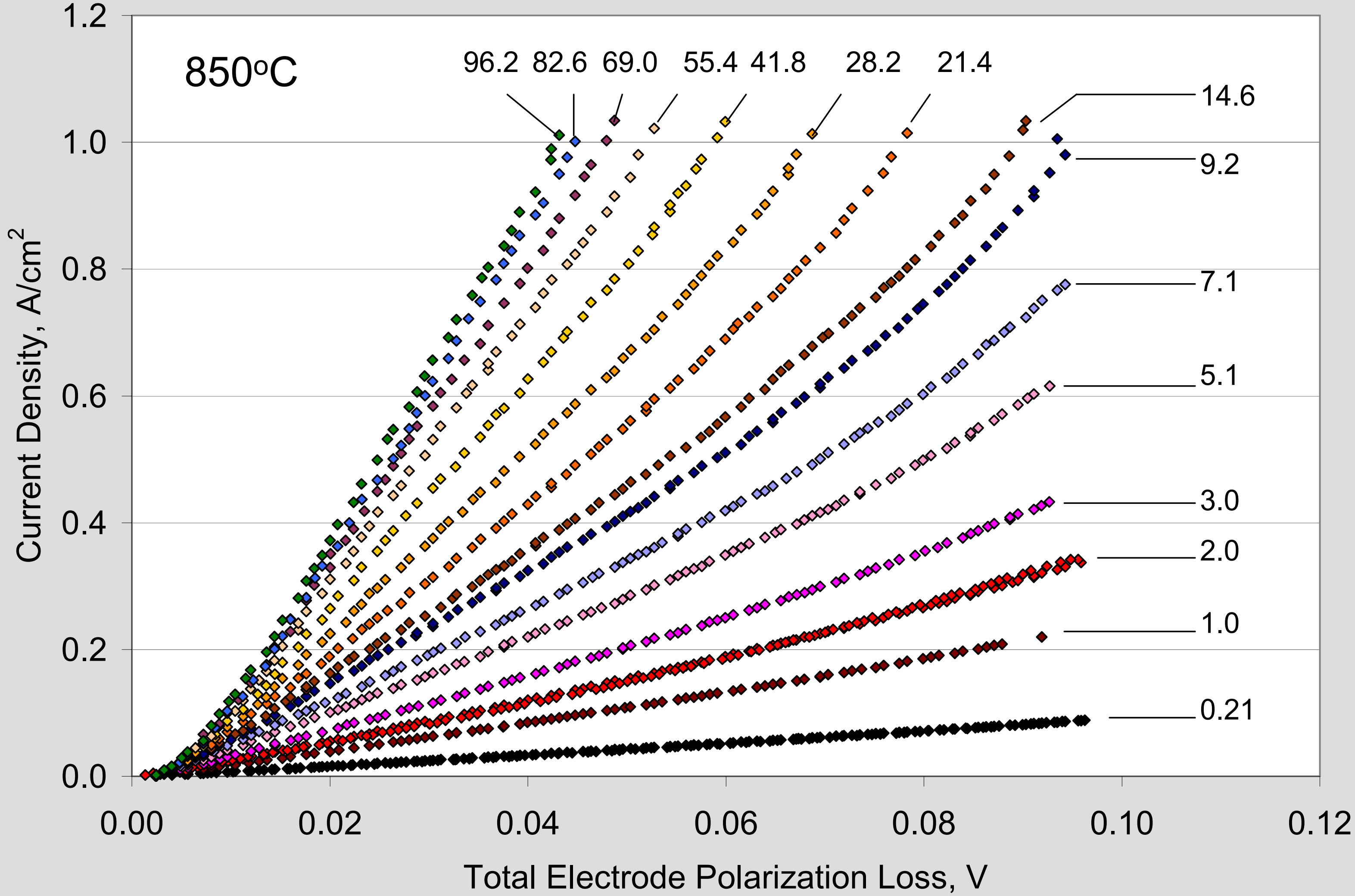
- If few adsorption sites are filled (usually at low pressure), performance should increase with pressure, yielding a -1/4 $PO_2$ dependence is expected if $\alpha_a \approx \alpha_c$ (-1/2 for associative model)

$$R_{CT} \approx 1/I_o \approx (P_{O_2})^{-\alpha_a/2(\alpha_a+\alpha_c)}$$ (dissociative model)

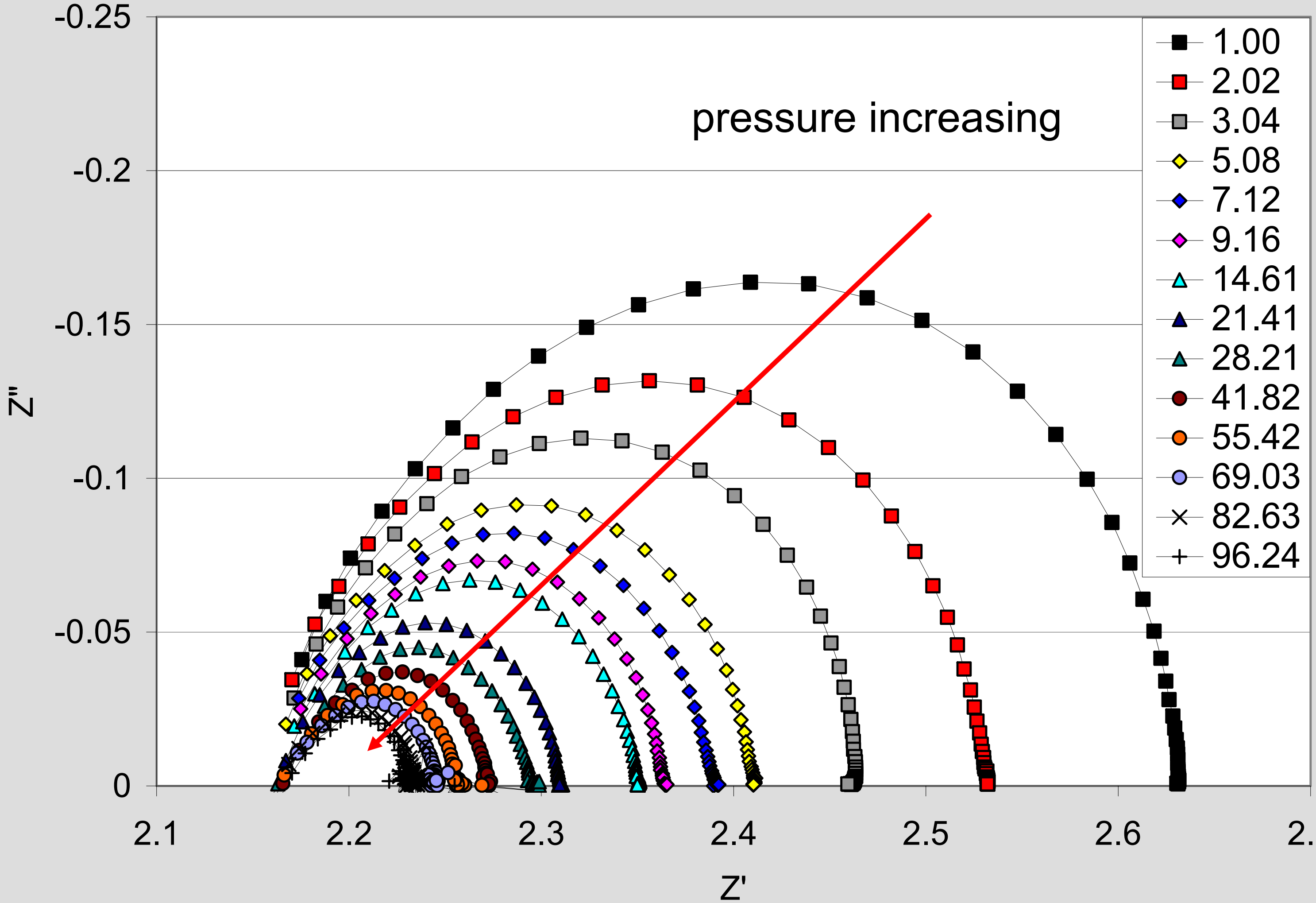
- Langmuir adsorption isotherm (dissociative):

$$\theta = \frac{K_{ad} P_{O_2}^{1/2}}{1 + K_{ad} P_{O_2}^{1/2}}$$

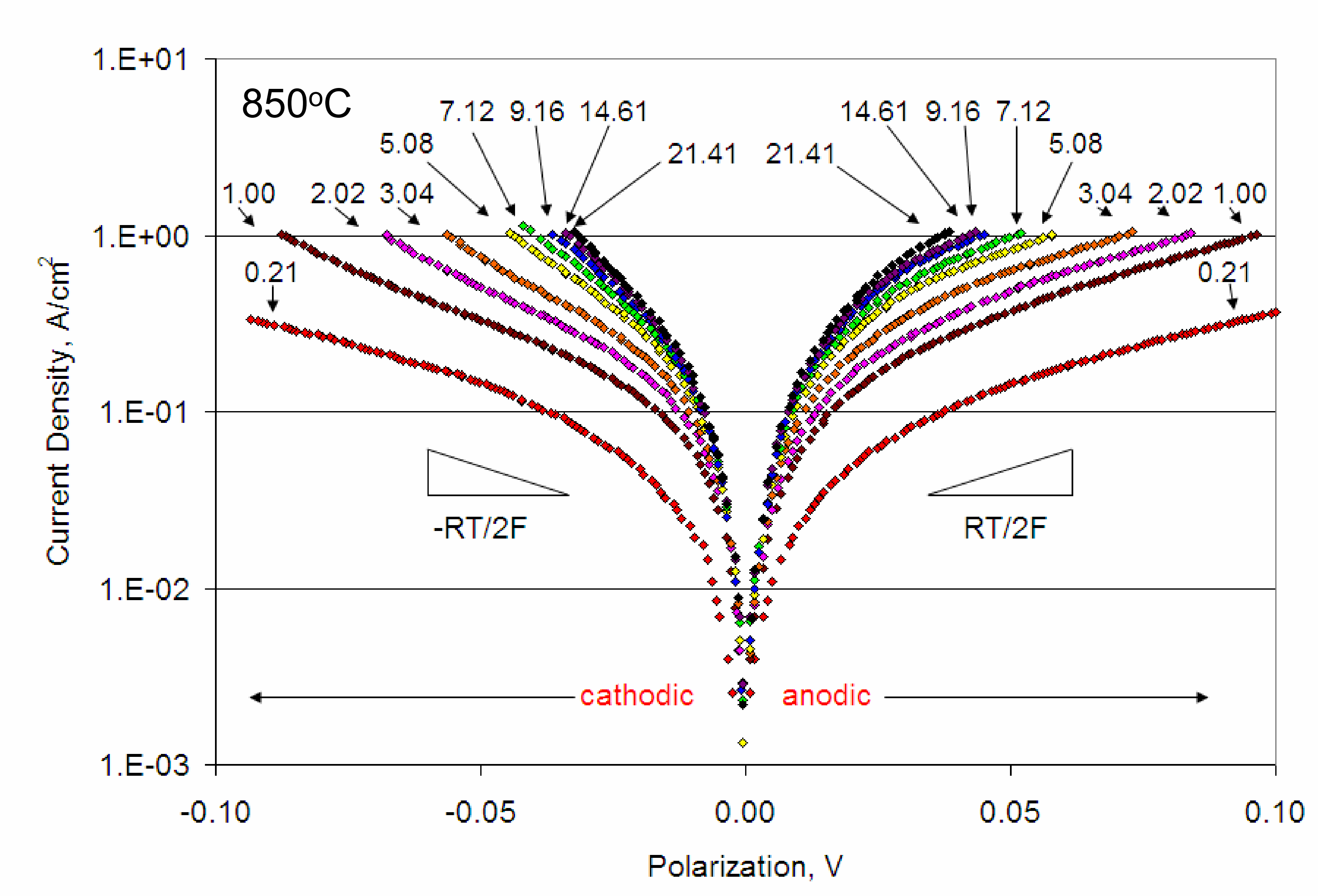
# Polarization Curves for Symmetric LSM-20/ YSZ/LSM-20 Cell at Various Oxygen Pressures



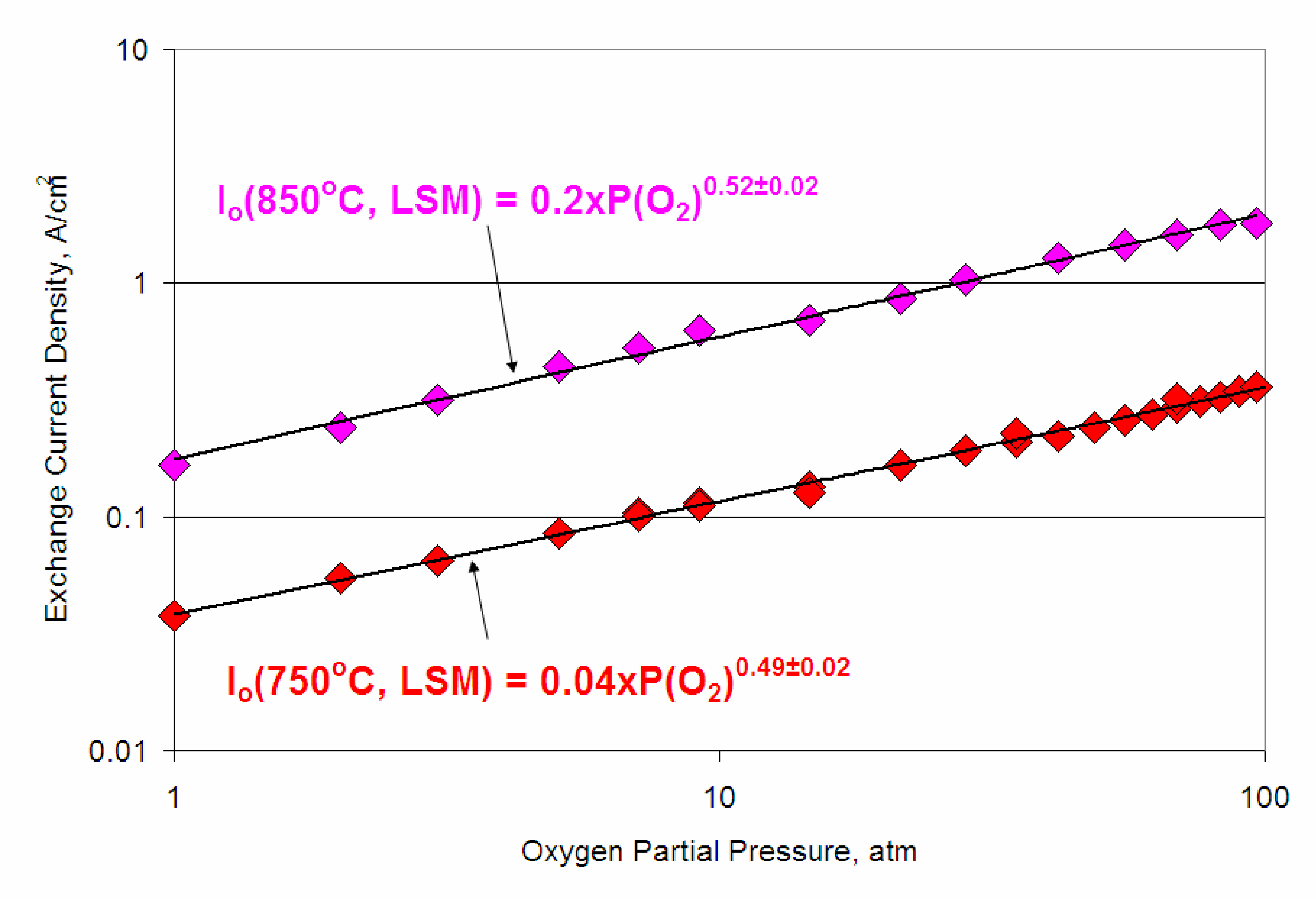
# EIS Shows Diminished LSM-20 Electrode Losses with Increased Oxygen Partial Pressure; Ohmic Contributions are Constant (OCV)



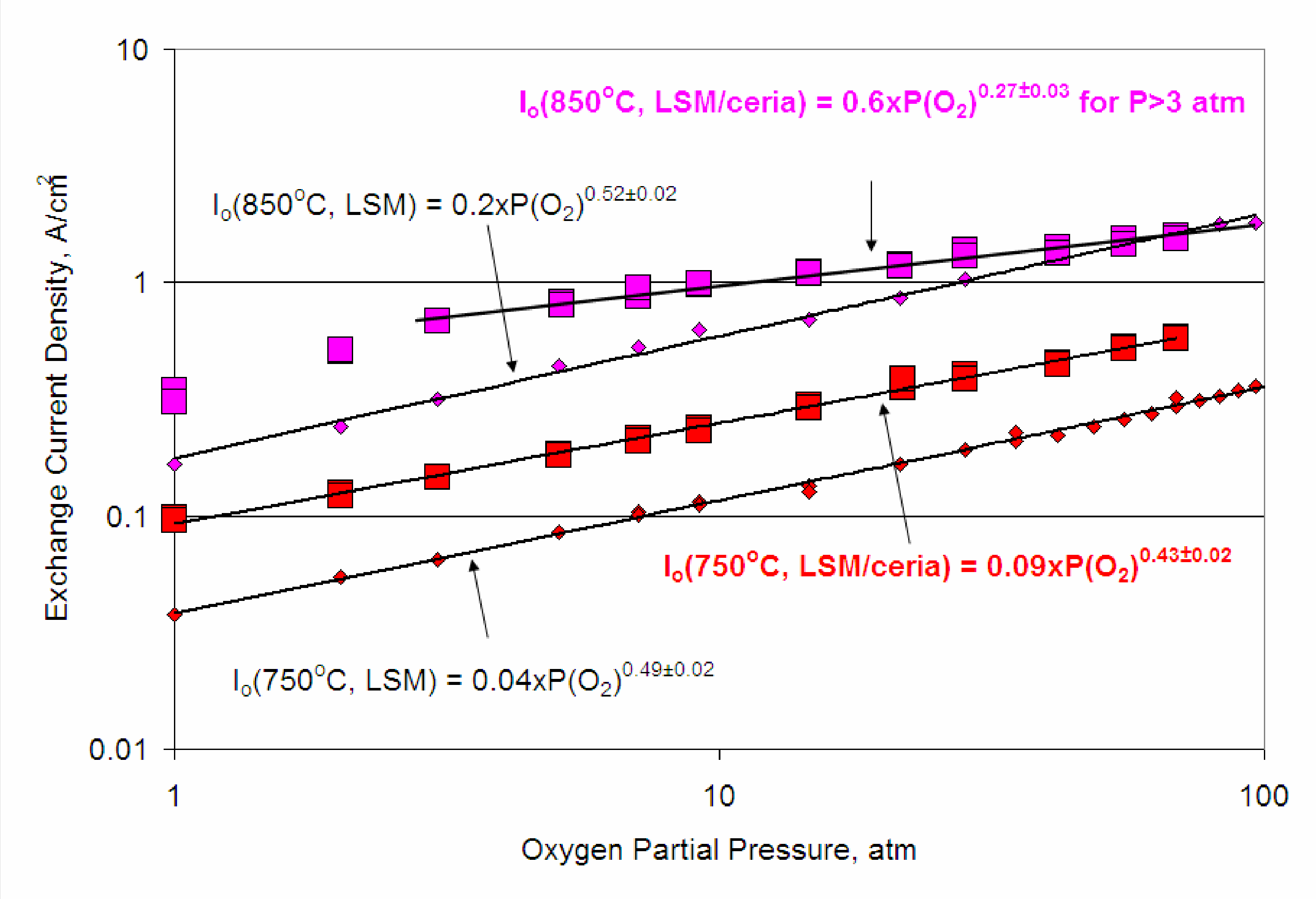
# Half-Cell Measurements for LSM-20/YSZ Show Symmetric Cathodic and Anodic Performance



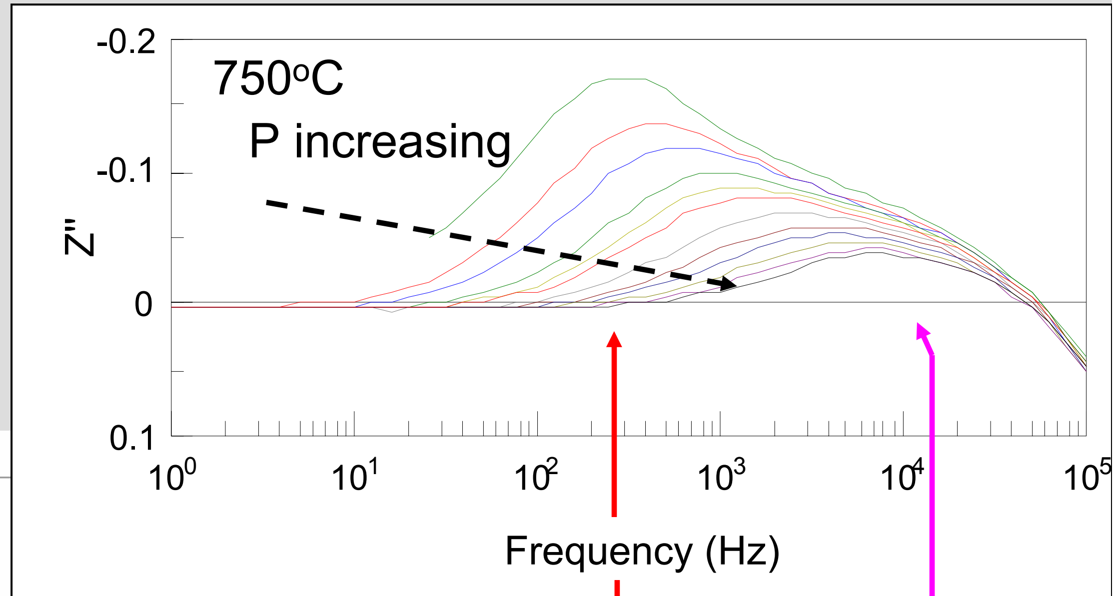
# Performance of LSM-20 Improves as $P(O_2)^{1/2}$ Over Wide Pressure Range in Oxygen

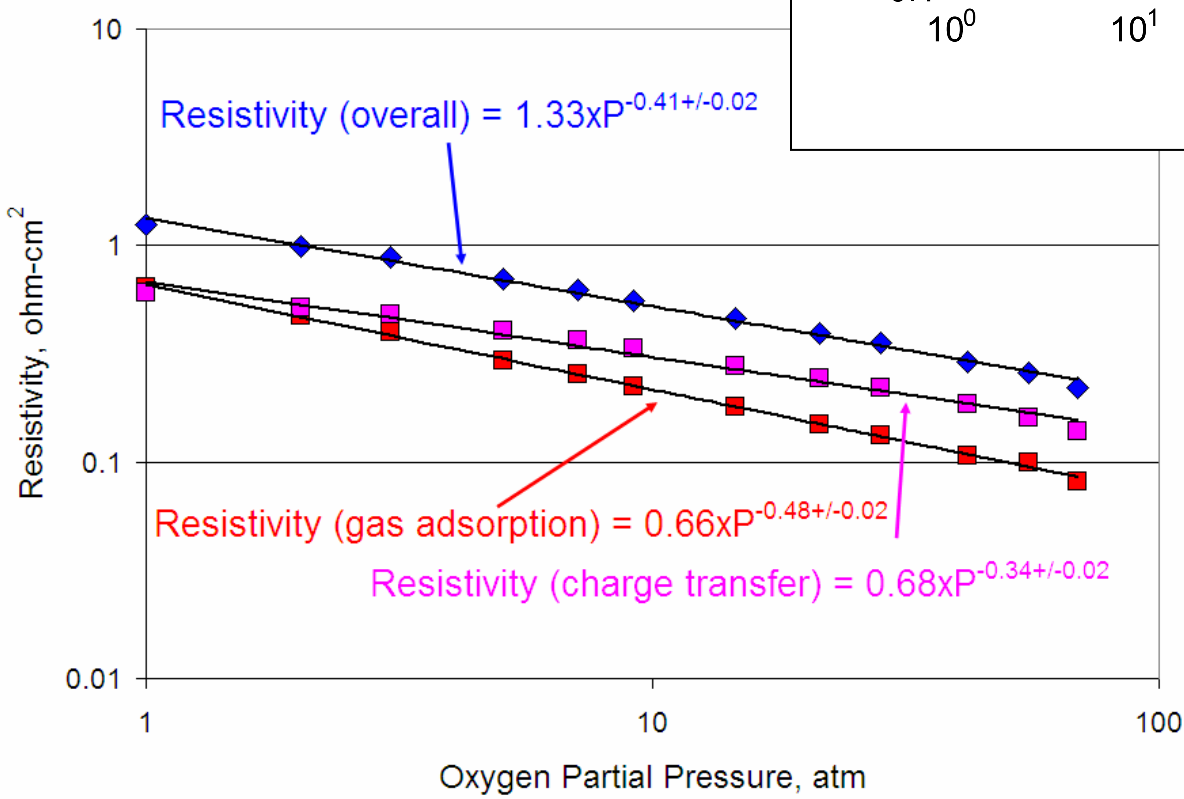


# Smaller $P(O_2)$ Dependence Found for Mixed-Conducting LSM-Ceria Composite



# EIS Results for LSM-Ceria – Gas Adsorption versus Charge Transfer

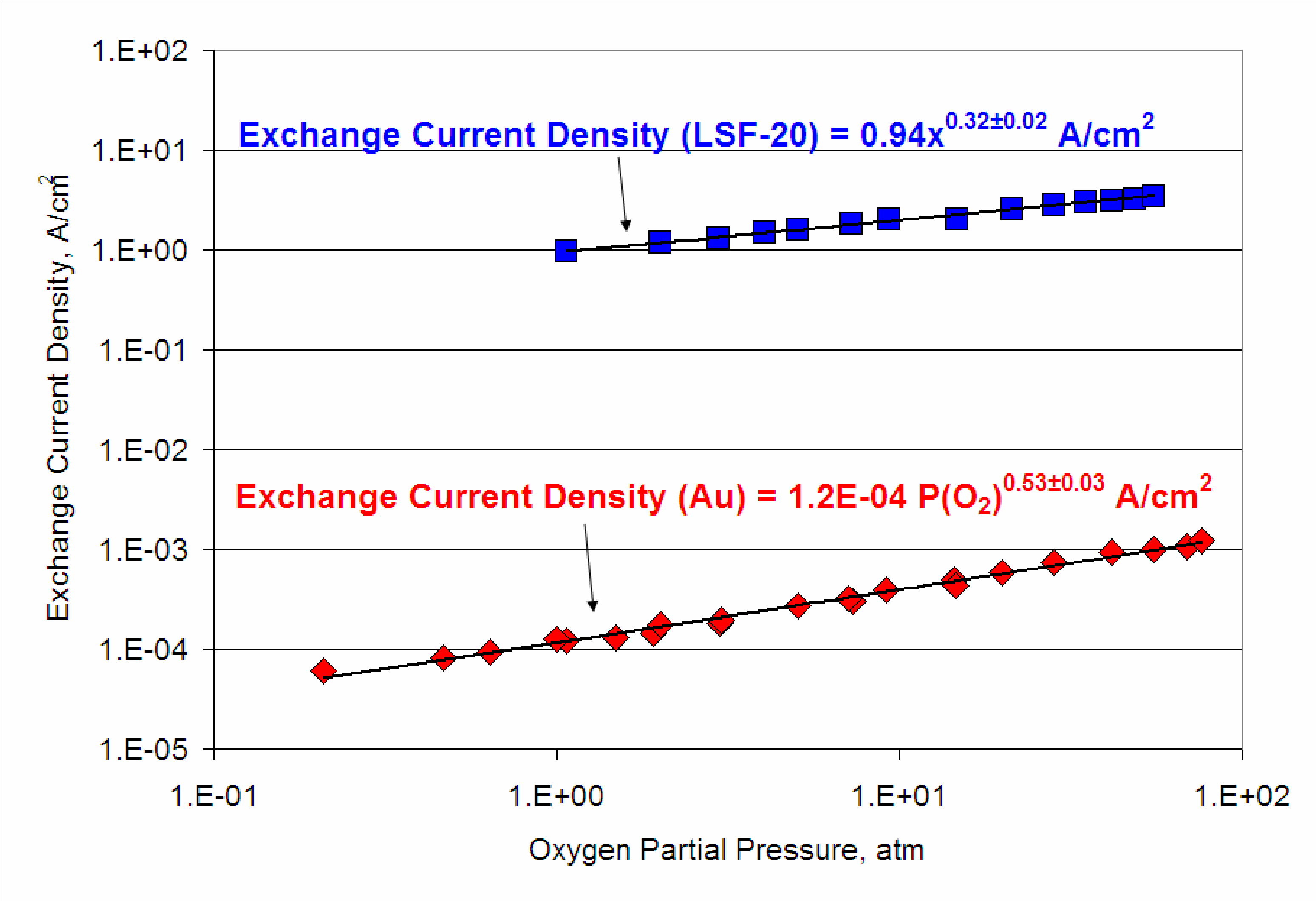



A – Low frequency arc arising from adsorption, dissociation, $\sim P^{1/2}$ dependence

B – High frequency arc arising from charge transfer processes, $\sim P^{1/4}$ to $P^{1/3}$ dependence

# LSF-20 Shows Low P Dependence – Greater Charge Transfer Contribution; Au Results Consistent With Greater Gas Adsorption Contribution



# Conclusions and Future Work-High Pressure Studies

- Cathode performance was found to improve with increased pressure, to ~100 bar $O_2$ partial pressure
  - For LSM and Au, exchange currents followed a $P^{1/2}$ dependence over broad pressure ranges, attributed to dominant gas adsorption processes
  - For more active LSM/ceria and LSF, a lower P dependence was found, attributed to relatively greater charge transfer reaction contributions
- Future studies will address pressure effects on anode performance
  - Concentration polarization expected to play greater role
  - High absolute steam concentrations in coal gas
  - Role of coal gas contaminants at high pressure
  - Comparison to/validation of anode modeling e.g. Gemmen and Trembly JPS 2006 model

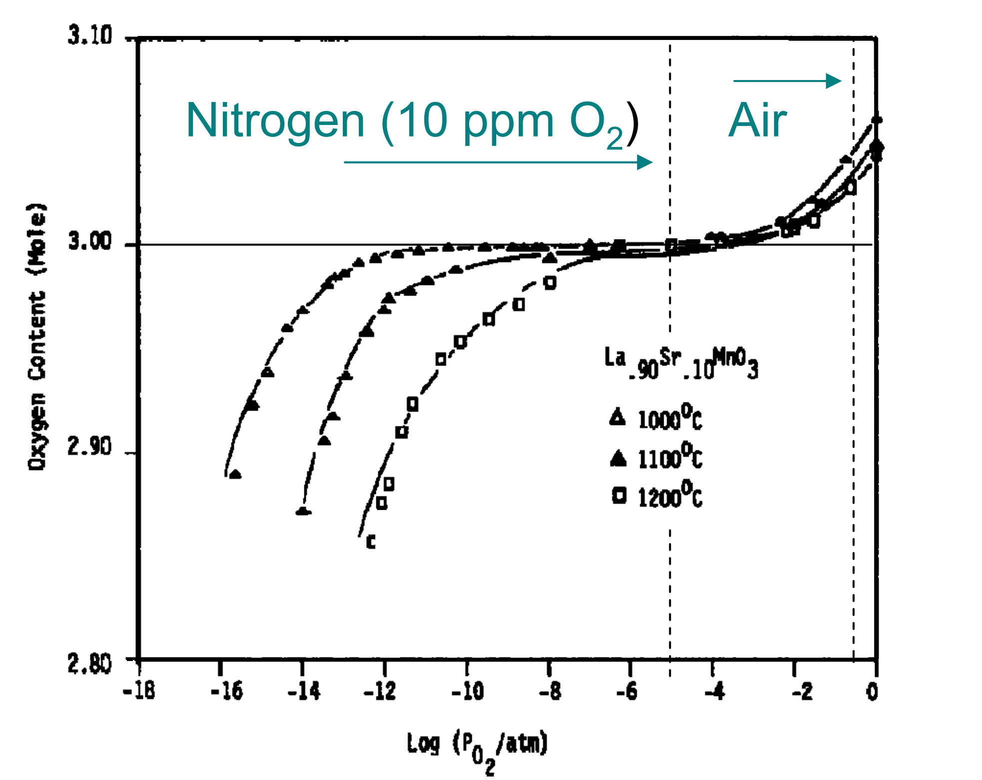
# LSM Sintering at Low Temperature

- Objectives: develop an electrically conductive, chemically and physically compatible, and stable contact paste to bond the SOFC cathode to the interconnect plate.
- Approach: Use LSM
  - Use alternating air and nitrogen flows to densify LSM at temperatures far below those usually required, exploiting that material's unusual defect chemistry.
  - Evaluate mechanical strength of bonds formed to the cathode and to the spinel-coated ferritic steel interconnect, electrical properties, and interfacial phase stability.
  - Work with SECA modeling tasks to establish contact paste performance criteria, implement in stack.
- Conclusions:
  - LSM can be densified by alternating air/nitrogen cycles.
  - The effect decreases with increased Sr content.
  - Bond strengths to spinel-coated ferritic steel of ~2 MPa or greater achieved in a few hours – process not yet optimized.

# Background – LSM Sintering at Low Temperature

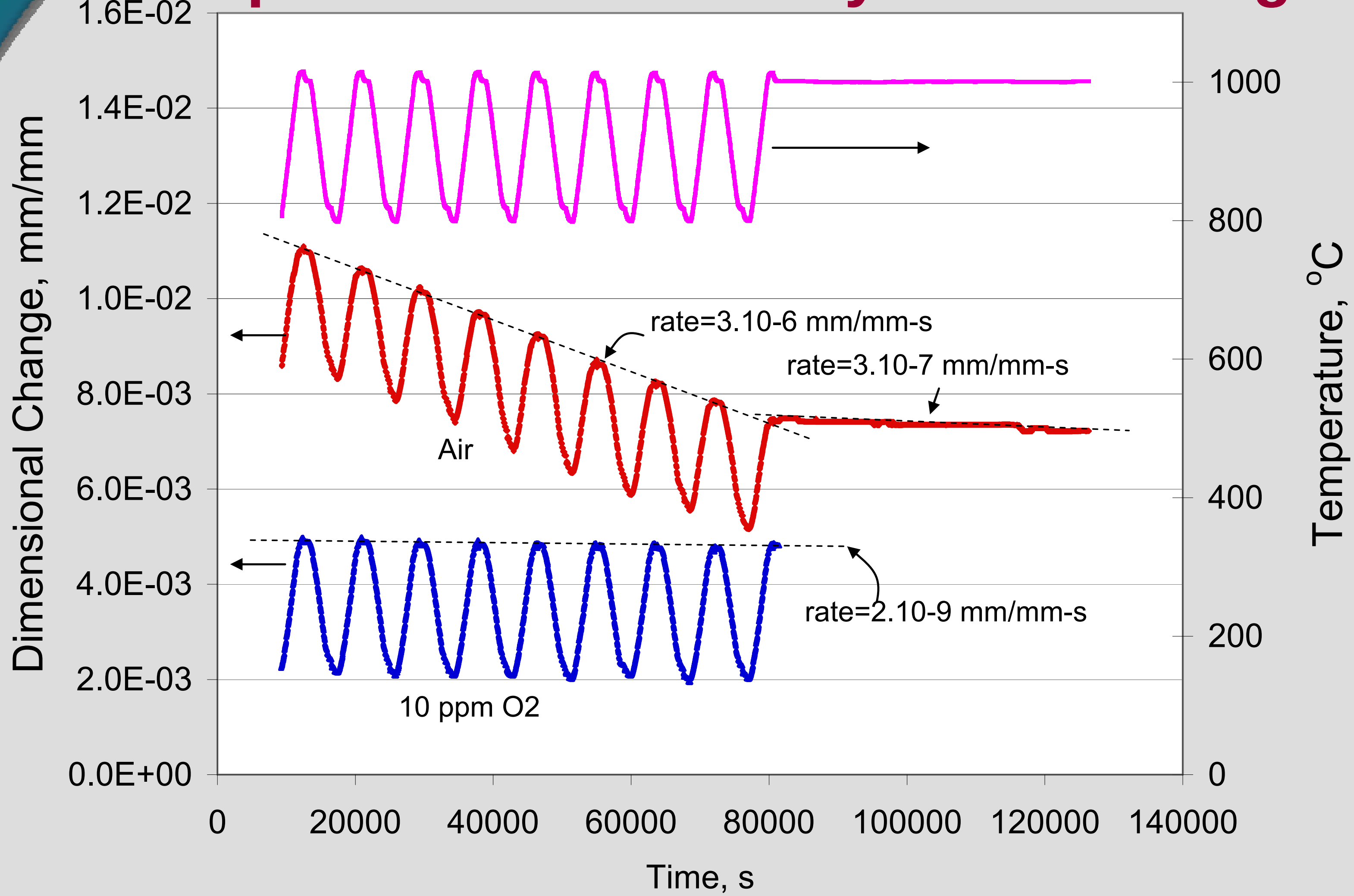
- LSM exhibits “excess” lattice oxygen in air, expressed as metal vacancies (no oxygen interstitials in perovskite).
- Thermal cycling previously shown to enhance LSM densification:
  - *Series of recent publications by Mori, ascribing mechanism to phase changes associated with oxygen gain/loss*
  - *1997 patent by Kuo et al. on suppression of effect by aliovalent cation substitution on both A-and B-sites.*
- Our work focuses on $PO_2$ cycling (air/nitrogen), expected to affect lattice oxygen concentrations more strongly than thermal cycling.

**Oxygen Non-Stoichiometry in LSM-10**



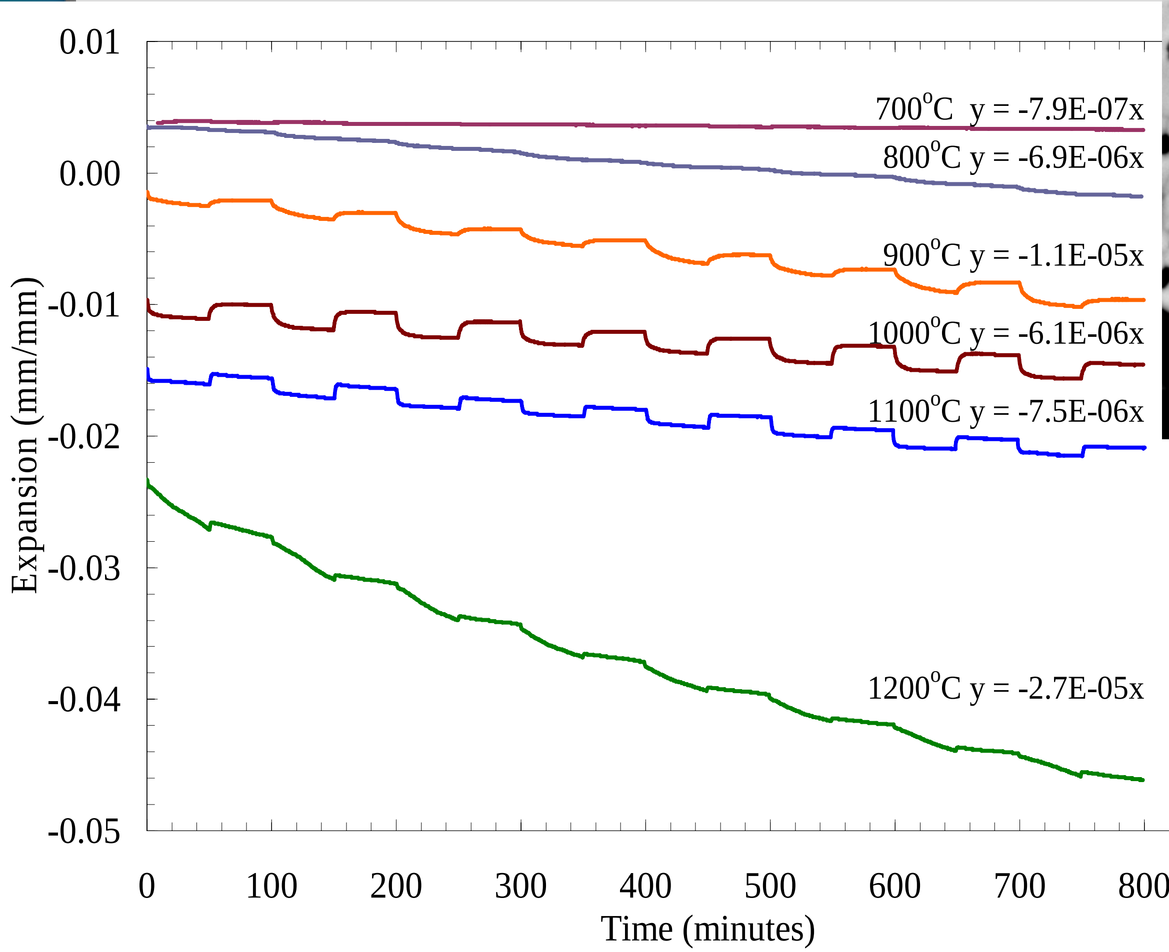

*Kuo et al. J Solid State Chemistry, 1989; 83(1): 52.*

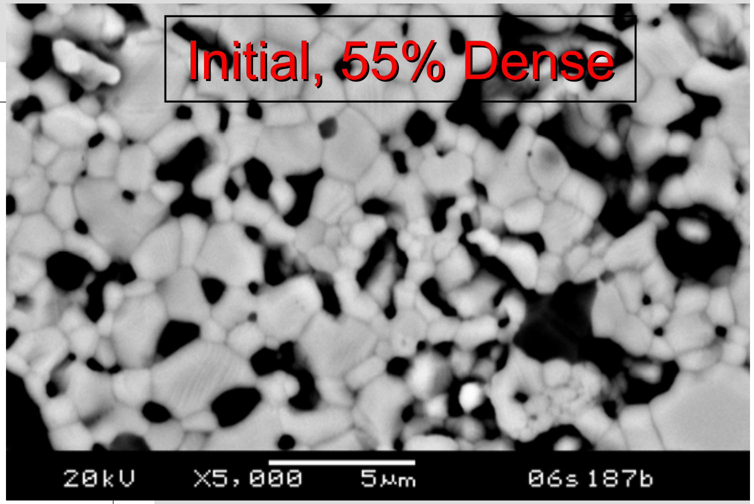
# Enhanced Shrinkage of LSM-10 Occurs When Thermally Cycled in Air, Minimal at Constant Temperature or When Cycled in Nitrogen

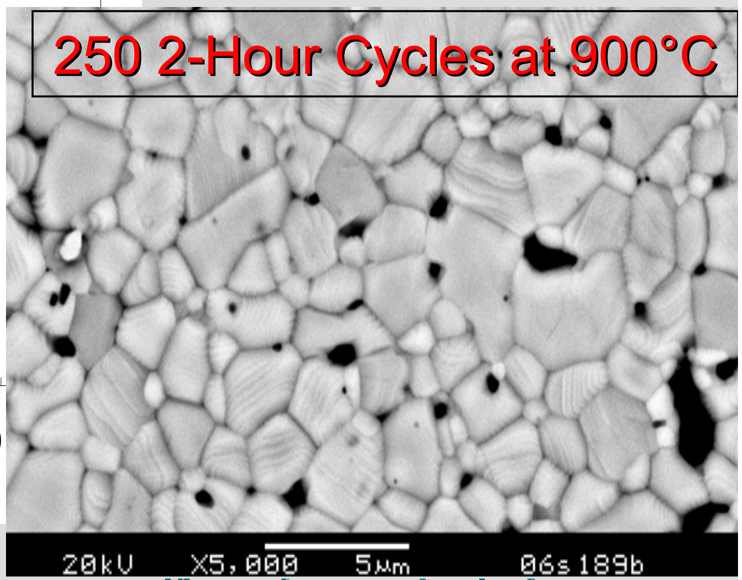



Initial sintered density = 55 percent

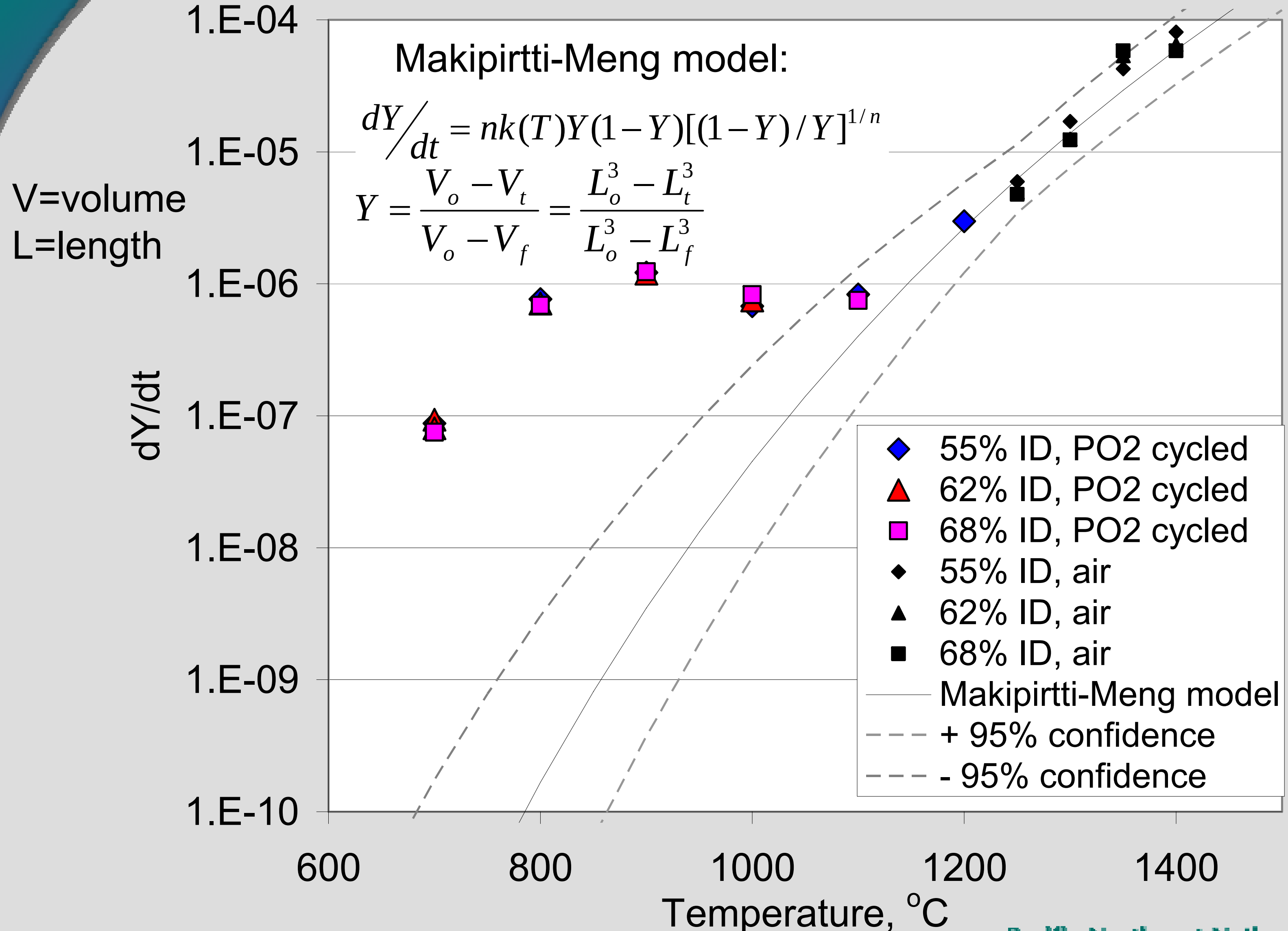
# Air/Nitrogen Cycles Also Results in LSM-10 Shrinkage, Effect Visible as Low as 700ºC



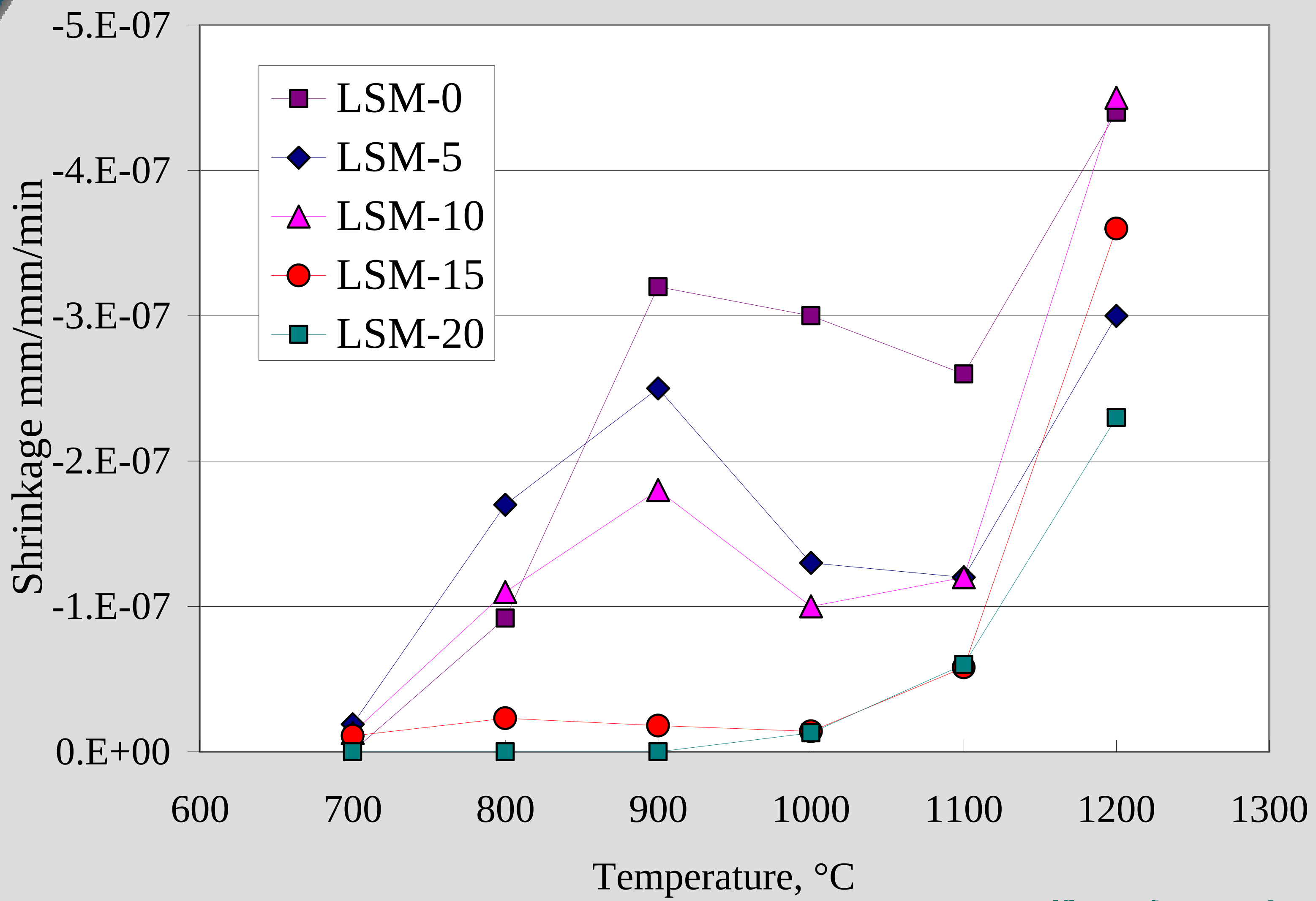



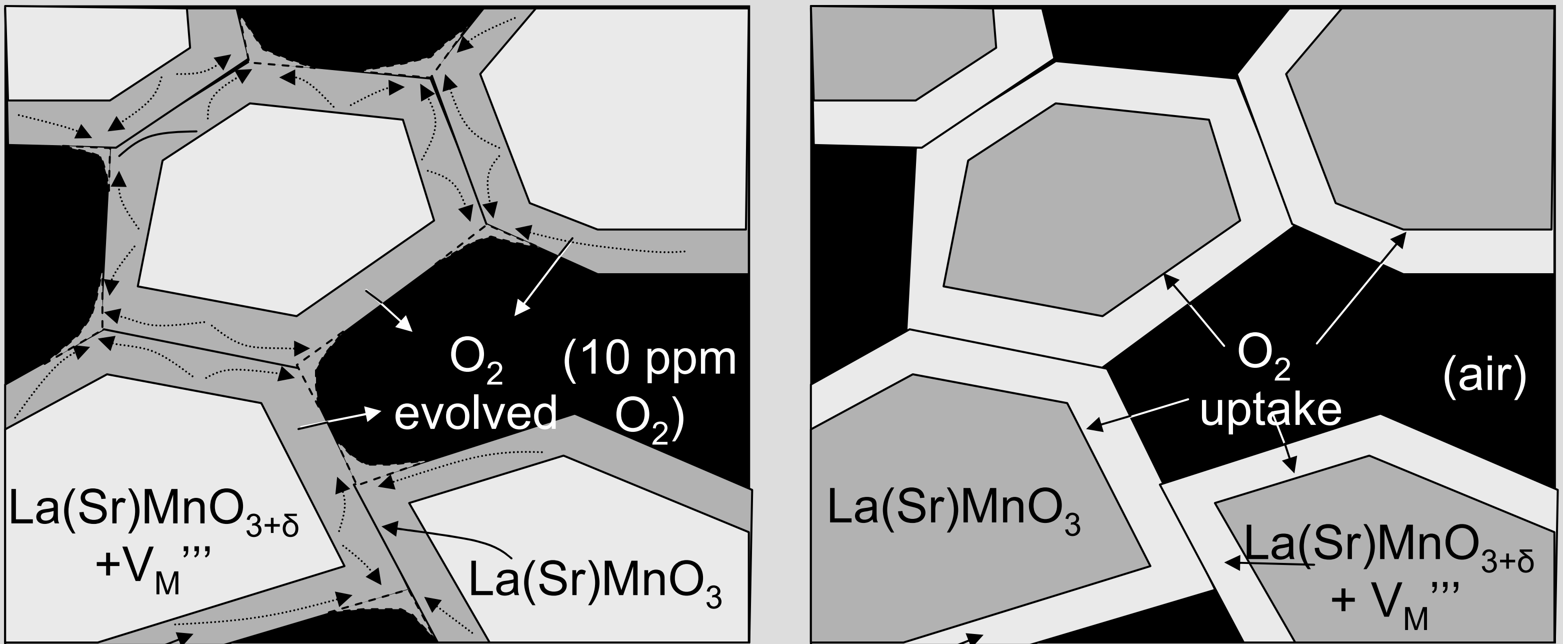
# Comparison of Enhanced Sintering Rates due to $PO_2$ Cycling to Expected Rates for LSM-10



# $PO_2$-Cycling Shrinkage Suppressed by Sr Substitution



# Transient Coexistence of Oxygen and Metal Vacancies Leads to Enhanced Mobility




$V_M''', V_O^{\bullet\bullet} > equilibrium$ $\quad$ $V_M''' < equilibrium$

stoichiometric

oxygen-excess

pore

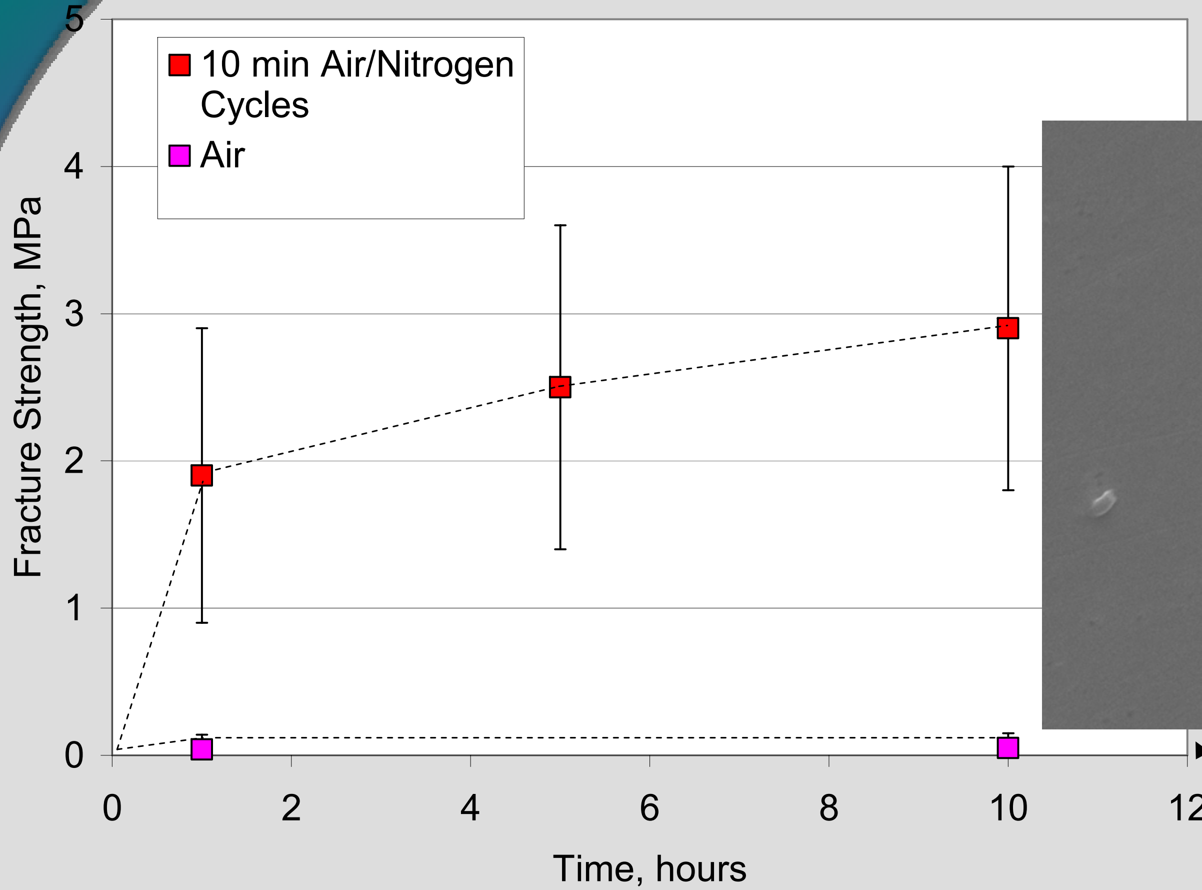
## Air → Nitrogen:

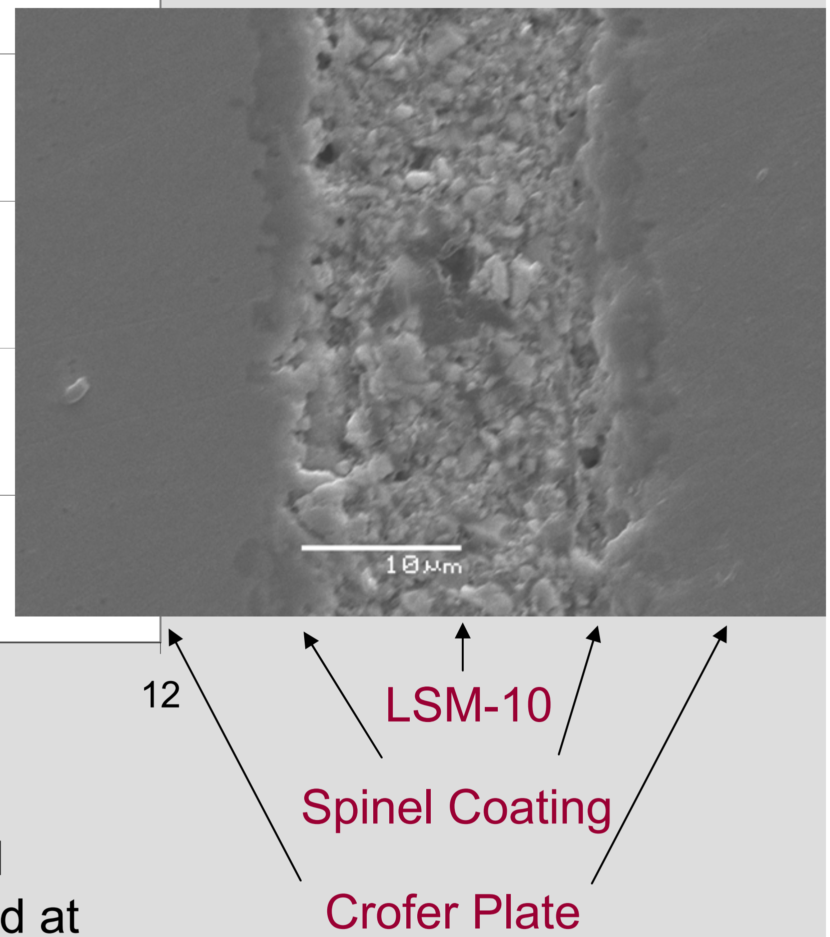
- Excess metal and oxygen vacancies present
- Shrinkage occurs

## Nitrogen → Air:

- metal vacancies less than equilibrium
- Minimal shrinkage

# LSM Contact Paste Sintering at 900ºC: Air/Nitrogen Cycles Results in Bonding




- Five specimens measured for each condition
- Coverage was incomplete – ink not optimized
- LSM bond strength to spinel coating estimated at >8 MPa (fractured at epoxy bond)

# Conclusions – LSM Sintering at Low Temperature

- Alternating air/nitrogen cycles is an effective way to induce LSM sintering at low temperatures
  - Orders of magnitude higher rates than expected for air sintering for T<1000$^{o}$C
  - For LSM-10, maximum sintering rate at 900$^{o}$C due to air/nitrogen cycling
  - Shrinkage rates decrease with increased Sr content – LSM-20 shows no enhanced shrinkage
- The mechanism of sintering is defect chemistry-driven: coexistence of transient oxygen vacancies with metal vacancies leads to enhanced mobility; no effect for stoichiometric or oxygen-deficient compositions such as LSF
- Bond strengths between spinel-coated ferritic steel coupons of ~2 MPa or greater achieved in a few hours with un-optimized inks, incomplete coverage; estimated LSM-10 to spinel bond strength >~8 MPa (failed at expoxy bond)

# Future Work – Low Temperature Sintering of LSM-Based Contact Pastes

- Improve ink formulations, burn-out/sintering procedures to achieve more uniform coverage and higher strength
- Evaluate mechanical bonding strength to coated interconnect coupons and to porous cathodes
- Evaluate long-term electrical properties using fixture developed by Yang et al. (two paste/interconnect interfaces, two paste/porous cathode interfaces); evaluate long-term interfacial stability
- Work with SECA modeling tasks to establish contact paste performance criteria, optimize contact paste placement and coverage in a stack, evaluate critical stresses
- Implement contact paste compositions and processing methods in SECA stack tests

# Acknowedgements

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