Sintering of LSM Contact Pastes at Low Temperature

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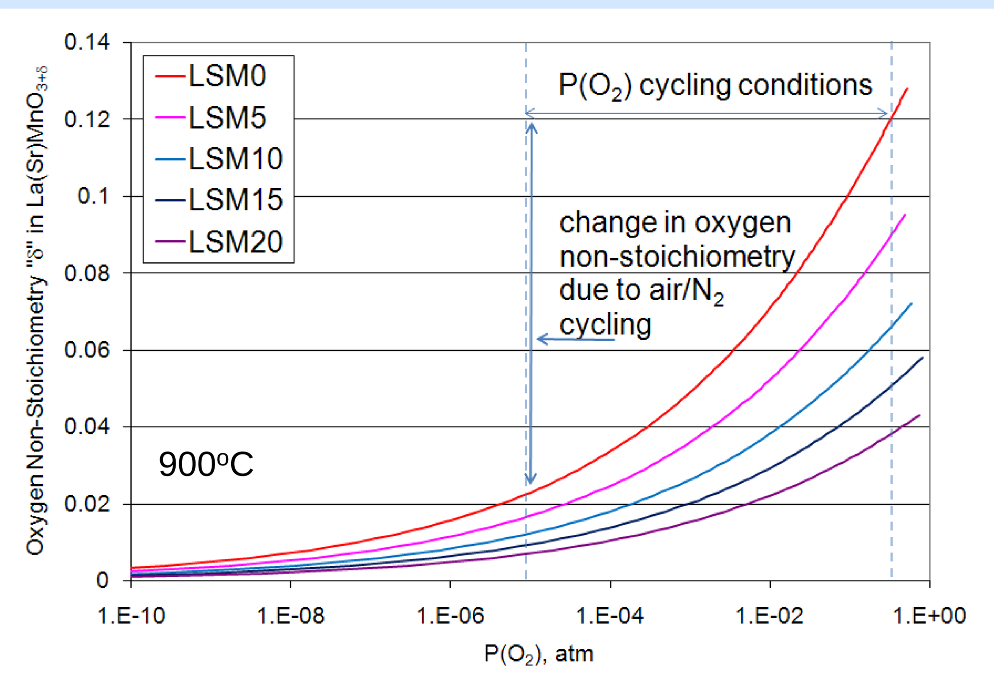
Purpose and Approach

Develop cathode-side contact paste that :

- can be sintered at temperatures similar to those needed for glass seal processing,
- contributes minimally to cell and stack resistance,
- provides good interfacial stability with the cathode and interconnect,
- provides a good thermal expansion match to other fuel cell components, and
- is of low cost

The unique defect chemistry of $La_{1-x}Sr_xMnO_3$ ($x \leq 0.1$) provides an opportunity for low temperature sintering:

- contains "excess" oxygen, expressed in the lattice as cation vacancies
- cation vacancy concentrations are sensitive to $P(O_2)$ and to temperature
- $P(O_2)$ as well as thermal cycling creates cation concentration gradients, resulting in accelerated sintering
- requires no sintering aids, stable against further sintering in air



Sintering Mechanism

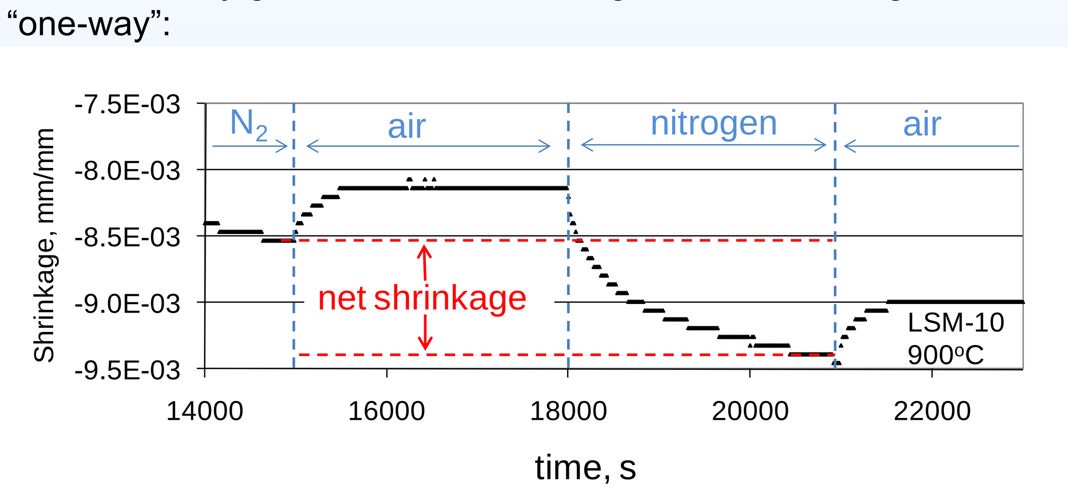
The sintering rate depends on mobility of cation vacancies, D_v, and excess cation vacancy gradient dC/dx

$$Rate = -D_v \frac{dC}{dx}$$

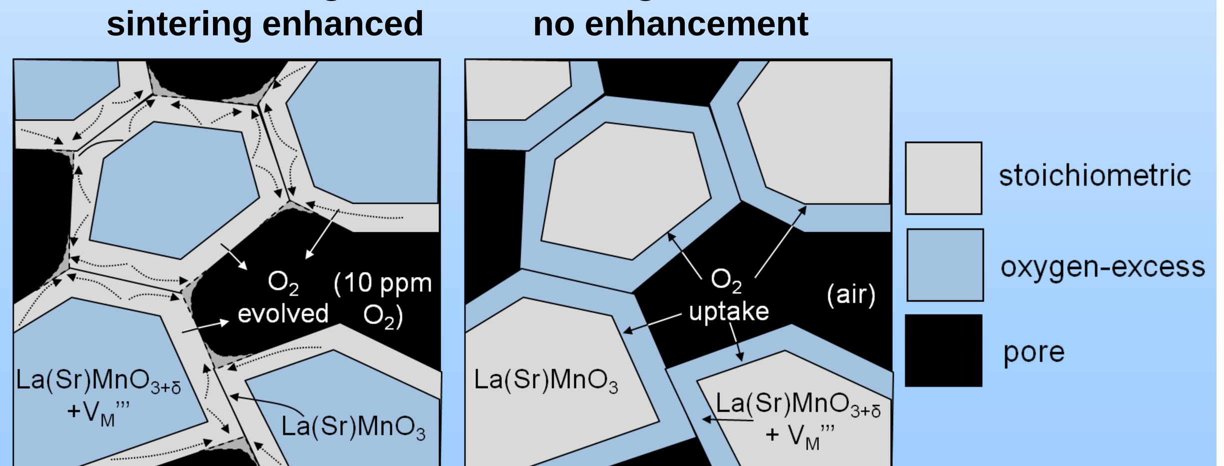
Oxygen content in LSM and cation vacancy concentration are related

$$3O_o^x + 2[V_{La}'''] + [a_{Mn}^x] + 6[\bullet] \rightarrow 3/2\,O_2(g) + [a_{La}^x]$$

The cation vacancy gradient and thus driving force for sintering is transient and "one-way":



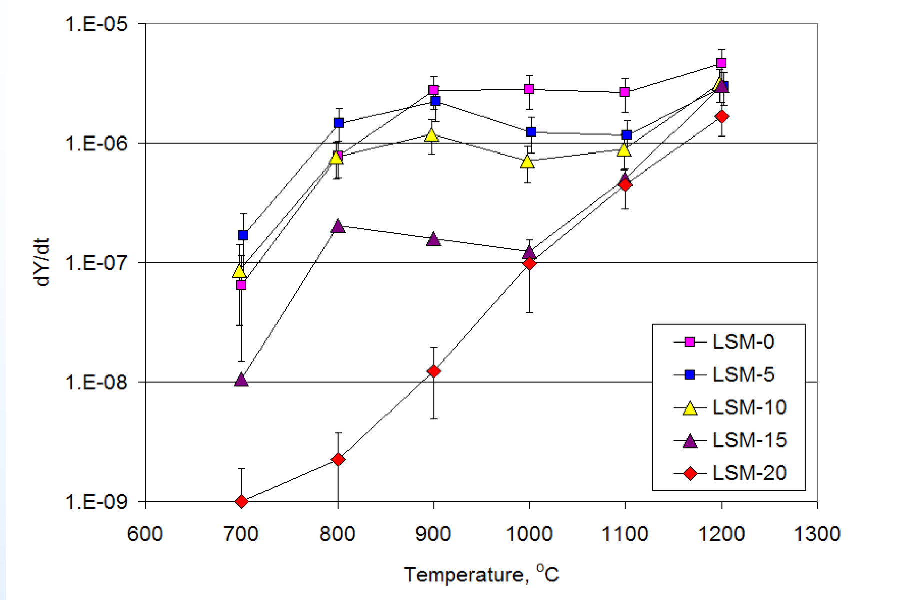
Air→ Nitrogen sintering enhanced | **Nitrogen→ Air no enhancement**



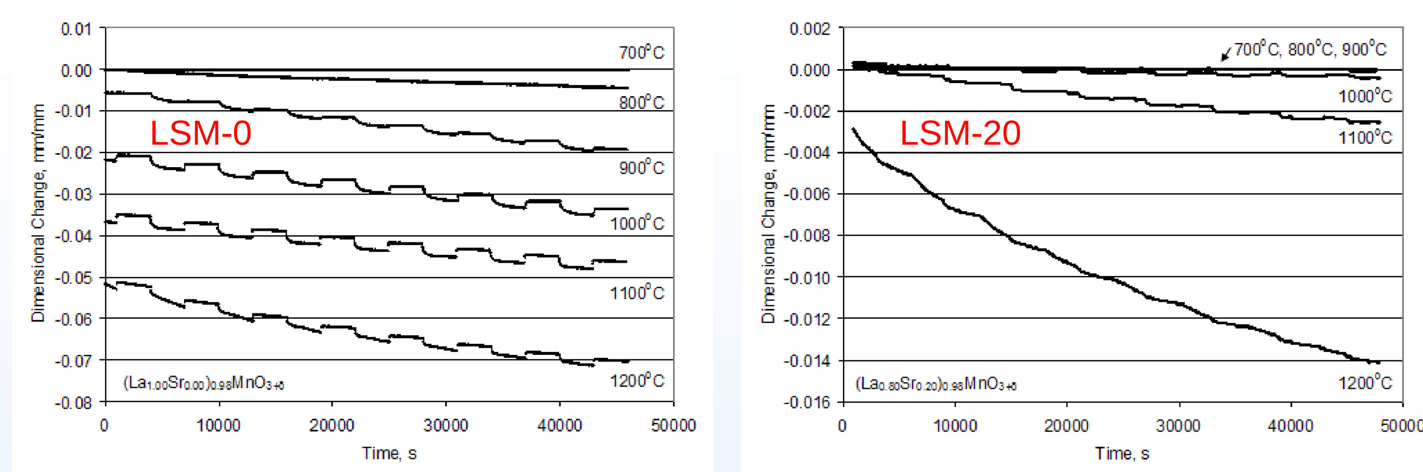
As oxygen is evolved, excess cation vacancies must migrate or annihilate to re-establish equilibrium. Excess cation vacancies are not formed during oxygen uptake.

Sintering Kinetics – Experiment and Model

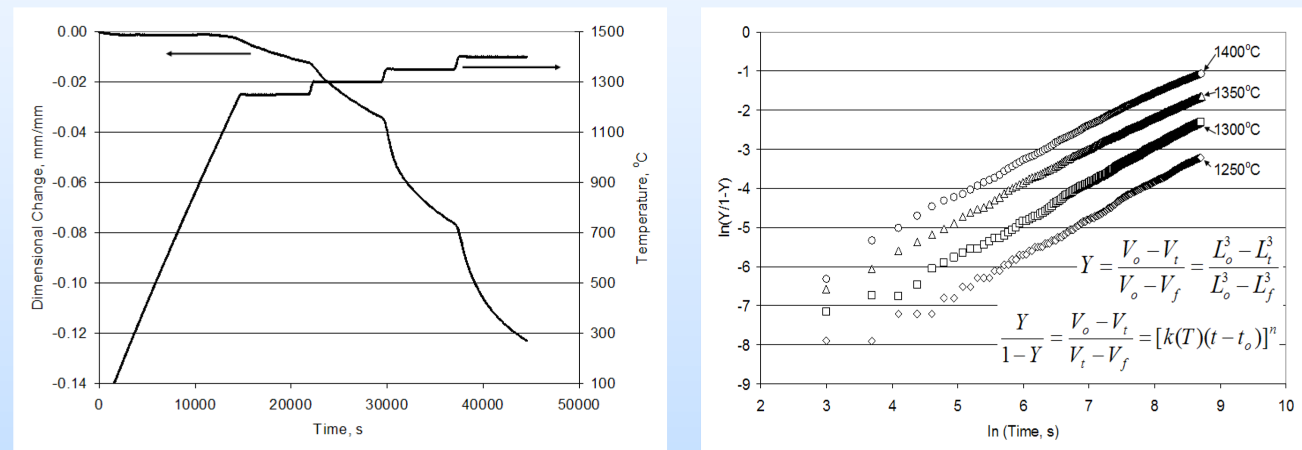
Sintering of LSM-0>LSM-5>LSM-10>LSM-15>LSM-20, follows same trend as extent of oxygen non-stoichiometry



Dilatometry curves show high sintering rates for LSM-0 in alternating air/nitrogen for LSM, and negligible shrinkage for LSM-20, a widely used cathode material



From isothermal dilatometry, kinetic parameters for air sintering are extracted



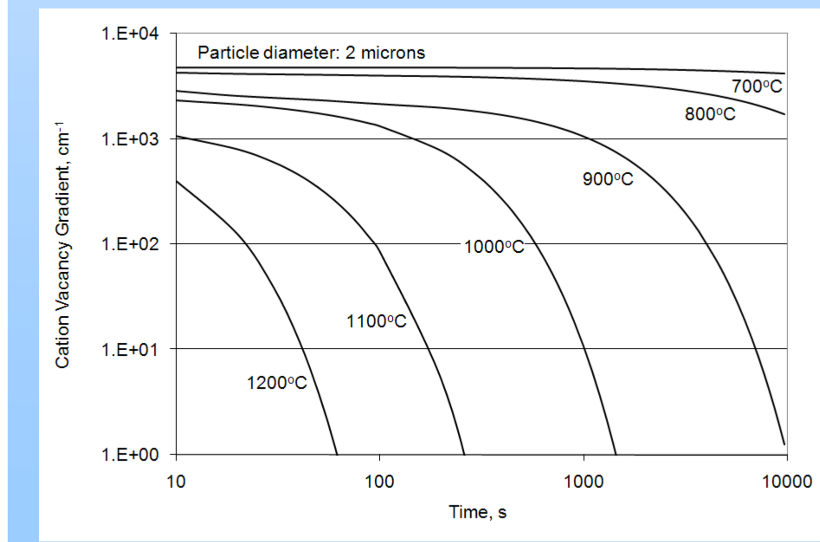
Enhanced sintering is attributed to the creation of a transient cation vacancy gradient as oxygen is gained and lost by LSM. For finite particles of radius a, that gradient is:

$$\frac{dC_{vM}}{dx} = \frac{12(C_0 - C_1)}{\pi^2 a}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\left[e^{-\frac{Dn^2\pi^2 t}{a^2}}\right]\left[n\pi\cos\left(\frac{n\pi}{2}\right) - 2\sin\left(\frac{n\pi}{2}\right)\right]\sin\left(\frac{n\pi}{2}\right)$$

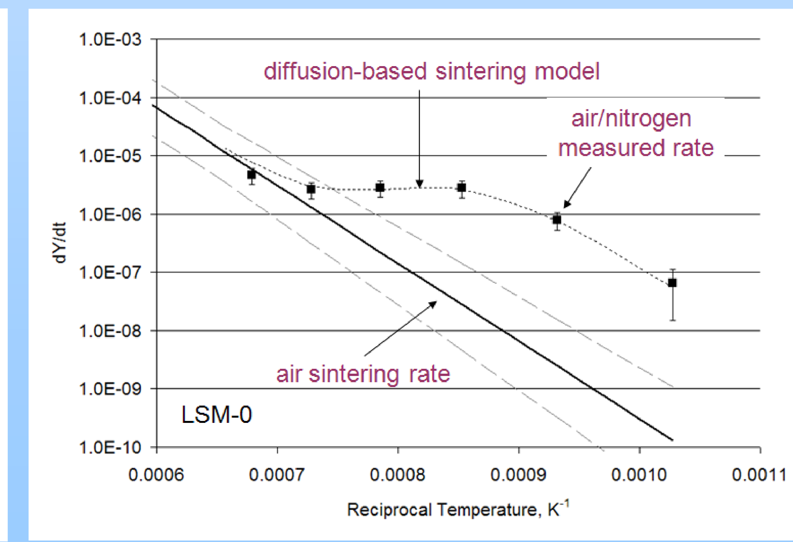
Sintering rates are modeled as the sum of the rate in alternating air/nitrogen plus the rate in air.

$$\frac{dY}{dt} = \left(\frac{dY}{dt}\right)_{air} + \left(\frac{dY}{dt}\right)_{air/N_2} = \left(1 + A\frac{dC}{dr}\right)\left(\frac{dY}{dt}\right)_{air}$$

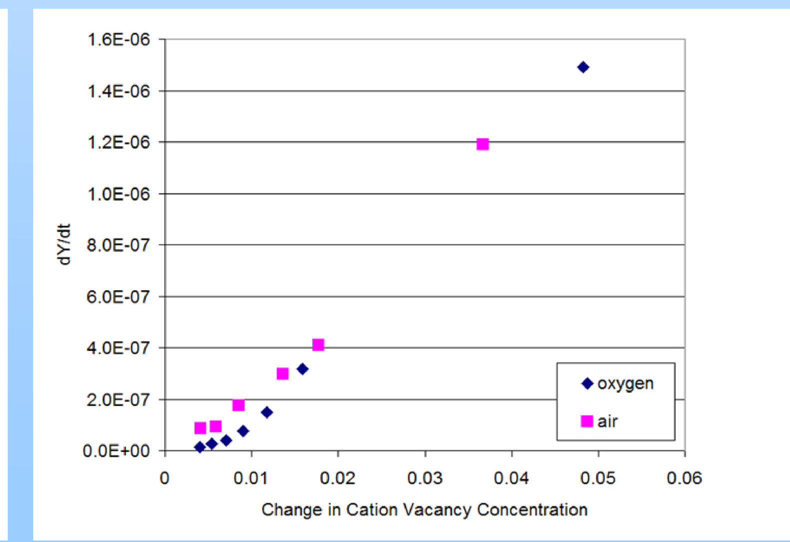
Calculated cation vacancy gradient versus time



Diffusion-based model in good agreement with experimental observations

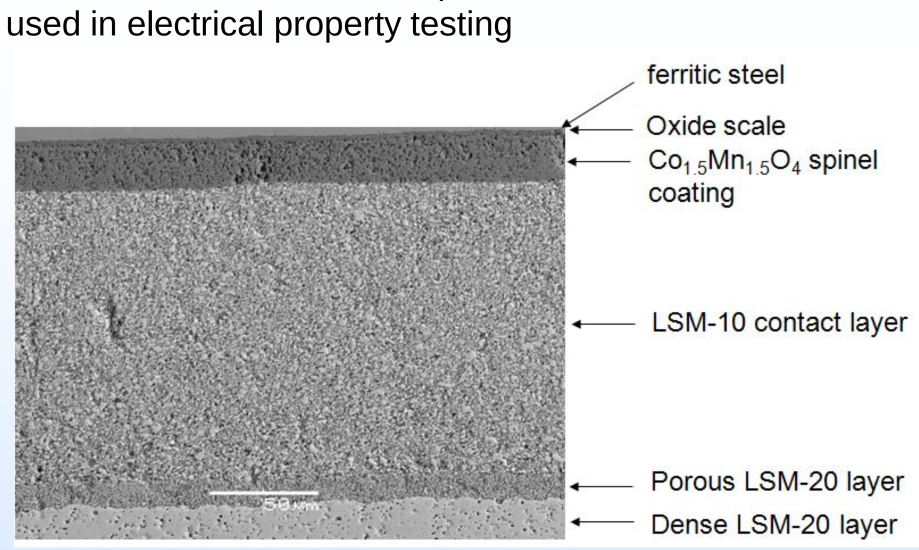


Sintering rates correlate with cation vacancy concentration changes in diluted air/oxygen alternated with nitrogen

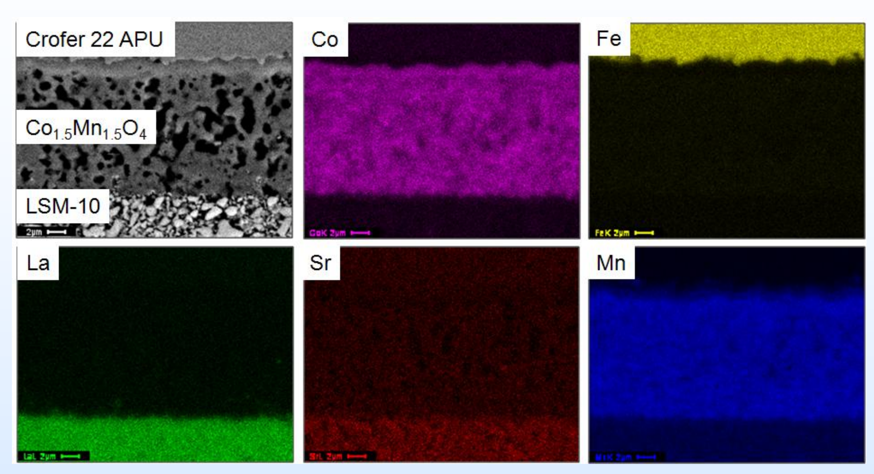


Structure, Strength, and Electrical Properties

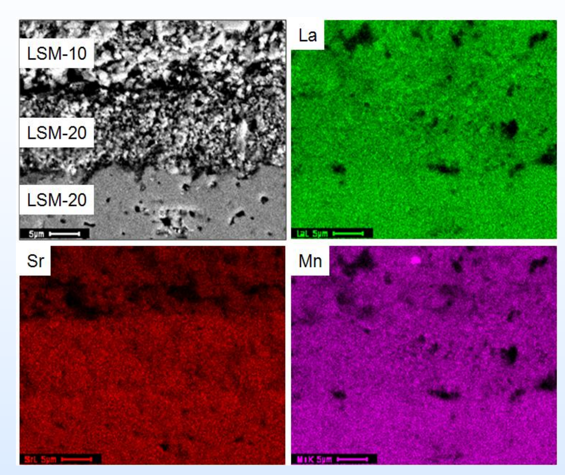
Cross-section of sandwich specimen used in electrical property testing



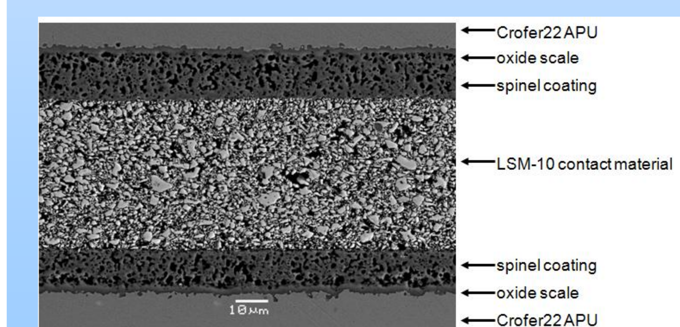
Elemental maps of (Co,Mn)3O4 spinel/LSM contact paste interface reveal distinct boundary



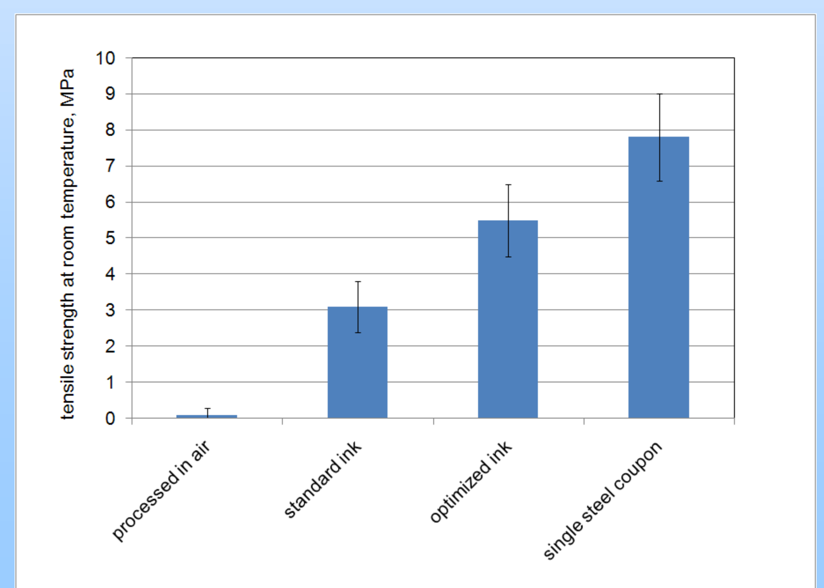
LSM-10 contact paste/ LSM-20 cathode boundary remains distinct



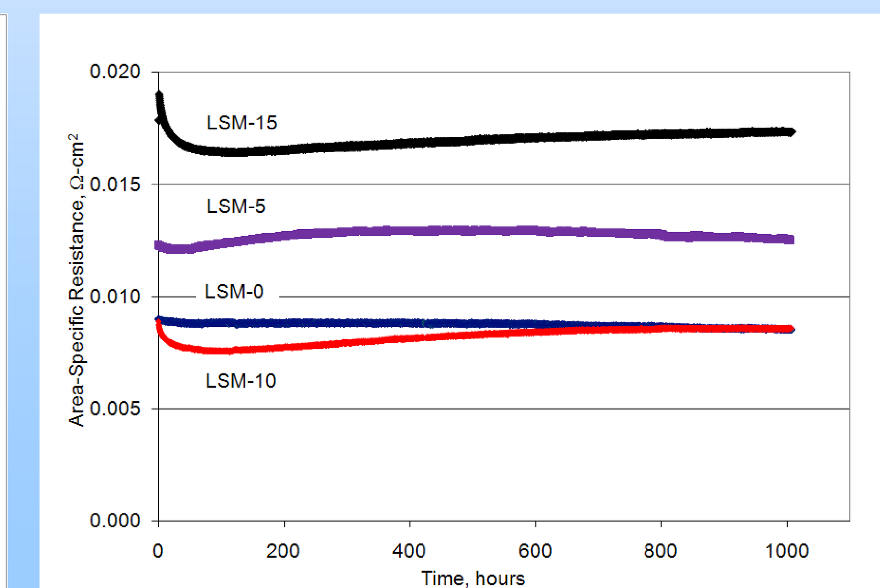
Configuration of specimens used in tensile strength measurements



Room-temperature tensile strengths obtained for spinel-coated ferritic steel coupons bonded with LSM-10 contact paste, processed at 900ºC, 2 hours



Electrical resistivity of ferritic steel/spinel/LSM contact paste/LSM-20 cathode/LSM contact paste/spinel/ ferritic steel sandwich specimens at 800ºC in air



Summary

- LSM-x contact pastes, where x≤10, can be sintered effectively below 1000ºC in alternating air and nitrogen in ~2 hours without the use of sintering aids. Under these conditions, neither LSM-20 nor LSCF-6428 cathodes are densified.
- Tensile bond strengths >5 MPa at room temperature have been achieved for spinel-coated ferritic steel coupons bonded with LSM contact pastes. Higher bond strengths are believed to be possible. Detailed studies of the mechanical properties of contact pastes are underway at ORNL (E Lara-Curzio) and PNNL (EV Stephens, BJ Koeppel), including bond strength evaluations at high temperature.
- Electrical resistivities of LSM contact pastes generally meet performance targets in 1000 hour tests.
- A sintering model has been developed that is in good agreement with experimental sintering kinetics results. Sintering rates are related to a calculated transient excess cation vacancy gradient that results from oxygen uptake/loss during alternating air/nitrogen cycling.
- The efficacy of air/nitrogen cycling as a means of sintering LSM contact pastes has been demonstrated in stack tests using the Core Technology Programs planar test fixture (XD Zhou), as well as in button cells.

Acknowledgement

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