Sintering of LSM Contact Pastes at Low Temperature
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Sintering Mechanism
The sintering rate depends on mobility of cation vacancies, Dn, and excess cation vacancy gradient dC/dt.

\[
\text{Rate} = D_n \frac{\partial C}{\partial t}.
\]

Oxygen content in LSM and cation vacancy concentration are related

\[
3O_2 + 2 \left[ 3/2 \cos \left( \frac{n \pi}{2} \right) + 3/2 \cos \left( \frac{n \pi}{2} \right) \right] \rightarrow 3/2 \cos \left( \frac{n \pi}{2} \right) + 3/2 \cos \left( \frac{n \pi}{2} \right).
\]

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

\[
\text{Calculated cation vacancy gradient versus time}
\]

\[
\begin{align*}
\frac{\partial C}{\partial t} &= f \left( \frac{\partial C}{\partial t} \right) \text{ in nitrogen,} \\
\frac{\partial C}{\partial t} &= g \left( \frac{\partial C}{\partial t} \right) \text{ in air.}
\end{align*}
\]

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

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

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

Summary

- LSM-x contact pastes, where x<16, can be sintered effectively below 1000°C 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 (EY Stephens, BJ Koeppl), 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/diss 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.

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