Composite Cathode Contact Development: An Investigation of $LSCo/Al_2O_3(f)$ Composite

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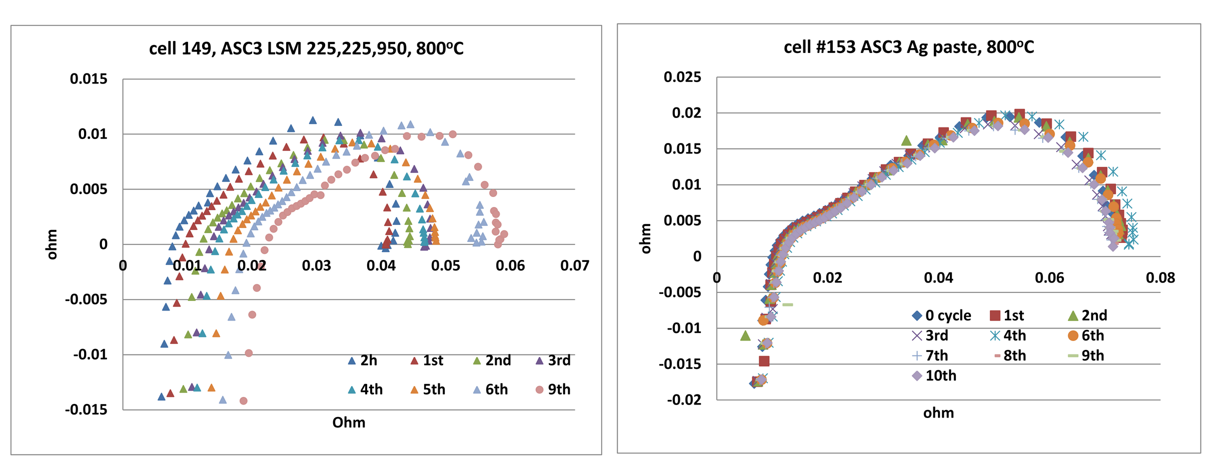
Introduction:

Cathode contact has been observed as the weakest link in solid oxide fuel cells (SOFC) when using highly conductive $LaSrCoO_3$ (LSCo) ceramics. The poor bonding strength was due to (1) mismatch in CTE, (2) poor solid-state sintering at low stack firing temperatures. This often leads to loss of ohmic contact during routine thermal cycling as compared to precious metal based contact (e.g., Ag - see figures below). In previous work, we have adopted mechanical interlocking by roughening cathode surface, as well as impregnated zirconia fiber material to enhance the strength. Both approaches demonstrated improvement in thermal cycle stability; however, these work was focused on the low-conductivity LSM materials.

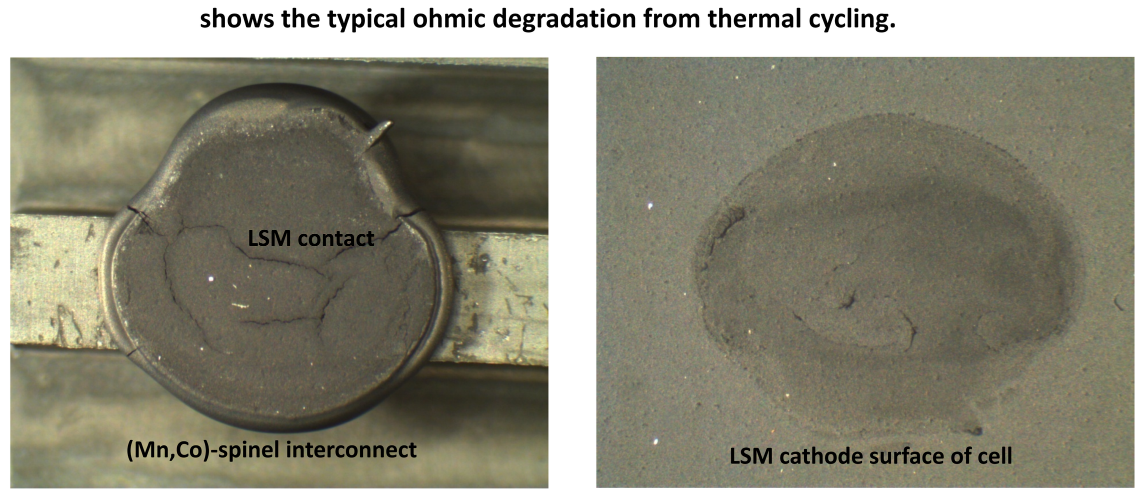
In this work LSCo is chosen as the contact material due to its high electrical conductivity. However, LSCo also has very large CTE (~$18x10^{-6}$/°C) compared to cell and interconnect (~$12\text{-}13x10^{-6}$/°C). As a result, large mismatch in CTE leads to large residual stresses and would damage the contact bonding during thermal cycling. In previous work, we tested a composite approach to tailor the CTE of LSCo by using low CTE mullite as fillers. Results showed composites' CTE can be greatly reduced at large fractions of mullite; however, the contact strength showed minimum improvement. FY20 we the fiber approach to strengthening the contact using the strong and inert Al_2O_3 fibers. The planed work:

Q1: bulk strength and densification of $LSCo/Al_2O_3$ system
Q2: contact strength evaluation: as-sintered and thermal cycled
Q3: durability of electrical conductivity and contact strength (isothermal ageing 800°C 1000h) *postponed*
Q4: validation test with generic stack fixture and post-mortem analysis (2"x2" LSM-based cell 800°C1000h followed 5-10 deep thermal cycles) *postponed*

Common Problem in Thermal Cycling



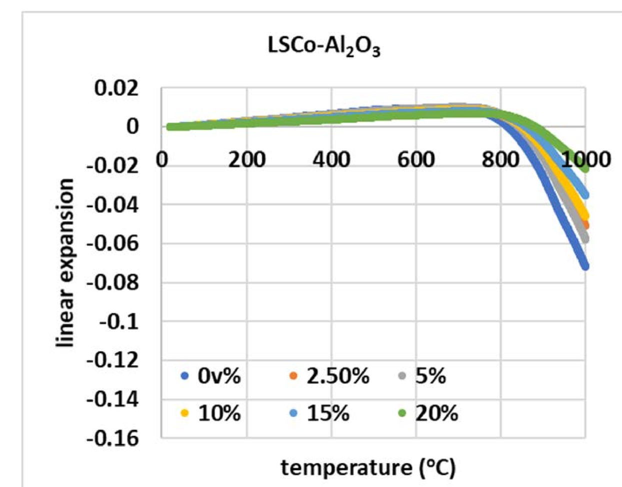
EIS of single cell testing with a ceramic contact (left) and a precious metal (right) shows the typical ohmic degradation from thermal cycling.

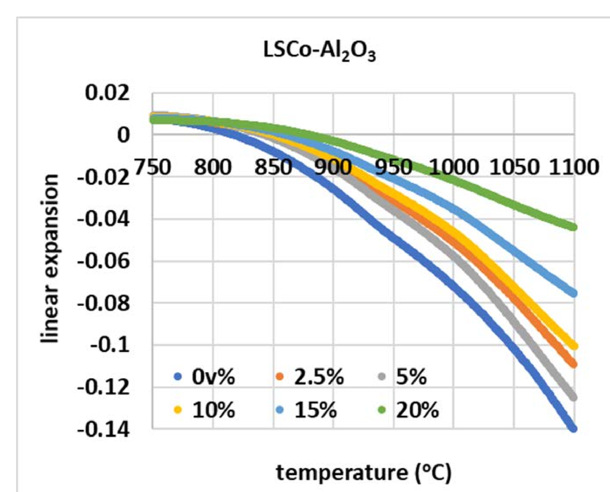


Matching fracture surface shows the weak link of LSM contact (left) at the LSM cathode surface (right) of a cell in stack fixture test. Note the LSM contact materials was completely de-bonded from LSM cathode surface, due to poor solid-state sintering at 930°C (stack firing temperature), as compared to the normal sintering of LSM at ~1100°C.

1. Sintering Behavior of LSCo/Al2O3

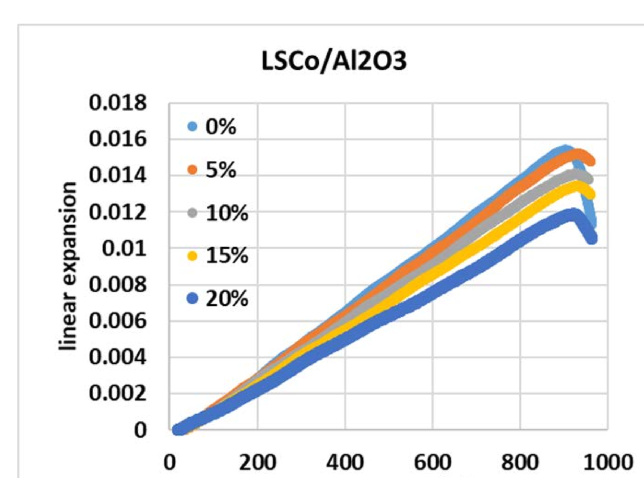
- ❖ Al_2O_3 short fibers at 2.5, 5, 10, 15, 20 v%
- ❖ Shrinkage monitored at ramp rate of 2°C/min in air





Sintering curves of LSCo/Al2O3 (f) composite

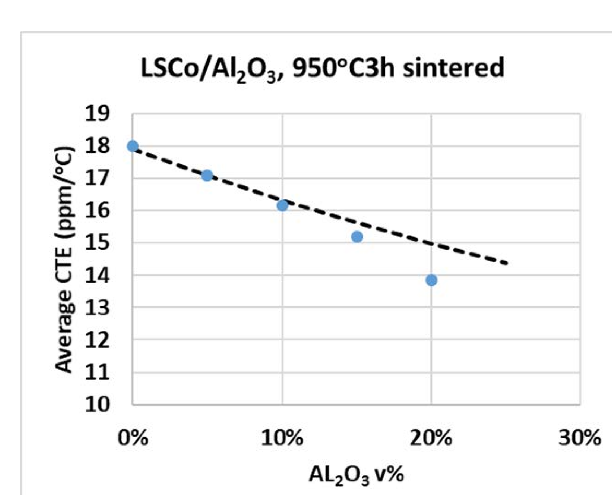
Thermal expansion behavior of LSCo/Al2O3



CTE prediction by model

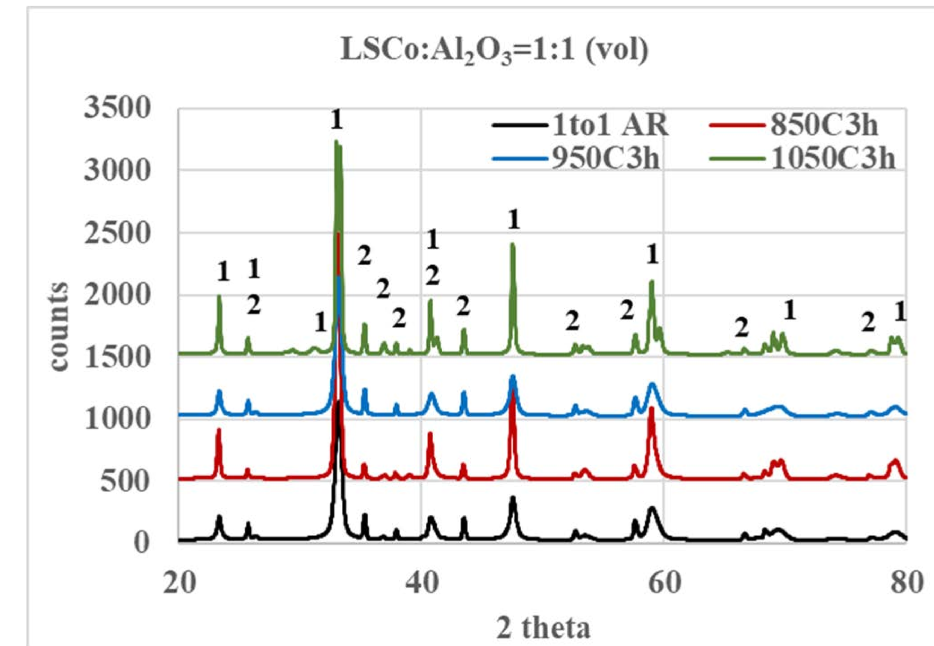
$$\alpha_{comp} = (\alpha_1K_1F_1/\rho_1+\alpha_2K_2F_2/\rho_2)/(K_1F_1/\rho_1+K_2F_2/\rho_2)$$

(Turner, hydrostatic tension and compression only)
K: bulk modulus, G: shear modulus, F: mass fraction, ν: Poisson ratio, ρ: density



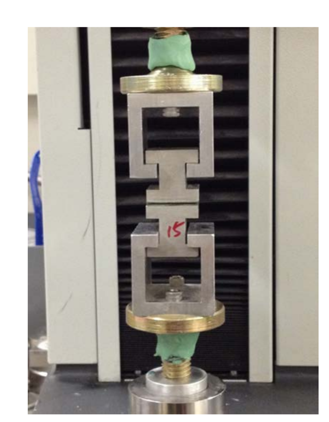
2. Chemical Compatibility

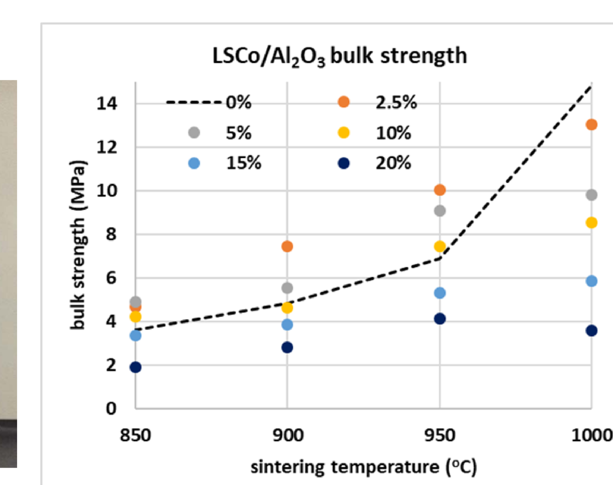
- ❖ LSCo:Al2O3=1:1 and sintered 850, 950, 1050°C 3h
- ❖ Characterized by XRD
- ❖ No 2[nd] phases identified

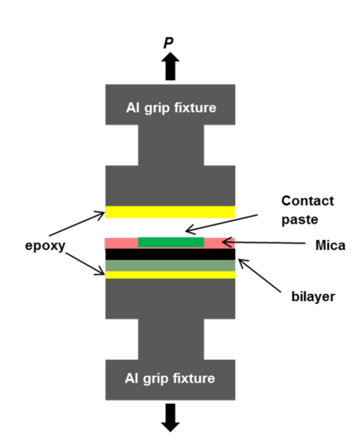


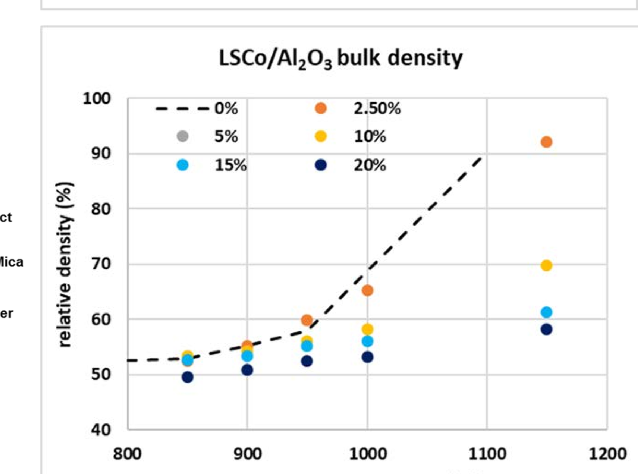
3. BUlk/ and Contact Strength Evaluation

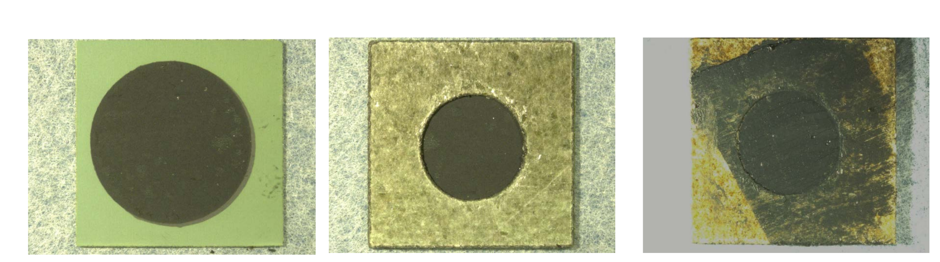
- ❖ Sintered (850-1000°C3h) pellets for bulk strength by diametral compression
- ❖ Contact strength tested in tension with paste on bilayer and sintered 850 or 950°C3h, no contact load applied in as-fired and thermally cycled





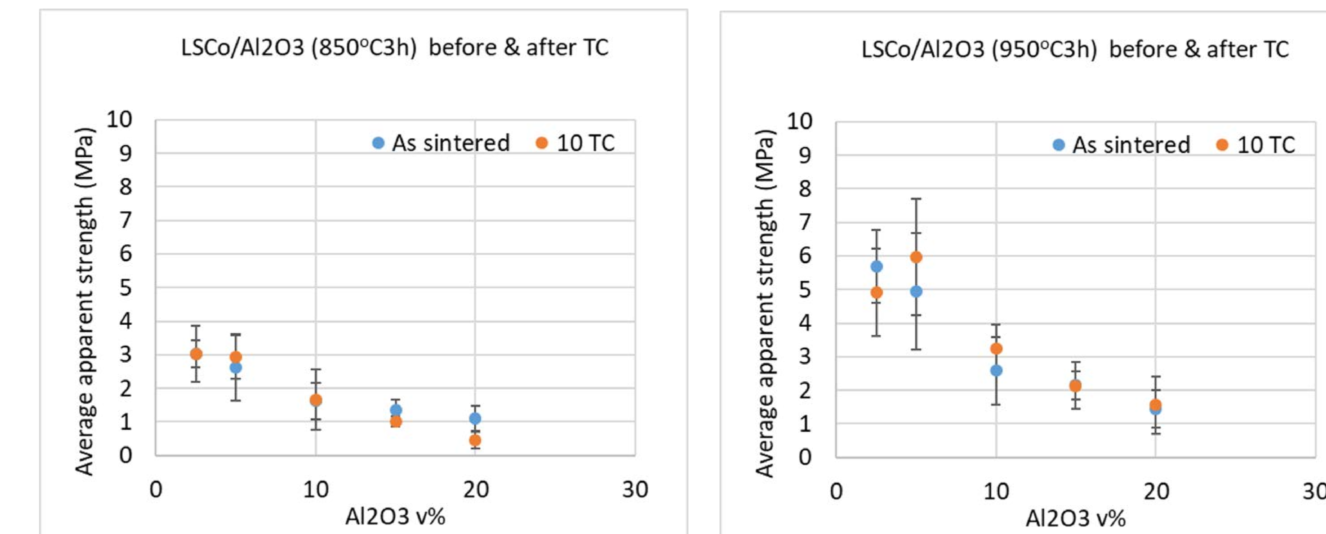




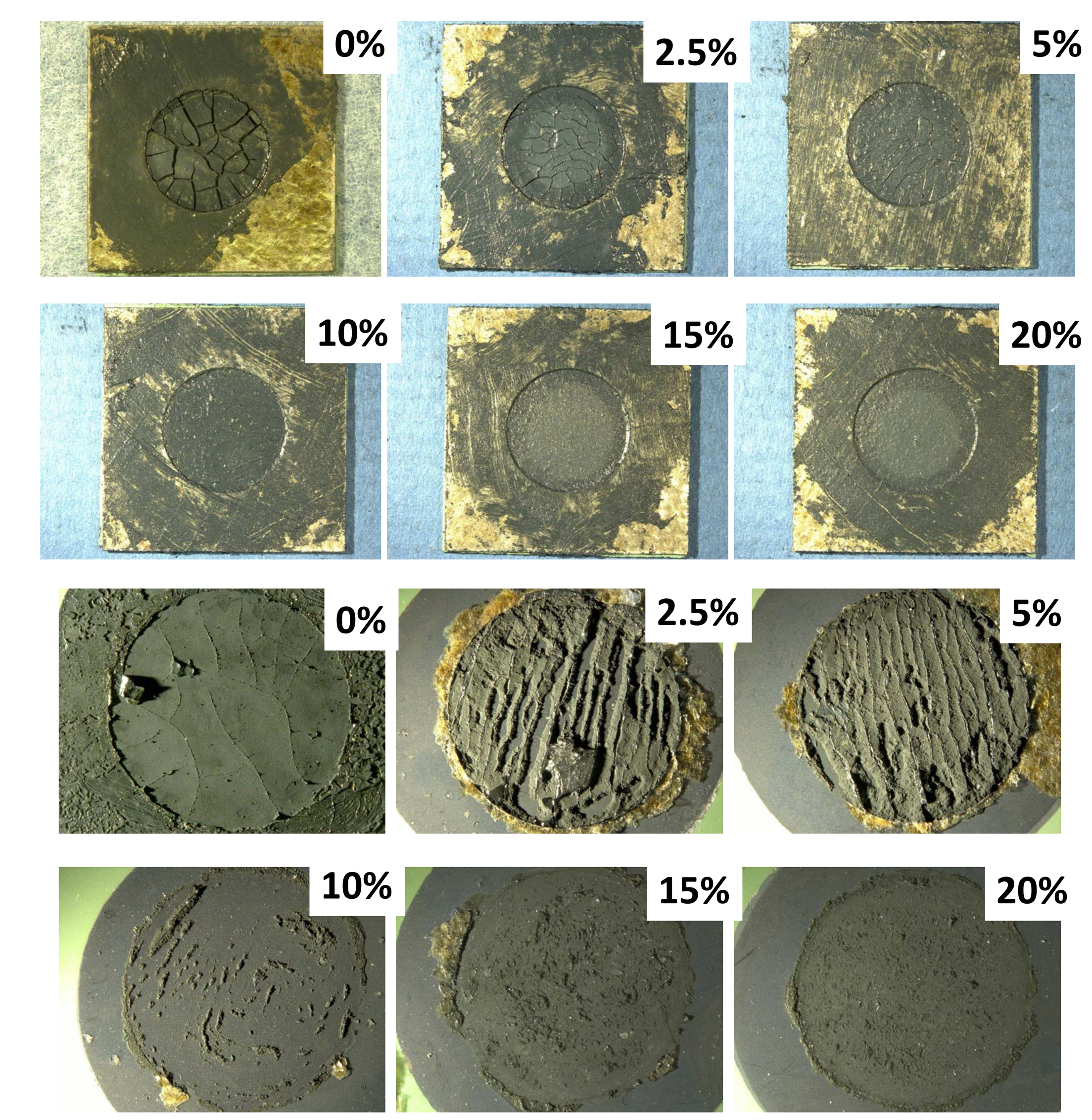


Micrographs show the preparation of samples: bilayer (left), mask on bilayer (middle), and paste applied (right)

Contact strength of as-sintered and after 10 deep thermal cycles



4. Fracture Surface Observation of Fiber Strengthening



Summary and Conclusions

- Composite contact materials of $LSCo/Al_2O_3$ (f) with vol.% of 2.5, 5, 10, 15, and 20 were investigated.
- Sintering study showed the retardation effect in densification increased with increasing alumina fiber content.
- CTE results showed linear behavior with decreasing averaged CTE with increasing Al_2O_3 v%, consistent with model prediction.
- XRD analysis of 850-1050°C sintered $LSCo/Al_2O_3$(1:1) composite found no secondary phases, implying good chemical compatibility.
- Bulk strength showed strengthening effect of Al_2O_3 fibers at low vol.% and low sintering temperatures where densification was not aggressive. At high v% fibers, likely reached percolation limit, densification was severely hindered, resulting low strength for all temperatures.
- Contact strength test showed strengthening effect by alumina fibers at low v% and no strength degradation after 10 thermal cycles.
- Fracture surface analysis revealed strong bonding at interface for composite with low v%, consistent with strength tests.

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