Composite Approach to Tailor CTE of LSCo-based Ceramic Cathode Contact for Solid Oxide Fuel Cells

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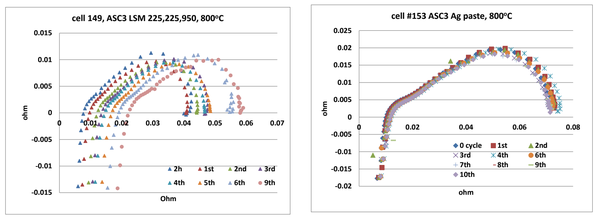
Introduction:

Cathode contact was identified as the weakest link in solid oxide fuel cells (SOFC) when using ceramic materials such as LSM, LSCo etc. The poor bonding strength was due to (1) mismatch in CTE, (2) poor solid-state sintering at low stack firing condition. This often led to loss of ohmic contact during routine thermal cycling as compared to precious metal based contact (e.g., Ag). 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, the work was focused on the low-conductivity LSM materials.

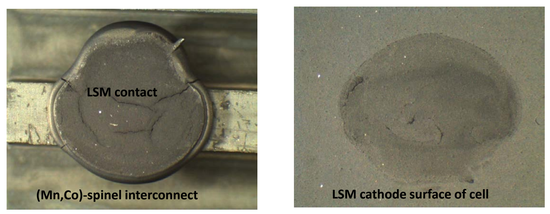
As LSCo has much higher electrical conductivity than LSM, use of LSCo as cathode contact would likely improve cell performance. However, a major hurdle presented to employ LSCo is its higher CTE (~18x10^{-6}/^{o}C) than typical cell and metallic interconnect materials (~12-13x10^{-6}/^{o}C). Such large mismatch in CTE would lead to large residual stresses and damage the contact bonding during thermal cycling. In FY18, we proposed a composite approach to tailor the CTE of LSCo-based contact by using low CTE and potentially inert mullite as fillers. The work will be divided in three sections:

- Effect of mullite volume fraction (0, 0.1, 0.2, 0.3, and 0.4) on CTE of the LSCo composite
- Electrical conductivity measurement of LSCo composite at elevated temperatures
- Bonding strength evaluation of joined couples on as-joined and thermally-cycled ones

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.

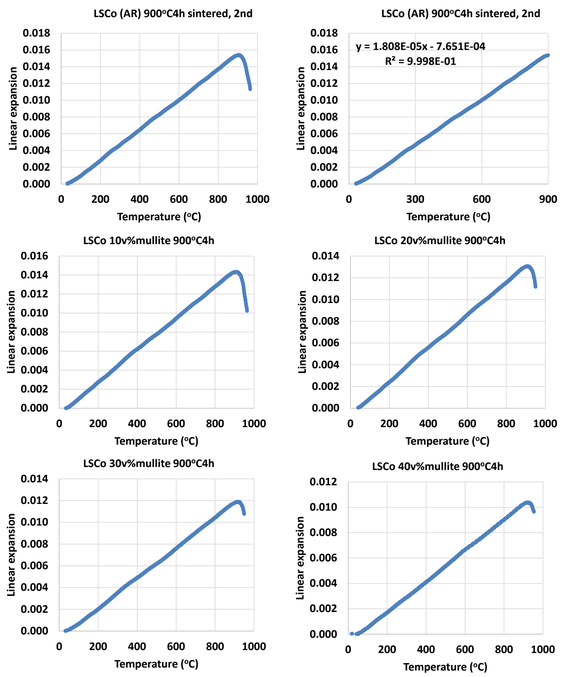


Matching fracture surface shows the weak link of LSM contact (left) at the LSM cathode surface (right) of a cell in stack fixture test. Note the LSM contact materials was completely de-bonded from LSM cathode surface, due to poor solid-state sintering at 930^{o}C (stack firing temperature), as compared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

1. Effect of Mullite Volume Fraction on CTE of Composite LSCo Contact

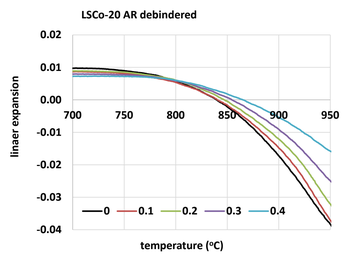
- Objective was to determine optimum volume fraction to decrease CTE without losing electrical conductivity as well as microstructure/phase stability
- Candidate LSCo powders were ball-milled with Mullite powders at 0, 0.1, 0.2, 0.3, and 0.4 volume fractions.
- Mixed powders were pressed into cylinders and sintered at 900^{o}C4h in air to mimic stack final firing conditions
- Dilatometry was used to obtain CTE at a ramp rate of 2^{o}C/min in air to 950^{o}C, 2 samples were used for each volume fraction

Typical thermal expansion behavior



Presence of mullite showed decrease of linear expansion with increasing volume fraction. In addition, the filler may also retard the intrinsic densification of LSCo at ~900^{o}C. Average CTE was therefore calculated up to 900^{o}C.

Composite sintering behavior



Presence of mullite showed decreased densification with increasing volume fraction of mullite.

Model Prediction for CTE of Composite

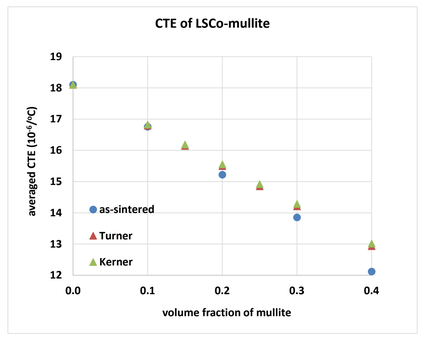
$\alpha_{comp} = (\alpha_1 K_1 F_1/\rho_1 + \alpha_2 K_2 F_2/\rho_2)/(K_1 F_1/\rho_1 + K_2 F_2/\rho_2)$
(Turner, hydrostatic tension and compression only)

$\alpha_{comp} = \alpha_1 + \nu_2(\alpha_2 - \alpha_1)(K_1(3K_2+4G_1)^2 + (K_2-K_1)(16G_1^2+12G_1K_2)/(4G_1+3K_2)(4\nu_2 G_1(K_2-K_1)+3K_1K_2+4G_1K_1)$
(Kerner, including shear stress)

K: bulk modulus, G: shear modulus, F: mass fraction, ν: Poisson ratio, ρ: density

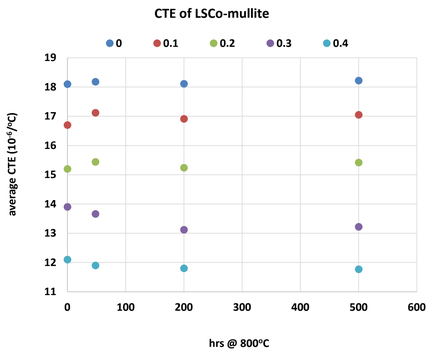
Property	LSCo	mullite
E (GPa)	142.4	230
G (GPa)	54	93
K (GPa)	140	146
α (10^{-6}/^{o}C)	18.1	5.5
poisson ratio	0.33	0.24

2. Measured versus Model Prediction



Presence of mullite showed relatively linear decrease with Increasing volume fraction, consistent with both model predictions, implying no severe and substantial reaction occurred between LSCo and mullite. Some deviation observed at highest V_f=0.4 for the as-sintered composites.

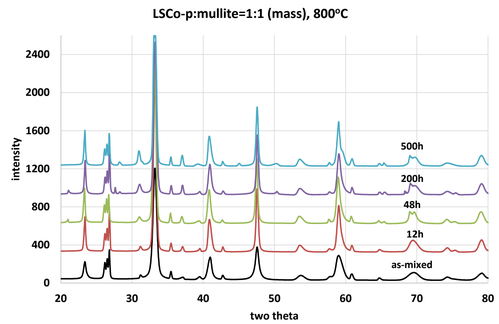
3. Effect of Ageing on CTE



Isothermal ageing in air showed minimum changes of CTE of LSCo-mullite composite over 500h in air. Composite with mullite of Vf=0.3 showed the largest change ~7% after 200h ageing. Overall, the composite appears thermally stable.

4. Crystalline Phase Analysis

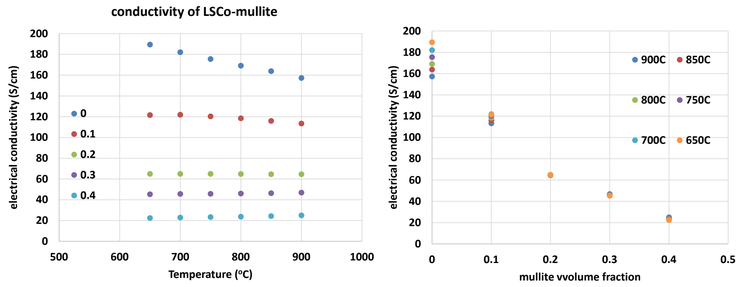
- LSCo:mullite=1:1 mixture pressed pellets and sintered at 800^{o}C for 12, 48, 200, and 500h in air



No other phase was identified besides LSCo and mullite phases, implying good chemical compatibility.

5. Electrical Conductivity at Elevated Temperature

- Sintered LSCo/mullite disc composite samples were measured with Pt plates and Pt wires in 4-pt at elevated temperatures (650-900^{o}C) in air
- Compressive load was applied to ensure good contact



Summary and Conclusions

1. Sintering study of LSCo-mullite mixture showed some retardation of sintering behavior where the onset temperature of shrinkage slightly increased with increasing mullite content.
2. Thermal expansion results all showed linear behavior with temperature, suggesting no substantial reaction between LSCo and mullite.
3. Adding mullite into LSCo can greatly reduce CTE of the composite from ~18x10^{-6}/^{o}C (v_f=0) to ~12.1x10^{-6}/^{o}C (v_f=0.4).
4. Measured average CTE was found consistent with model predictions with largest deviation of ~7% at v_f=0.4.
5. The average CTE remained fairly constant over 500h isothermal ageing at 800^{o}C, implying good chemical compatibility between mullite and LSCo.
6. Electrical conductivity showed decreasing behavior with increasing mullite content.
7. Future work will be focused on contact strength evaluation and microstructure analysis.

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