Mitigation of Cr Poisoning: An Investigation of LSCo/LSCF4628 Composite

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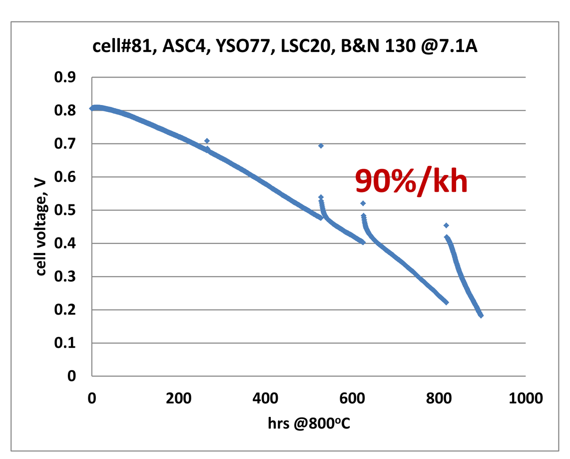
Introduction:

Cr is known to cause severe cell degradation in solid oxide fuel cells (SOFCs). Volatile species such as $CrO_2(OH)_2$ and CrO_3 have been identified as the leading poisons. Many attempts have been made to mitigate the problem by coatings of metal parts, and their protection has been proven successful for short to mid-term operations.

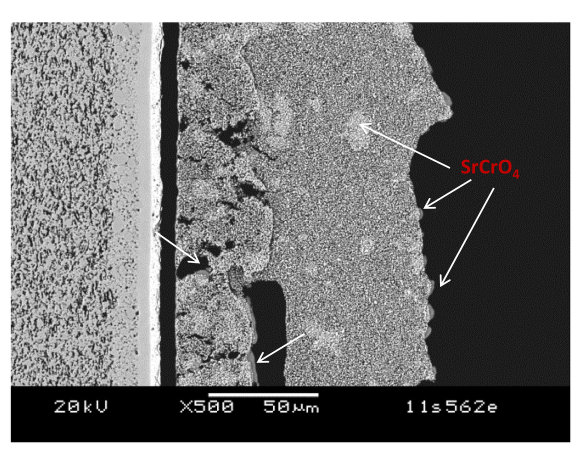
In addition to coatings where the long-term stability remains to be verified, we propose Cr-gettering materials (whether in upstream or on-cell) as a parallel means to mitigate the Cr issues. LSCF is currently used as a leading SOFC cathode materials, and has demonstrated much higher electrochemical performance than LSM-based cells. In previous work of LSCF-based cells, substantial amount of $SrCrO_4$ was found throughout the entire cathode. Reaction study also showed rapid reaction of LSCF and was proposed as Cr-gettering materials. For on-cell application, high conductivity is needed and In FY20 we focused on LSCo/LSCF4628 series. Properties of CTE, electrical conductivity, and chemical compatibility are most important. The work is divided in these areas:

- CTE study of LSCo20/ LSCF4628 composites with LSCF volume fractions from 0.1 to 0.4
- Isothermal ageing (800°C/1kh) on composites' CTE
- Electrical conductivity at elevated temperatures
- Microstructure and phase characterization
- Validation test in generic stack test fixture using 2"x2" cell (on-cell application)
- Complete post-mortem microstructure analysis

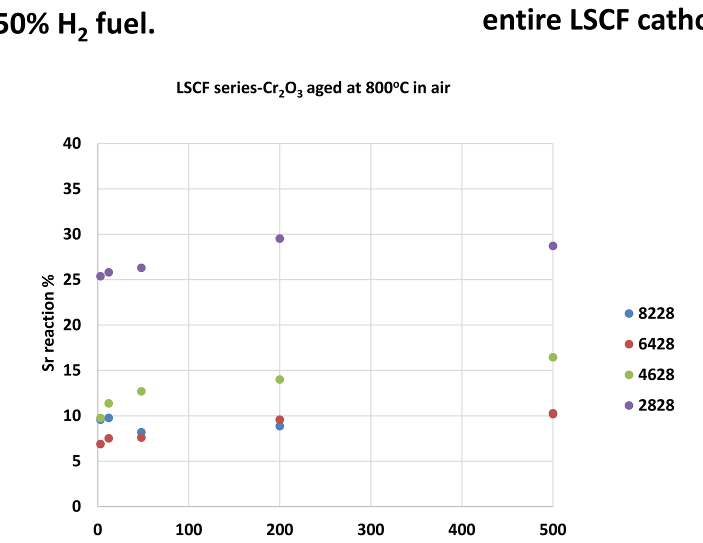
Evidence of Cr-Gettering by LSCF



LSCF6428-based cell (2"x2") shows very large degradation (90%/kh) during stability tests at constant current mode at 800°C with Cr sources in humid air and 50% H_2 fuel.



Post-mortem microstructure of LSCF6428-based cell (2"x2") after 800°C 1000h stability test showed substantial formation of $SrCrO_4$ throughout the entire LSCF cathode layer.

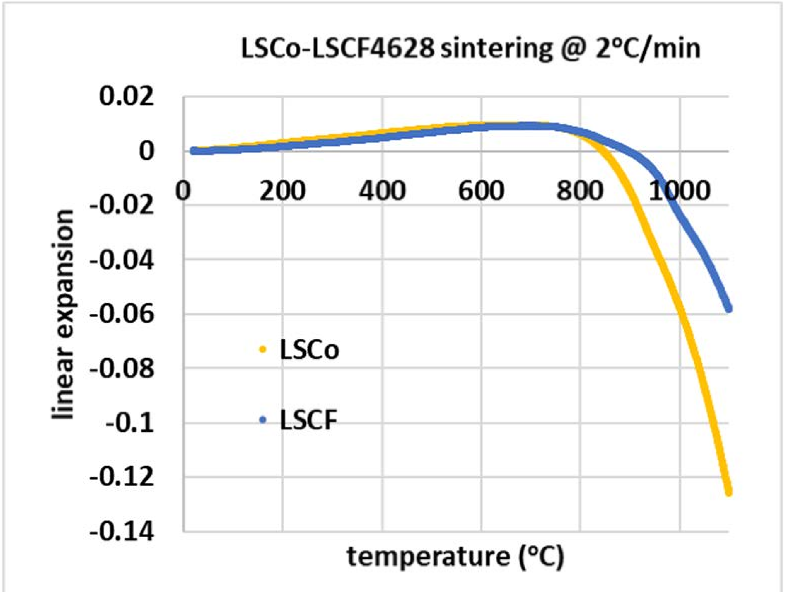


Quantitative XRD analysis showed the reaction between LSCF and Cr_2O_3 at 800°C is very rapid (in minutes) and the reactivity order is LSCF2828 > LSCF4628 > LSCF6428 ~ LSCF8228.

1. : Sintering Behavior

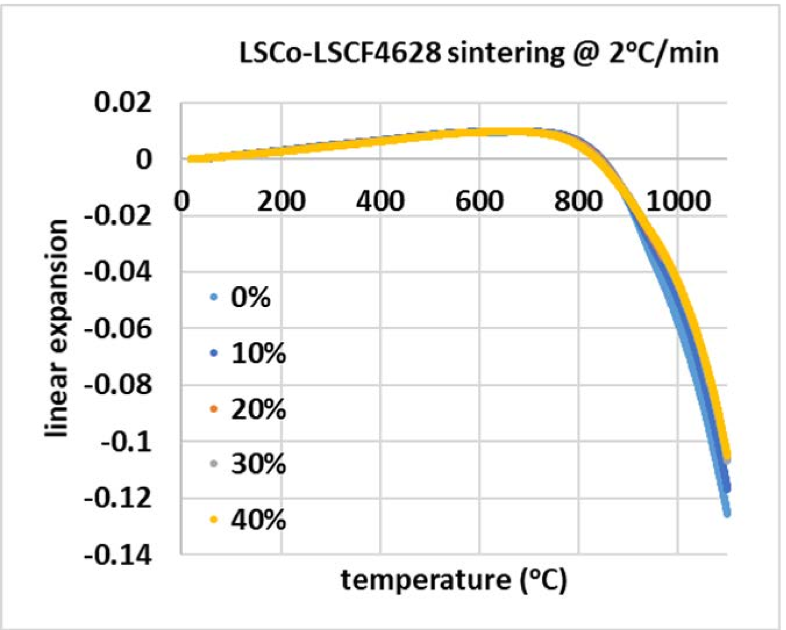
- LSCo20 mixed with LSCF4628 at volume fractions of 0.1, 0.2, 0.3, and 0.4.
- Bars are pressed and sintered at 950°C 3h in air
- CTE measured on sintered (950°C3h) bars at ramp rate 2°C/min

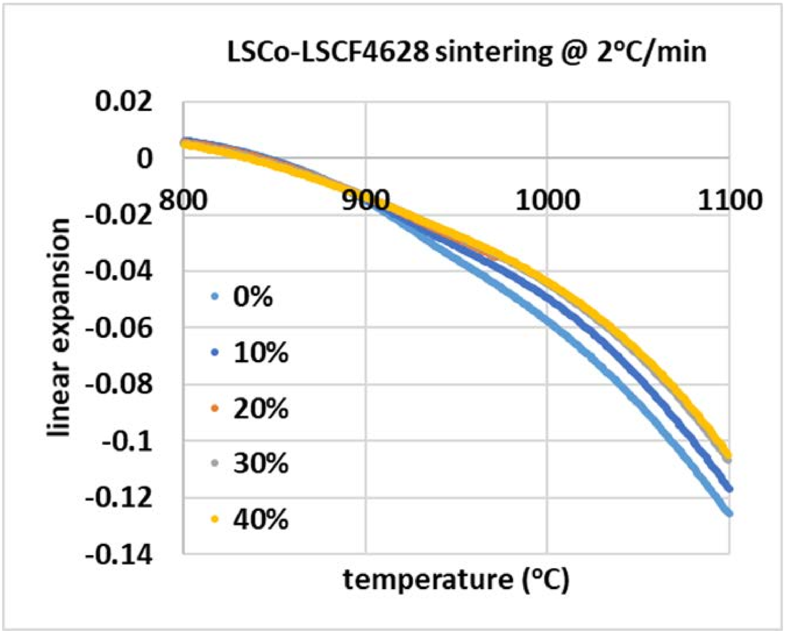
As-received LSCo and LSCF4628



Similar onset of shrinkage while LSCo shows a better sintering behavior

LSCo/LSCF4628 composites





No distinct retardation in densification of LSCo matrix by addition of LSCF4628 powders

2. Effect of Ageing on CTE of LSCo/LSCF4628 and Model predictions

- All samples initially 950°C3h sintered
- Isothermal ageing at 800°C 1000h in air
- CTE measured in both as-fired and aged

$$\alpha_{comp} = (\alpha_1 K_1 F_1/\rho_1 + \alpha_2 K_2 F_2/\rho_2)/(K_1 F_1/\rho_1 + K_2 F_2/\rho_2)$$

(Turner, hydrostatic stress only)

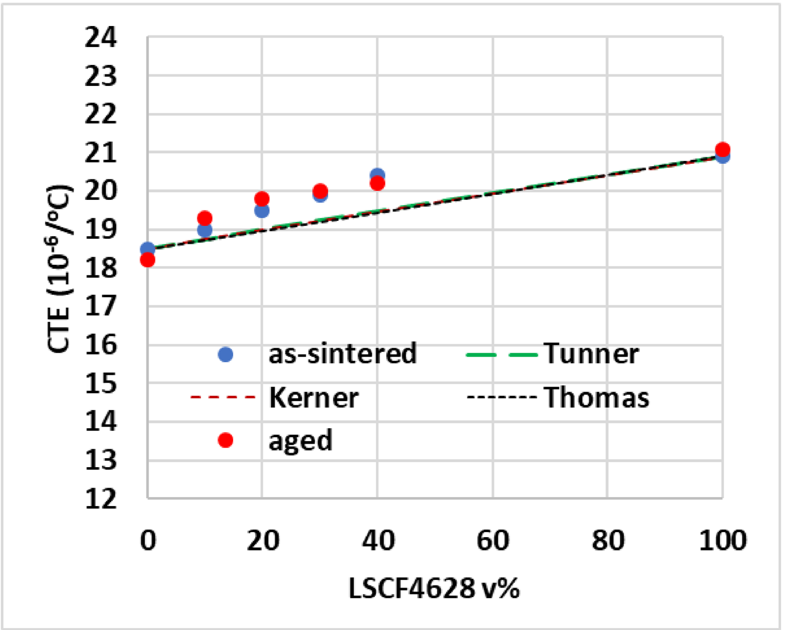
$$\alpha_{comp} = \alpha_1 + v_2(\alpha_2 - \alpha_1)(K_1(3K_2+4G_1)^2 + (K_2 - K_1)(16G_1^2 + 12G_1K_2)/(4G_1+3K_2)(4v_2G_1(K_2-K_1)+3K_1K_2+4G_1K_1)$$

(Kerner, including shear stress)

$$\alpha_{comp} = \alpha_1^{v1}\,\alpha_2^{v2}$$

(Thomas, empirical)

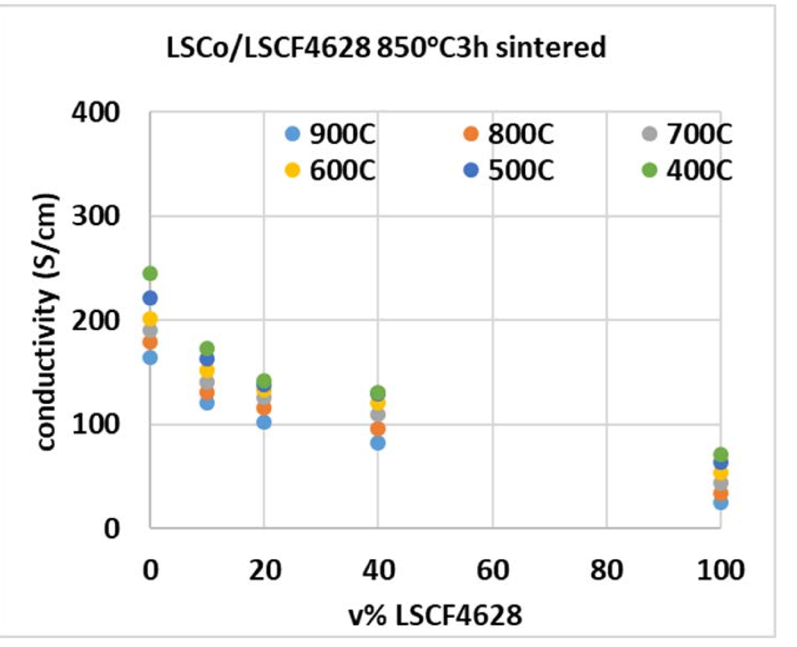
Property	LSCo	LSCF4628
G (GPa)	53.5	60.4
K (GPa)	140.3	145.8
α (10^{-6}/°C)	18.5	20.9
Poisson's Ratio	0.33	0.32

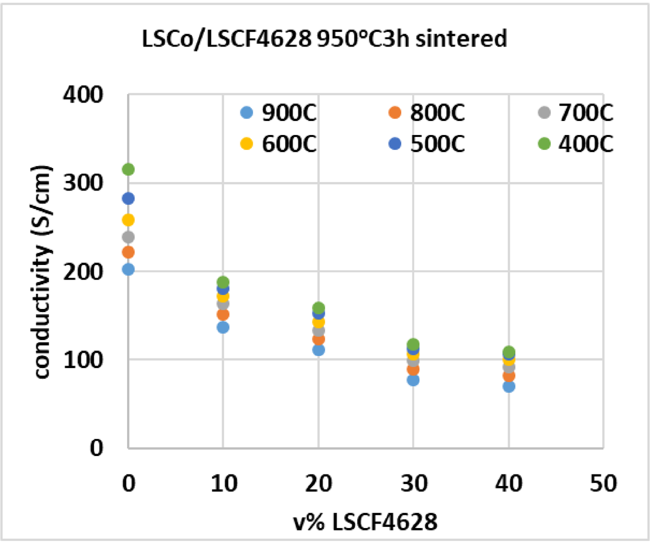


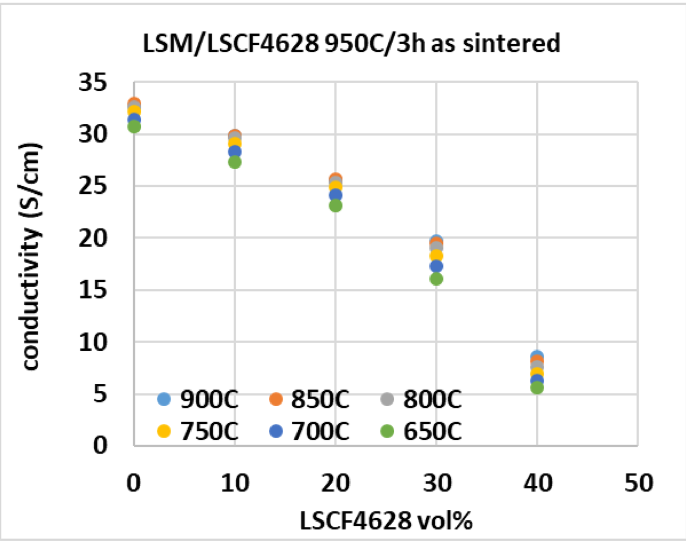
1. Effect of isothermal ageing appears minimum, suggesting no severe reactions between LSCo and LSCF4628
2. Small deviations (<5%) of averaged CTE between measured values and predictions, implying chemical compatibility

3. Electrical Conductivity

3.1 Effect of LSCF4628 v% on conductivity

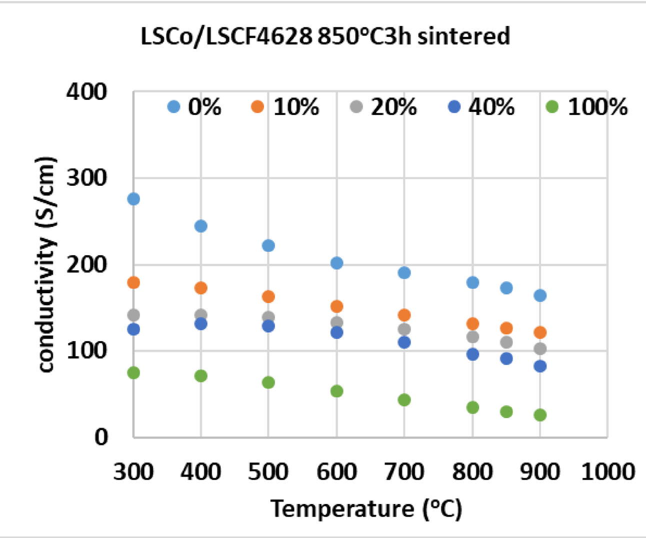


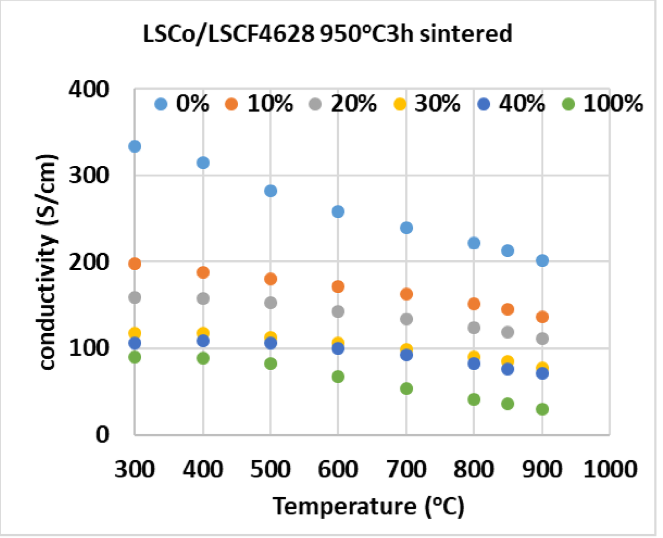




Much higher electrical conductivity of LSCo/LSCF composites than LSM/LSCF series

3.2 Effect of temperature on conductivity





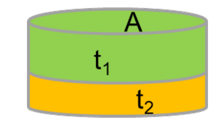
Metallic conduction behavior observed where conductivity decreases with increasing temperature

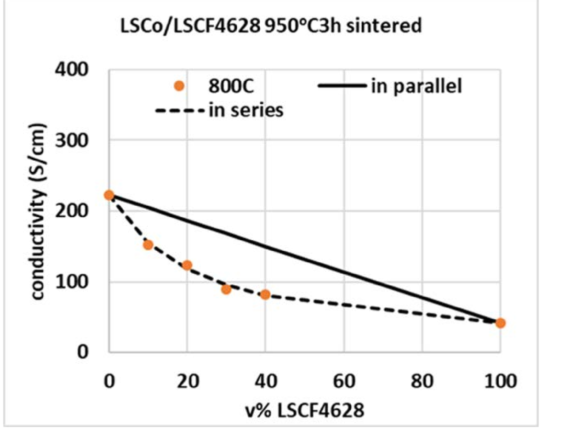
3.3 Comparison with model prediction

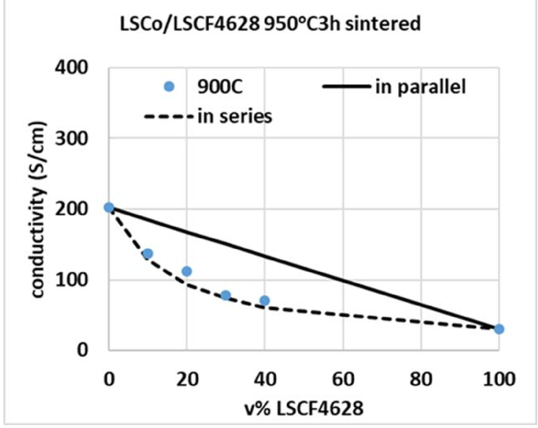
$$R_{comp} = R_1 + R_2$$

$$\rho_{comp}(t_1+t_2)/A = \rho_1 t_1/A + \rho_2 t_2/A$$

$$\rho_{comp} = \rho_1 v_1 + \rho_2 v_2$$







Good agreement of measured conductivity with simple resistor in series model

Summary and Conclusions

- ➢LSCo/LSCF4628 series at 10, 20, 30, and 40v% were investigated.
- ➢Sintering study showed minimal retardation in densification with the addition of LSCF4628 since both powders have similar onset temperature for sintering.
- ➢CTE results showed increasing trend with increasing LSCF v%, consistent with model prediction by 3 different models with errors less than 5%.
- ➢No substantial change in CTE after 800°C/1kh ageing, suggesting thermal and chemical stability.
- ➢Electrical conductivity also exhibited electronic conducting behavior of decreasing conductivity with increasing temperatures.
- ➢Nonlinear behavior of electrical conductivity vs LSCF v% appears in agreement with simple resistor in series model.
- ➢Future work will be mechanical property of LSCo/LSCF series sintered between 850-1000°C, validation in a generic stack fixtures, and optimization microstructure with strong short fiber reinforcement for thermal cycle stability.

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