

Cr Mitigation by LSCF-based Materials for Solid Oxide Fuel Cells



Pacific Northwest
NATIONAL LABORATORY

Y-S Chou, J.P. Choi, J. Bonnett, N. Canfield, and J. W. Stevenson
K2-44, Energy Processes & Materials, PNNL, Richland, WA 99354

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Introduction:

Cr is known to cause severe cell degradation in solid oxide fuel cells (SOFCs). Volatile species such as $\text{CrO}_2(\text{OH})_2$ 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 operation.

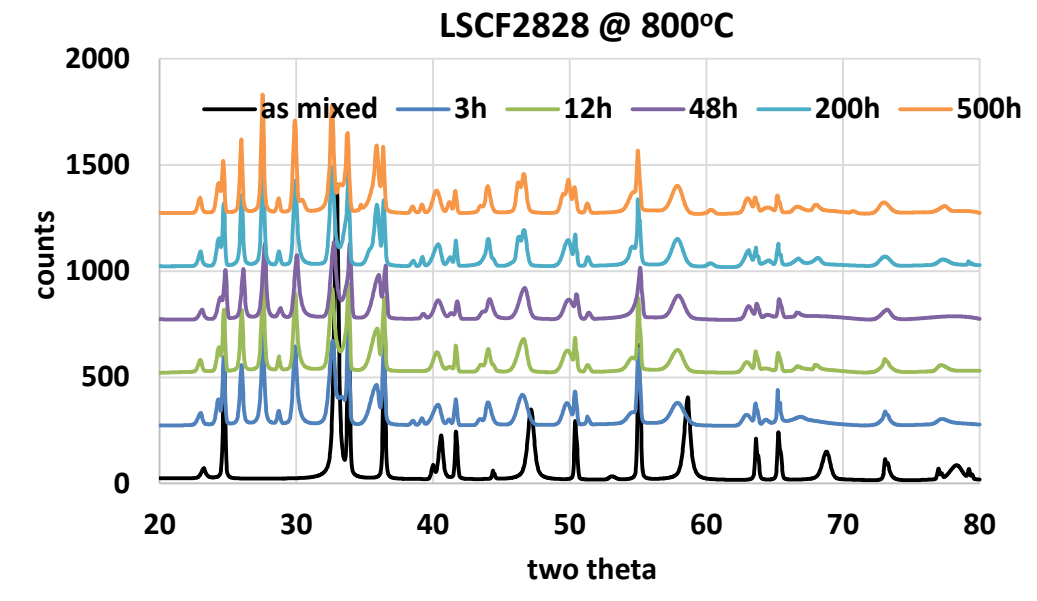
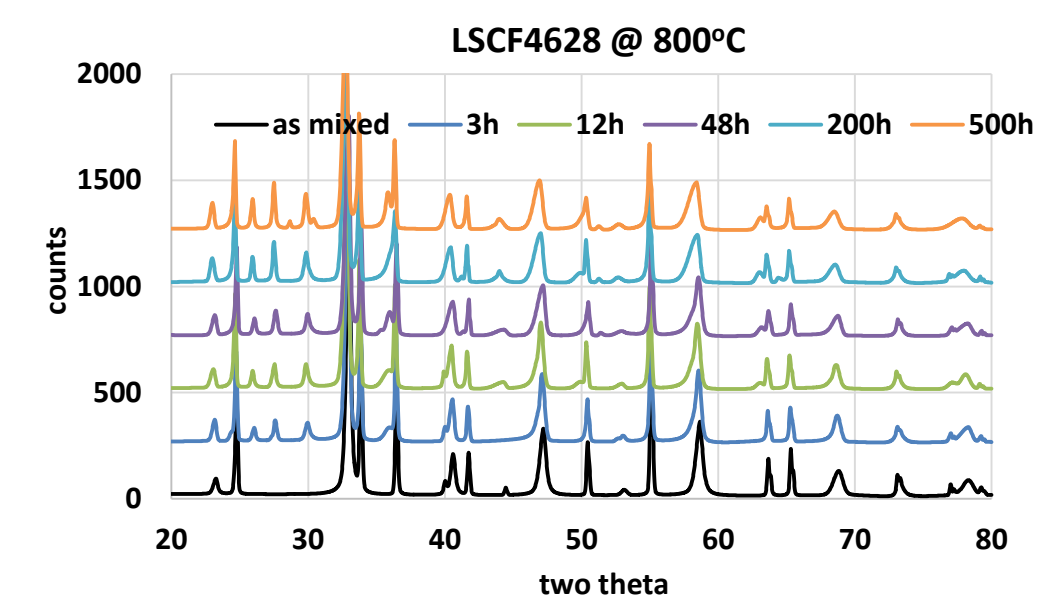
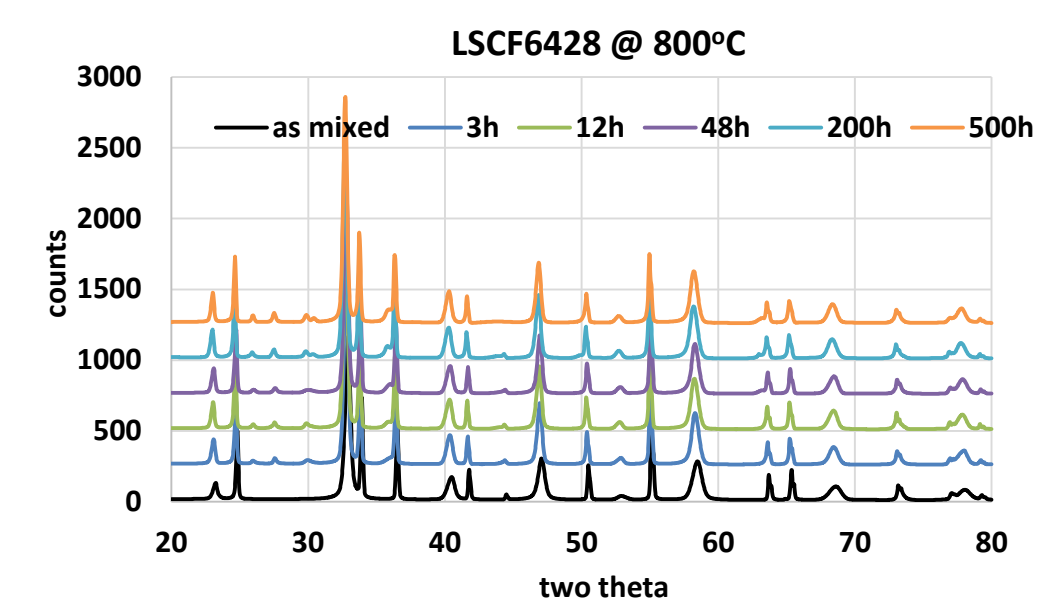
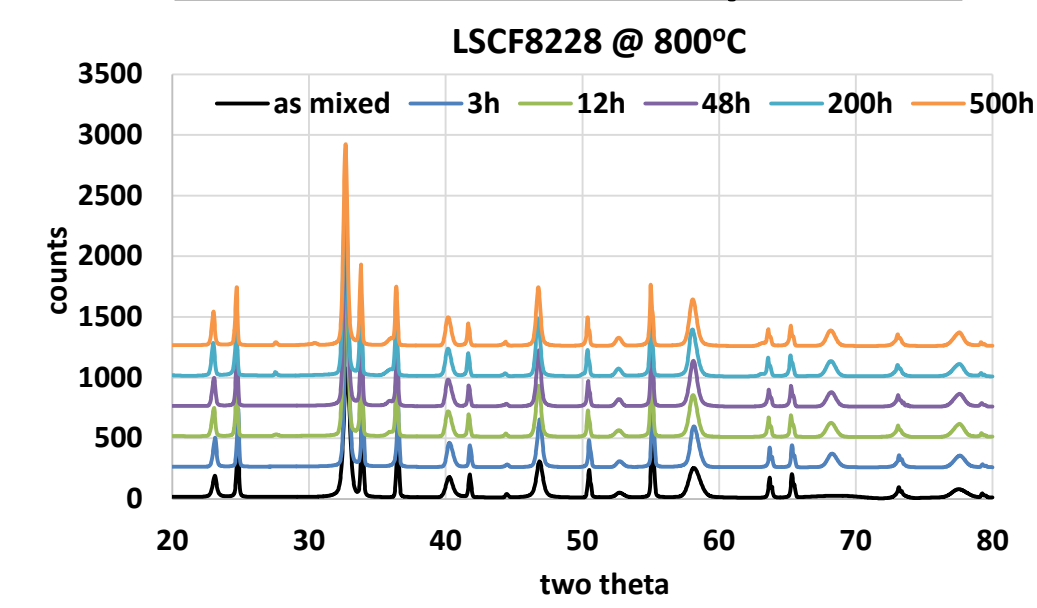
In addition to coatings, we propose Cr-gettering materials (whether in upstream or on-cell) as a means to mitigate the Cr issues. LSCF is currently used as a leading SOFC cathode materials, and has demonstrated much higher electrochemical performance than LSM-based cells. In previous stack testing of LSCF-based cells, substantial amount of SrCrO_4 was found throughout the entire cathode, and therefore LSCF was proposed as a good Cr-getter candidate. In FY18 we will study the chemical reaction kinetics and the effect of La/Sr ratio on SrCrO_4 formation to identify optimum candidates. The work will be divided as:

- Chemical reaction study of LSCF8228, 6428, 24628, and 2828 with Cr_2O_3
- Effect of isothermal ageing on chemical reaction
- Validation test in generic stack test fixture using 2"x2" cell (upstream, on-cell, or both)
- Complete post-mortem microstructure analysis

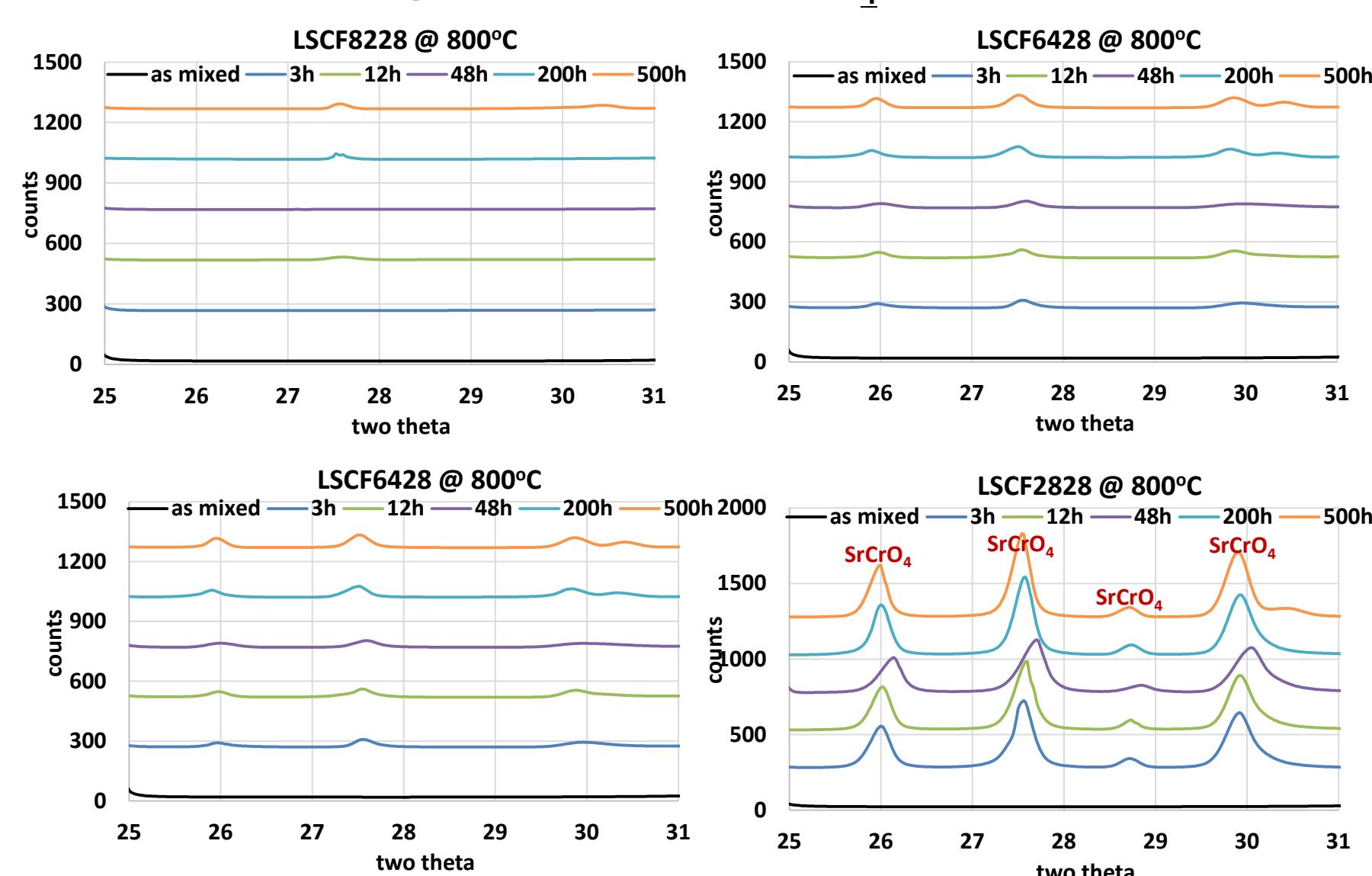
1. Chemical Reaction Study

- ❖ Objective was to study La/Sr ratio on SrCrO_4 formation
- ❖ LSCF8228, 6428, 4628, and 2828 powders were commercially obtained through combustion synthesis
- ❖ LSCF:Cr₂O₃ powders at 1:1 ratio were mixed in ball-mill and then pressed as pellet sintered at 800, 900, and 1000°C for 3h to 500h in air

Effect of Time and La/Sr Ratio

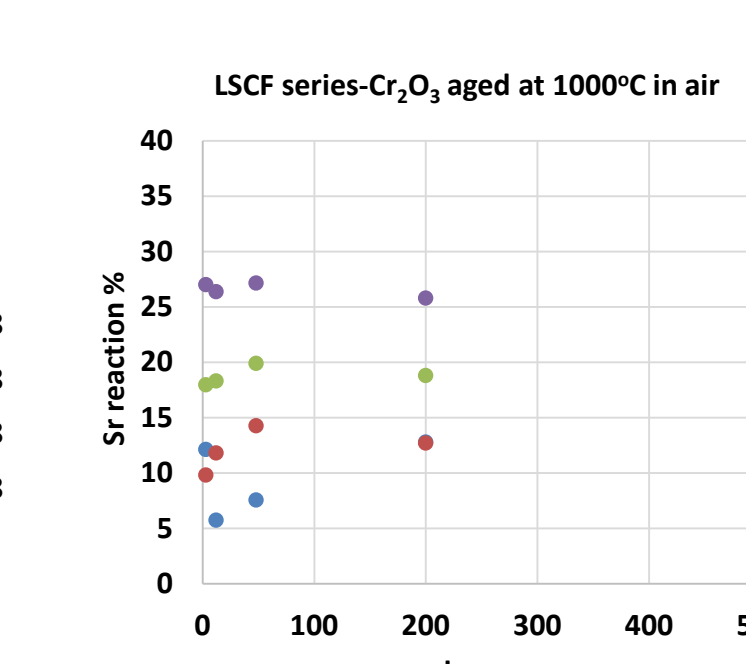
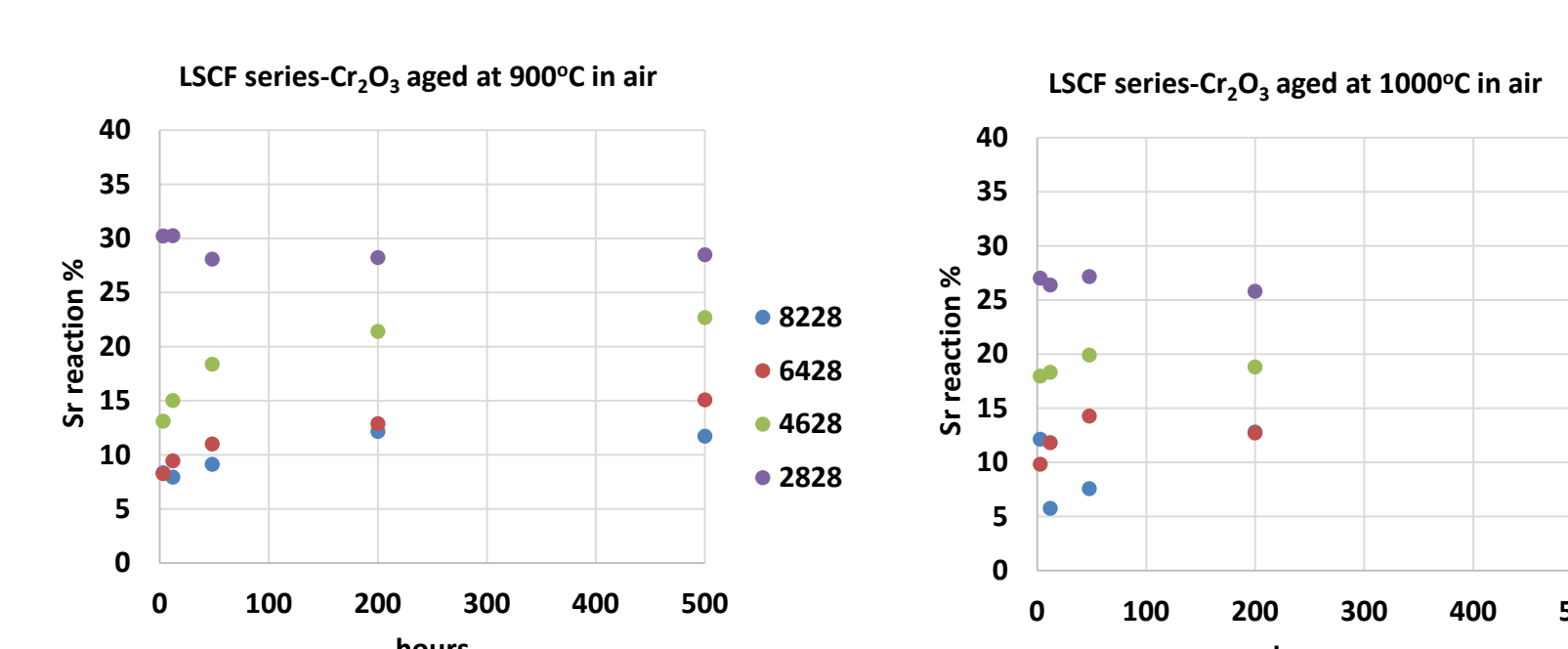
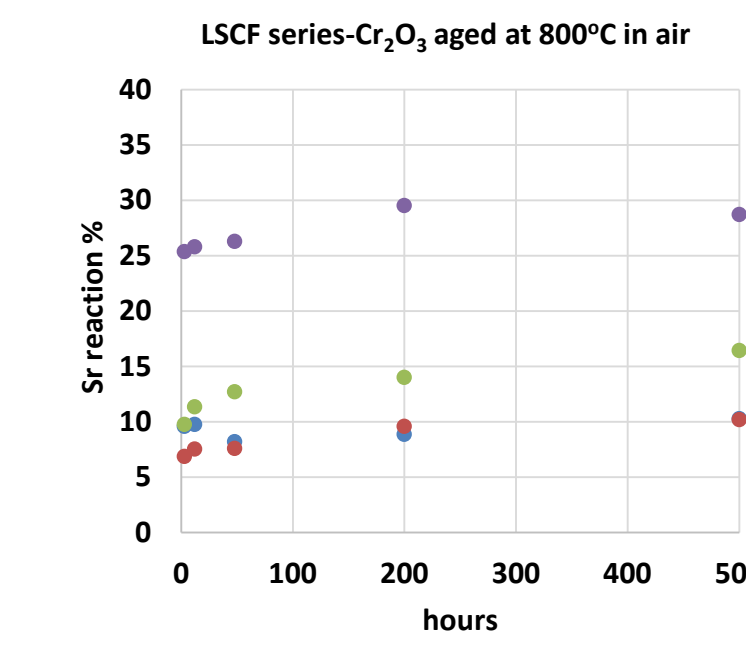
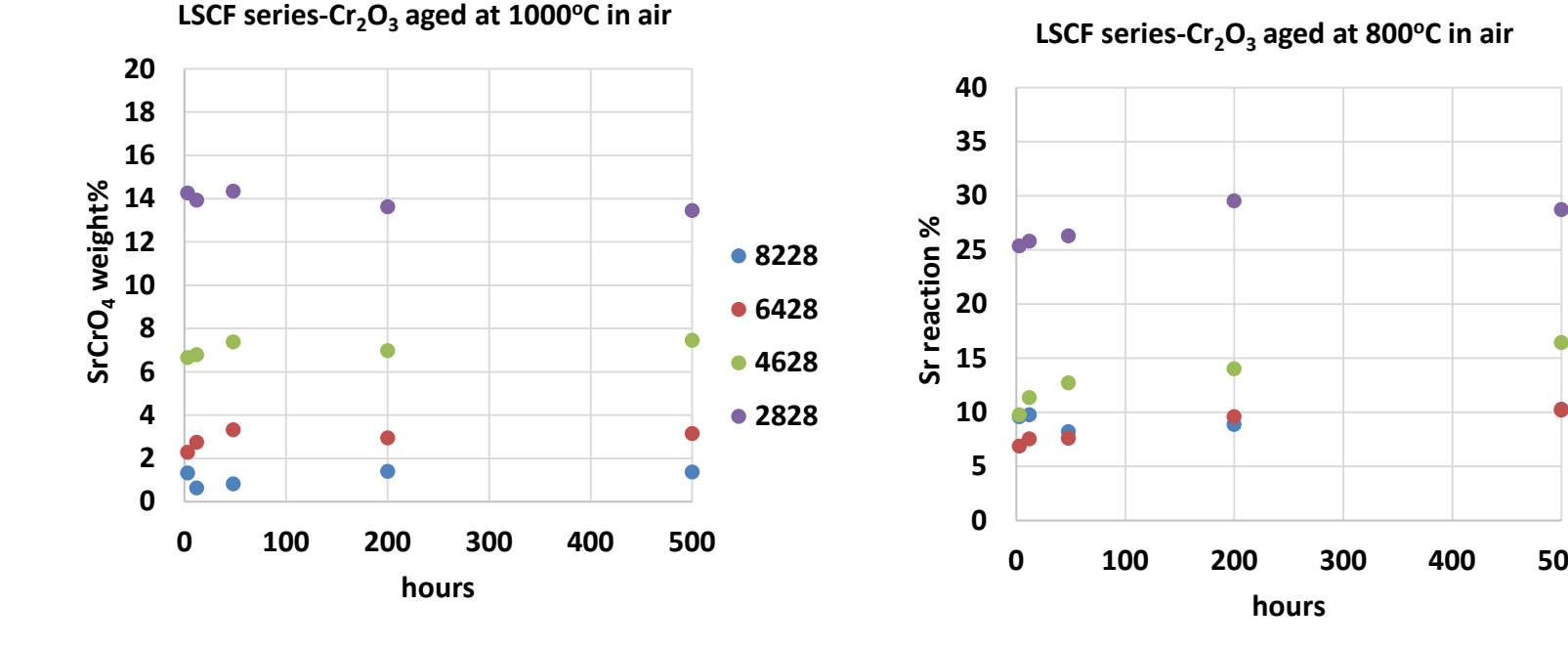
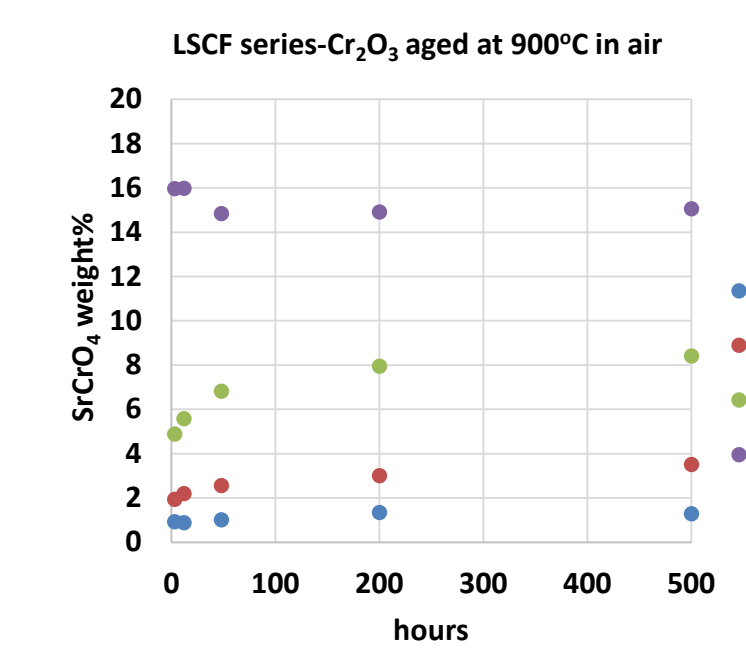
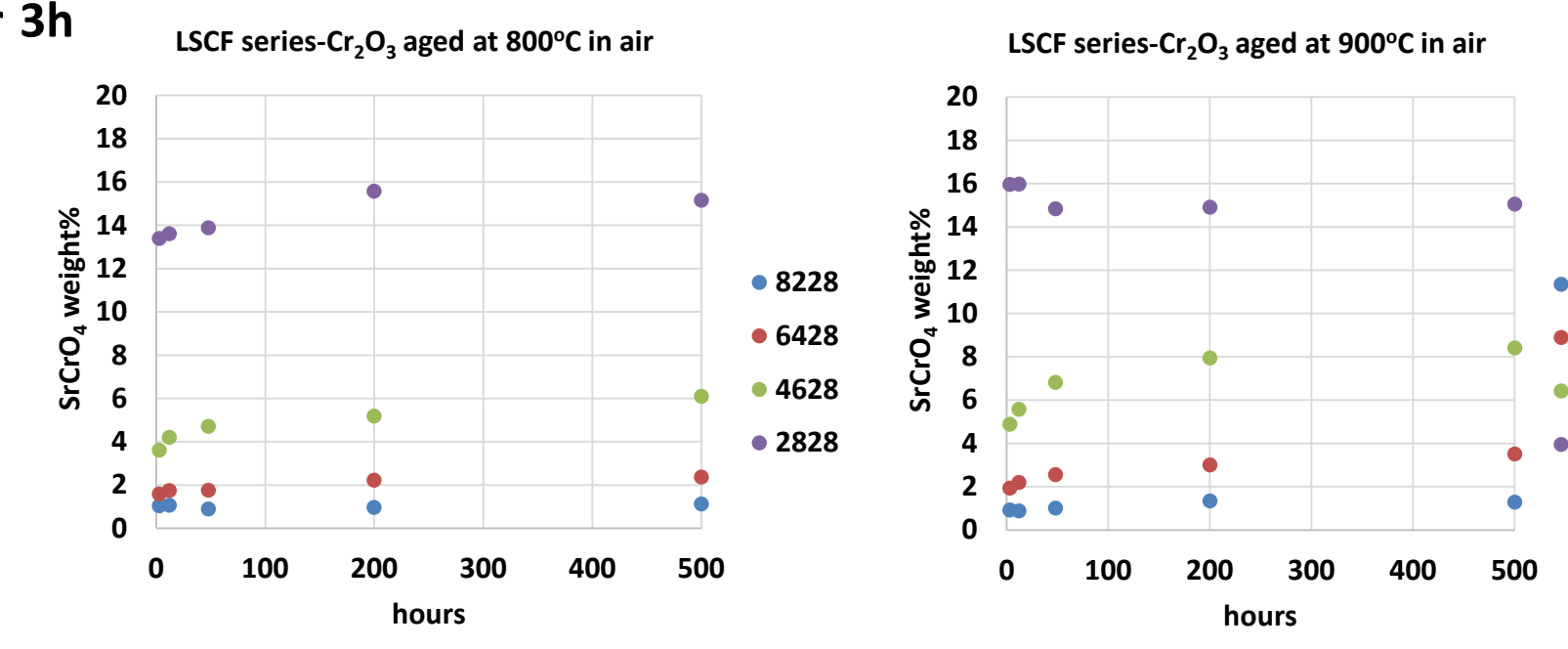


Enlarged View Shows SrCrO_4 Formation



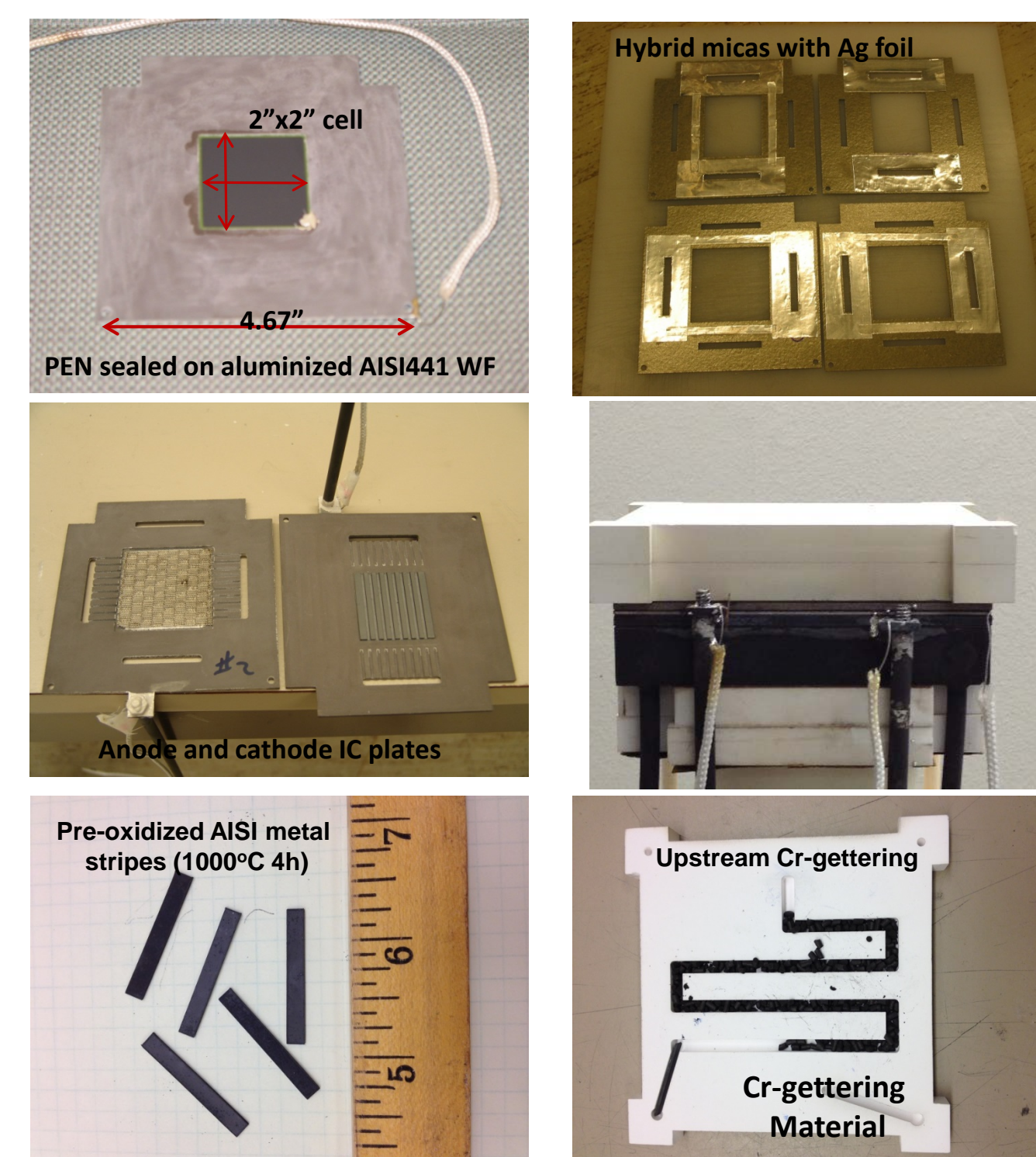
2. SrCrO4 Quantitative Analysis

- ❖ External calibration curve prepared with mixture of LSCF, Cr_2O_3 , and SrCrO_4 .
- ❖ Powder mixtures with SrCrO_4 at wt%, 2,4,6,8,12,16, and 20

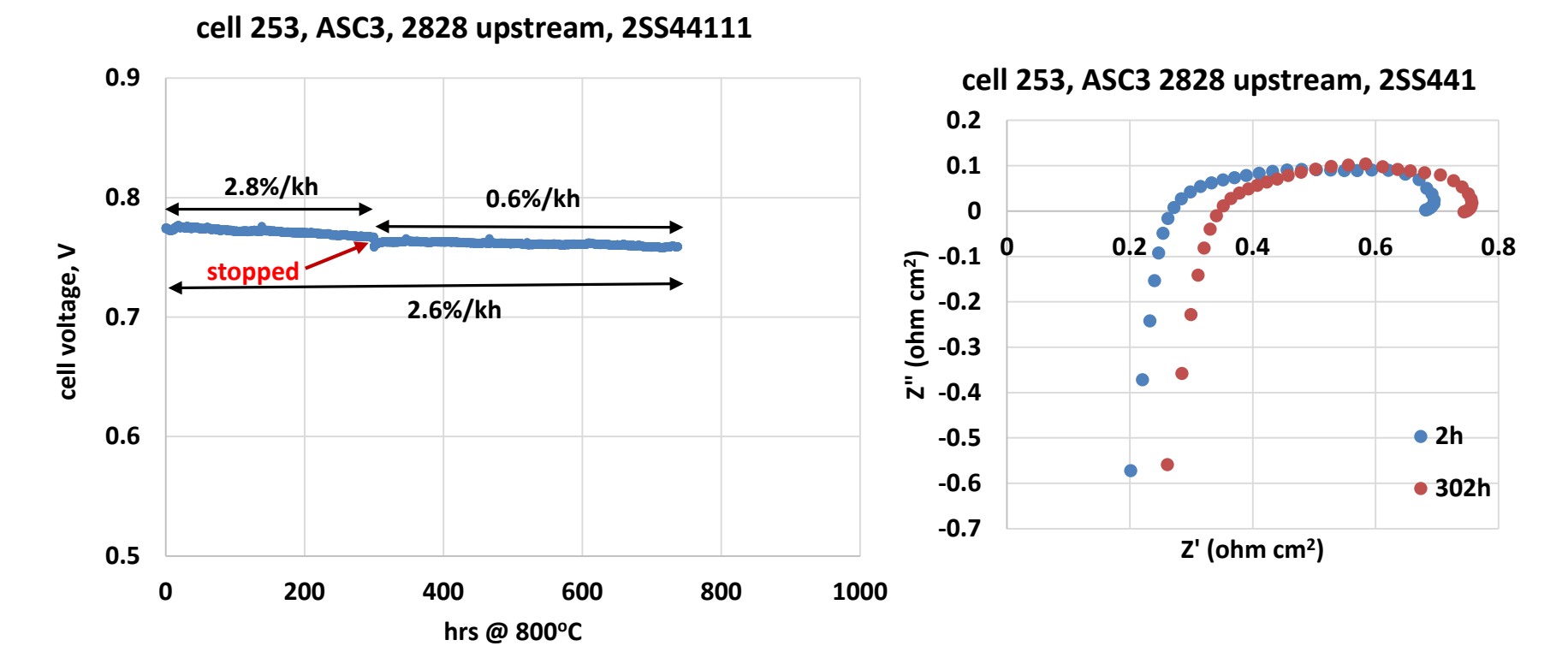


Quantitative analysis showed LSCF2828 is the most reactive to form SrCrO_4 at the presence of Cr source, while LSCF8228 is least reactive at all three temperatures. The reaction is rapid that 0.5h is almost complete.

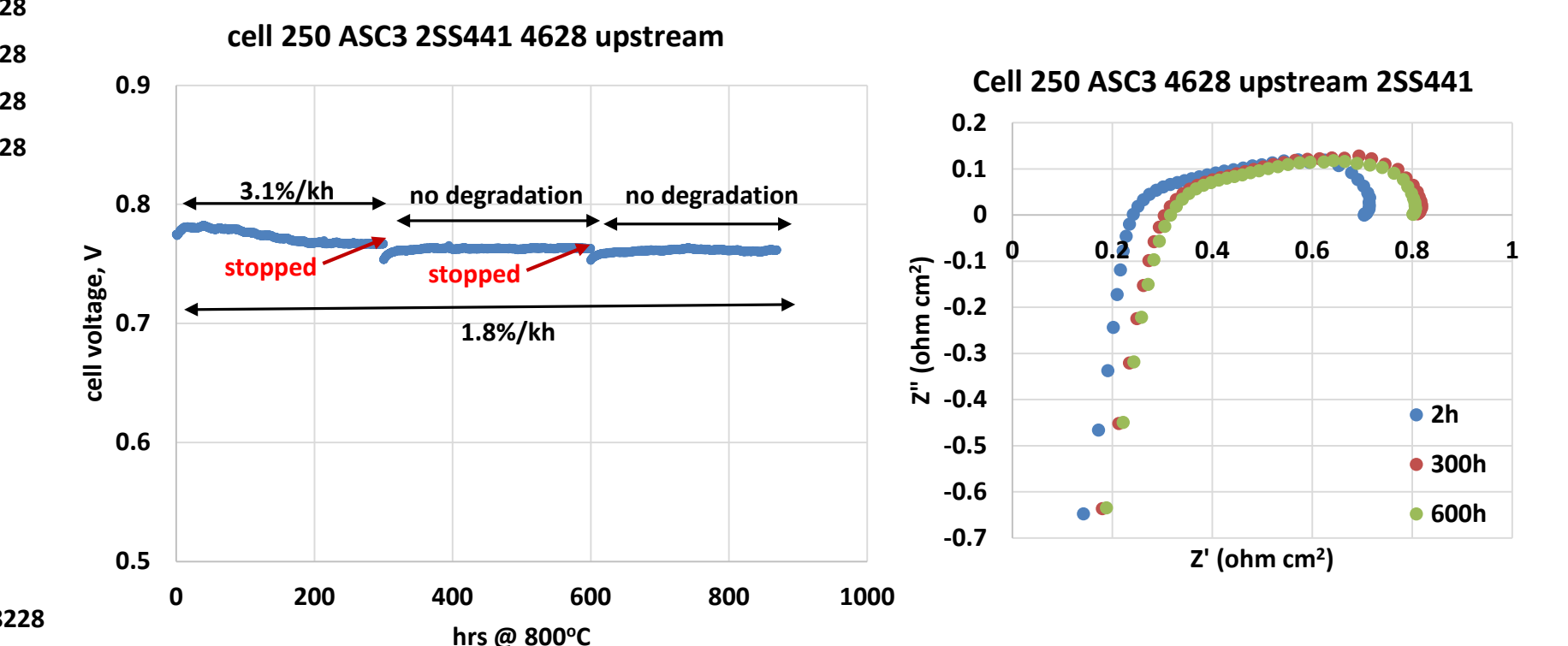
3. Validation in a Stack Test Fixture:



LSM-based Cell Performance at 800°C with Upstream Cr Source and LSCF-getters at Constant Current Mode and Humid Air

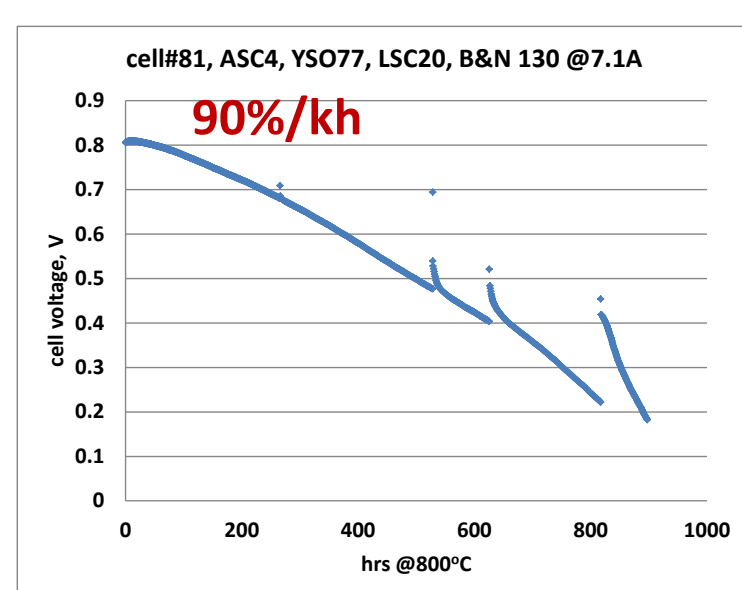


Validation cell test with LSCF2828 as Cr getter placed at upstream and tested at 800°C in humid air with un-coated SS441 as Cr source. Note that minor cell degradation was observed during first segment which was due to ohmic increase.

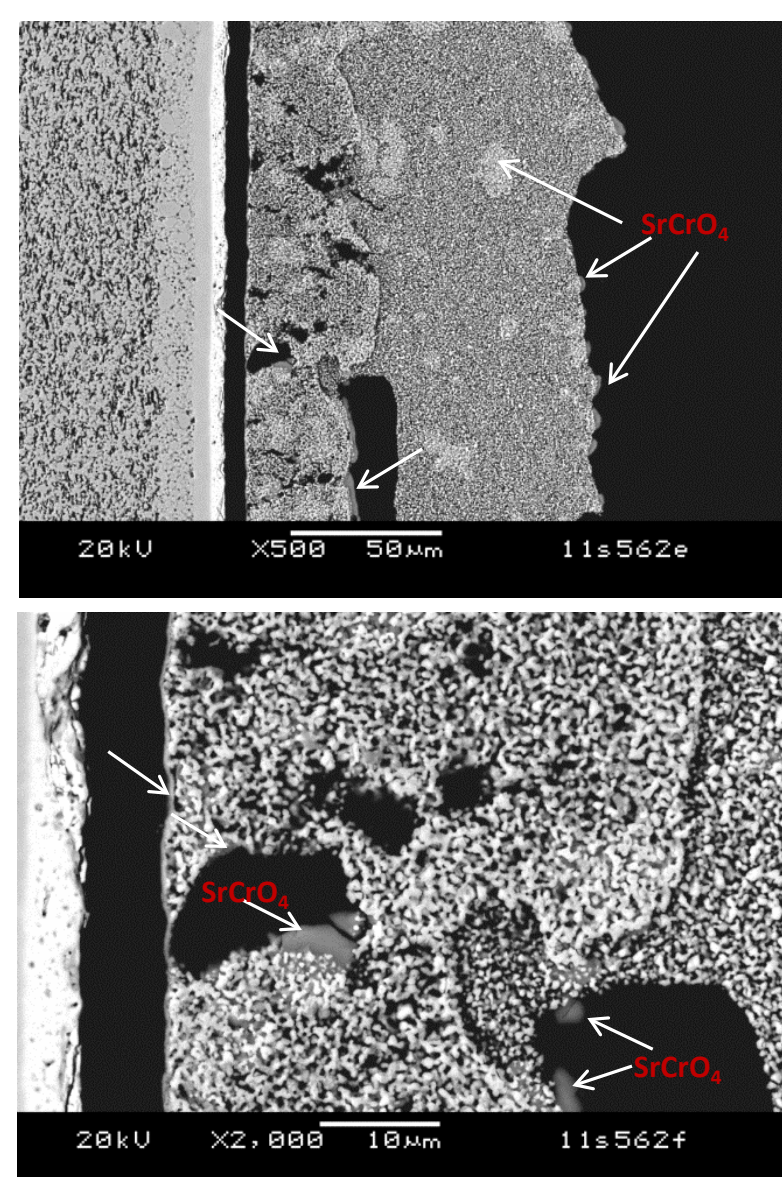


Validation cell test with LSCF4628 as Cr getter placed at upstream and tested at 800°C in humid air with un-coated SS441 as Cr source. Note no cell degradation was observed after first segment which was due to ohmic portion.

Previous Observations of LSCF-based Cell Exposed to Cr Sources in Stack Tests



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% H₂ 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.

Summary and Conclusions

1. Chemical reaction study of powder mixture of LSCF series with Cr_2O_3 in air showed the formation of SrCrO_4 in all LSCF series. LSCF with high La/Sr ratio (8/2) has the least reactivity while LSCF with low La/Sr ratio (2/8) formed the most chromate.
2. At all three temperatures, the formation of chromate is very rapid and complete in time as short as half an hour.
3. Quantitative analysis showed Sr in LSCF series reacted the most, ~30% for LSCF2828, and decreased with Sr in LSCF structure to ~24% for LSCF4628, ~15% LSCF6428, and ~12% LSCF8228 at 900°C after 500h.
4. Validation with LSM-based cells in stack test fixture showed desirable minimum degradation when LSCF2828 and LSCF4628 were placed at upstream as Cr getters.
5. Future work will continue validation tests with on-cell application and post-mortem microstructure analysis.

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ACKNOWLEDGEMENT

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