Surface & Grain Boundary Degradation of LSCF/SDC Electrode in SOFC and SOEC

Yun Chen,^{1,3} Yueying Fan,^{1,2} Harry Abernathy,¹ Gregory Hackett,¹ Xueyan Song^{1,3}

I Background & Motivation:

- The effect of moisture on cathode performance depends on electrochemical operation (including operation duration and current density). For LSCF, such moisture impact could be further complicated by the instability of Sr.
- No detailed nanostructure analysis exists on the impact of moisture on Sr segregation on the internal surface (where the electrochemical reactions taking place) of porous LSCF/SDC electrode from the commercial cells operated over long term (>2000 hours at ~750°C, with humidified air).
- Detailed analysis is also not available on the impact of the humidity on the nanostructure of the LSCF/LSCF and SDC/SDC grain boundaries.

Present Work: Understanding the nanostructure origin of SOFC performance degradation induced by moisture in the air.

- ✓ SOFC commercial cells were evaluated over long term electrochemical operation.
- Analysis of electrochemical chA commercial button cell with LSCF/SDC cathodes was examined in dry air at 750°C, at 0.6A/cm² for 4610 h.
- A commercial button cell with LSCF/SDC cathodes was operated in 10% humidified air at 750°C at 0.6A/cm² for 2571 h. ✓ Cell characterization focused on
- Nanostructure & chemistry of internal surface of the LSCF/SDC porous electrode, the LSCF/LSCF grain boundaries, SDC/SDC grain boundaries, induced by moisture in the air.
- Nanostructure degradation evolution as the function of their distance to the electrolyte/SDC barrier layer.
- ✓ Relevance of present SOFC study on SOEC work: Common nanostructure degradation between SOFC and SOEC.

II Degradation of LSCF/SDC Electrode in SOFC

Commercial cell, SOFC, Accelerated Degradation In Humidified Air



- For the cell Operated 4610 h dry air, @0.6A/cm², @ 750°C, the cell degradation rate was 24 mV per 1000 h.
- For the cell operated for 2640 h in 10 % humidified air @0.6A/cm², @ 750°C, degradation rate was 42.5 mV per 1000 h.

Without current flow & electrochemical reactions:

- LSCF has high oxygen vacancy concentration at high temperatures due to the substitution of Sr²⁺ for La³⁺.
- The Sr dopant is charge compensated by oxygen vacancies leading to ionic conductivity.
- The conductivity is further affected by the valence stability of Fe⁴⁺ and Co⁴⁺.

Nanostructure and chemistry of cell operated for 4610 h dry air, @ 0.6 A/cm², @ 750°C.





At%	0	La	Sr	Со	Fe	Sm	Ce	Formula			
1	74.62	7.44	4.89	2.4	10.65			(La0.60Sr0.40)0.94(Co0.18Fe0.82)Ox			
2	75.36	7.25	4.91	2.48	10			(La0.60Sr0.40)0.97(Co0.20Fe0.80)Ox			
3	76.98	7.05	4.44	1.79	9.75			(La0.61Sr0.39)1.00(Co0.16Fe0.84)Ox			
4	75.5	7.34	4.89	2.11	10.16			(La0.60Sr0.40)1.00(Co0.17Fe0.83)Ox			
5	57.19					5.02	37.8	Ce0.88Sm0.12Ox			
6	55.02					4.98	40	Ce0.89Sm0.11Ox			
7	55.47			10.25	1.24	2.6	30.43	Co0.89Fe0.11Ox+SDC			
8	58.02			2.67		3.2	36.11	SDC+CoOx			

Up to 100 nm from the internal surface to grain interior:

- Surface of the backbone is free of any coating layer. La:Sr ratio remained to be nominal of La:Sr of 0.6:0.4. $(La_{0.6}Sr_{0.4})/(Fe_{0.8}Co_{0.2})$ ratio is slightly lower on the surface than that of the grain interior
- There is no apparent Sr surface segregation on LSCF surface.
- LSCF Grain boundary and triple grain boundary junction areas are free of secondary phases. SDC grain boundary is without secondary phases, but Co & Fe segregation is observed.

Nielsen, J.; Hagen, A.; Liu, Y. L., SSI 2010, v181, p517. Bucher, E.; Sitte, W.; Klauser, F.; Bertel, E., SSI 2011, v191, p61-67.; Huang, Y.; Pellegrinelli, C.; Wachsman, *E.,* 2016, v163, F171.] [Nielsen, J.; Hagen, A.; Liu, Y. L., SSI 2010, v181, p517. Finsterbusch, M, A Lussier, JA Schaefer and YU Idzerda. "Electrochemically Driven Cation Segregation in the Mixed Conductor La0.6sr0.4Co0.2Fe0.8O3-Δ." Solid State Ionics 212, (2012): 77-80.

A.M. Svensson, S. Sunde, K. Nis, Mathematical Modeling of Oxygen Exchange and Transport in Air-Perovskite-Yttria-Stabilized Zirconia Interface Regions: II. Direct Exchange of Oxygen Vacancies, Journal of the Electrochemical Society, 145 (1998) 1390. S.B. Adler, J. Lane, B. Steele, Electrode kinetics of porous mixed-conducting oxygen electrodes, Journal of the electrochemical society, 143 (1996) 3554.

Evaluation of cation migration in lanthanum strontium cobalt ferrite solid oxide fuel cell cathodes via in-operando X-ray diffraction, J.S. Hardy, C.A. Coyle, J.F. Bonnett, J.W. Templeton, N.L. Canfield, D.J. Edwards, S. Mahserejian, L. Ge, B. Ingram, J. Stevenson, J. Mater. Chem. A, 6 (2018) 1787-1801.



¹ US Department of Energy, National Energy Technology Laboratory, Morgantown WV; ² NETL Support Contractor, Morgantown, WV; ³ West Virginia University, Morgantown WV;

Nanostructure and chemistry of cell operated for 2640 h in 10 % humidified air @ 750°C:





 $(La_{0.6}Sr_{0.4})/(Fe_{0.8}Co_{0.2})$ ratio of 1.26:1 Pocket region are Co- and Fe-enriched (Co:Fe = 0.3:0.7)



• Amorphous surface layer is mostly observed <1 mm from electrolyte.

• Pockets are at original LSCF/LSCF/LSCF triple grain junction area

At% (Average/StDev)	0	La	Sr	Со	Fe	Zr	Y	La:Sr	Co:Fe	(LaSr):(CoFe)	
Pocket area	47.92 /7.87	7.95 /1.87	4.93 /1.33	9.93 /3.85	26.67 /6.53	4.11 /0.7	0.7	1.61	0.37	0.35	(La _o
Bulk LSCF	65.31/3.76	10.38 /0.73	5.72 /0.81	2.44 /0.69	13.94 /0.85	-	-	1.82	0.2	0.98	(La _o
Amorphous coating	71.23 /5.98	4.16 /0.42	1.79 /0.34	0.42 /0.39	4.31 /0.44	15.19 /6.04	0.70	2.32	0.10	1.26	(La

Several microns away from the electrolyte/buffer

Co-Fe (no fixed Co:Fe ratio) phase present at both the LSCF/LSCF grain boundaries and triple grain junction regions.

Co:Fe (LaSr): Formula

(CoFe)

0.05 La_{0.05}(Co_{0.83}F

 $e_{0,17}O_{v}$



Stand Dev 42.61 1.14 0.00 0.92 1.18





Chemical composition of hulk ISCE

At%	0	La	Sr	Со	Fe	La:Sr	Co:Fe	(LaSr): (CoFe)	Formula
Average									(La _{0.62} Sr _{0.38}) _{0.96} (C
	73.92	7.92	4.89	2.32	10.96	1.62	0.21	0.96	o _{0.17} Fe _{0.83})O _x
Stand Dev	1 83	0 55	0 55	0.52	0 72				



Со

50.17 1.05 0.00 19.13 3.88 4.93

Fe

At SDC/SDC grain boundary, a ribbon-like Co-/Fe-enriched crystalline phase observed along grain boundary plane. SDC grain boundary secondary phase

At%	0	Со	Fe	Ce	Sm	Ce:Sm	(CoFe)Ox	
Average	74.28	4.01	6.41	13.60	1.70	7.99	(Co _{0.38}	Fe _{0.62})Ox
Stand Dev	2.07	2.08	3.63	3.67	0.31			
SDC								
At%	C)	Со	Fe	Ce	2	Sm	Ce:Sm
Average		76.99	-		- 2	0.35	2.67	7.63
Stand Dev		2.01	-		-	1.92	0.29	

Water vapor facilitated vaporization during the electrochemical operation:

✓ With electrochemical reaction in the presence of water, phase stability of LSCF & vaporization Species from LSCF

- The concentration of oxygen vacancies increases, the oxygen partial pressure above the sample surface decreases. These additional oxygen vacancies can be compensated by Co⁴⁺, reverting to Co³⁺. Increased oxygen reduction during operation further changes Fe and Co to lower valence states (i.e., Fe⁴⁺ to Fe³⁺ and Co⁴⁺ to Co³⁺ or even Co²⁺). The valence state changes of transition metal oxide could decrease the chemical stability of the LSCF with respect to water vapor.
- Sr can form volatile species $Sr(OH)_2$, which is greatly determined by the H_2O vapor pressure. For various oxides, when the equilibrium vapor pressure of a volatile species is 10⁻⁷ MPa or greater, material loss due to volatilization through a laminar gas boundary layer, becomes significant.
- The formation of various volatile hydroxides depends on both the water vapor and oxygen partial pressures. The active layer near the electrolyte are largely contributing to the ORR and is expected to be experiencing a more reducing atmosphere, and the volatilization of the different species could vary as a function of the distance to the electrolyte.
- ✓ <u>Surface and grain boundary degradation:</u>
- A uniform, conformal amorphous surface layer forms that contains all four cations of La, Sr, Fe, Co. The La: Sr ratio is higher than that of Co:Fe.
- There is formation of (CoFe)O, at LSCF/LSCF and SDC/SDC grain boundaries. The mixed conducting grain boundaries could possess higher ionic conductivity with a higher amount of oxygen vacancies, triggering lower valence states of Co and Fe at the grain boundaries. This is consistent with the formation (CoFe)O_x clusters at the triple grain boundary junctions that are presumably with the highest amount of defects and oxygen vacancies. (Close to the electrolyte)
- The morphology and nucleation of (CoFe)O, changes as function of the distance to the electrolyte and oxygen partial pressure changes. Next to the electrolyte: The presence of the amorphous and the small grains indicate the slow growth rate of the (CoFe)Ox phases. Several microns away from the electrolyte: The (CoFe)O_x experiences larger grain growth.

✓ Key new findings:

- The present study suggests the LSCF degradation is associated with changes in oxygen vacancy concentration and in the Co and Fe valence state dependent on the operation parameters and the distance of LSCF materials to the electrolyte.
- Co and Fe valence state changes under reduced oxygen partial pressure and high water vapor causes the volatilization of different species, including Sr, and the precipitation of (CoFe)O_x at the grain boundaries.
- It provides valuable insight into the degradation and decomposition mechanisms of LSCF.

At%

Average

0





(LaSr):(CoFe) _{0.62}Sr_{0.38})_{0.35}(Co_{0.27}Fe_{0.73})O_x _{0.65}Sr_{0.35})_{0.98}(Co_{0.17}Fe_{0.83})O_x a_{0.7}Sr_{0.3})_{1.26}(Co_{0.09}Fe_{0.91})O_x

III Degradation of LSCF/SDC Electrode in SOEC mode



 $(H_2O/H_2 \text{ ratio} = 1:2)$: 33% steam, 67% H_2 operated under SOEC at 0.5 A/cm², 800°C for 1360 h.

Co- or Fe-enriched (CoFe)Ox, some with Cr, are present at LSCF grain boundaries. The Co-Fe enriched grain boundary secondary phase appears to be ribbon-like elongated along the LSCF grain boundary planes.

There is no deposition or decomposition of the phases at the surface of the LSCF grains.

More severe degradation in SOEC mode and the formation of large-scale Co or Fe enriched oxide at SDC grain boundaries



Reversible 96 h each cycle with total 2378 h

with 13 SOFC & 12 SOEC cycles, @800°C 0.5

A/cm² and 50%H₂O and 50%H₂







Summary:

boundaries

✓ Common nanostructure degradation from LSCF/SDC oxygen electrode of SOEC cells operated at 750° C and 800° C.

- There is Co- or Fe-enriched (CoFe) O_x or (SmFe) O_x present at SDC grain boundaries.
- There is Co- or Fe-enriched (CoFe)O_x, some with Cr, present at LSCF grain boundaries.
- There is no deposition or decomposition of the phases at the surface of the LSCF grains.
- ✓ Common nanostructure degradation between fuel cell and electrolysis mode:
 - Presence of (CoFe)O_x at the LSCF grain boundaries or SDC grain boundaries, indicating the LSCF decomposition.
 - However, there is no similar amount of Sr- or La-enriched solid phase were discovered, indicating the possible evaporation of volatilization of La and Sr species.
- ✓ Ongoing work: systematic analysis of sets of operated SOECs to examine the impact of the following conditions on the cell degradation:
 - H_2O/H_2 ratio.
 - SOEC operation temperature, 750°C, 800°C, 850°C.
 - SOEC operation current density of 1 A/cm² and 0.5 A/cm².

Acknowledgement:

This technical effort was performed under the contract DE-FE0004000.

Disclaimer:

This project was funded by the Department of Energy, National Energy Technology Laboratory, an agency of the United States Government, through a support contract with URS Energy & Construction, Inc. Neither the United States Government nor any agency thereof, nor any of their employees, nor URS Energy & Construction, Inc., nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Science & Engineering To Power Our Future