Evaluation of Cr-Gettering Material in a Generic Stack Test Fixture at Pacific Northwest National Laboratory

Y-S Matt Chou, J-P Choi, and J. W. Stevenson, K2-44, Energy Processes & Materials, PNNL, Richland, WA 99354
C. Liang, Boxun Hu, Weyshla Rodriguez, Ashish Aphale, and Prabhakar Singh, U. Connecticut, CT 06269-5233

Pacific Northwest NATIONAL LABORATORY

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Introduction:

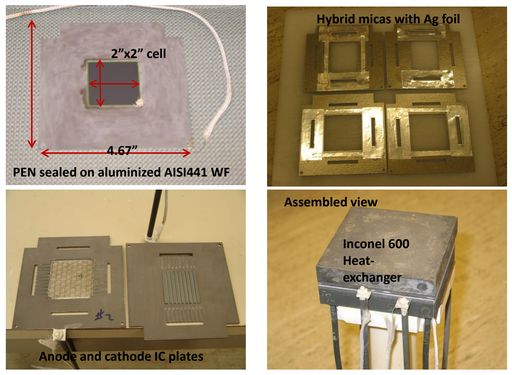
Cr is known to cause severe cell degradation in solid oxide fuel cells (SOFCs). Volatile species such as $CrO_2(OH)_2$ and CrO_3 have been identified as the leading poisons. Since Cr presence is unavoidable in ferritic stainless steel, leading metallic interconnect material, for oxidation resistance purposes. Many attempts have been made to mitigate the problem by coatings, and their protection has been proven successful for short to mid-term operation.

To further tackle the problem, U Conn. has proposed by employing Cr-gettering materials either at upstream and/or on-cell. PNNL has teamed up with U. Conn. in FY16 to investigate the effect of gettering materials. Candidate gettering materials will be synthesized at U. Conn., and PNNL will investigate its effect on LSCF-based cell performance in a generic stack text fixture both in upstream and on-cell arrangements. Overall the results will shed light in developing and engineering of novel and durable Cr-gettering for practical applications.

Materials and Processing

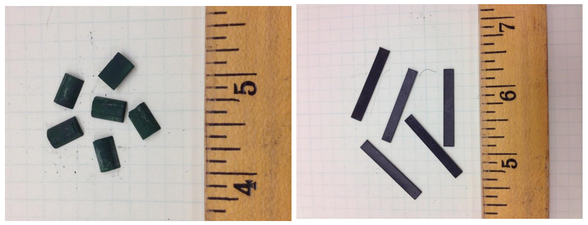
1. LSCF-based commercial cell (5cm x 5cm) with active cathode of 4cm x 4cm on NiO/YSZ anode support with thin YSZ electrolyte and Ceria barrier layer
2. Ce-(Mn,Co) spinel coating of AISI441 on cathode area
3. Aluminization of AISI441 interconnect and window frame plates
4. Refractory glass seal for WF/PEN at 930°C/2h
5. Hybrid phlogopite mica as perimeter compressive seal
6. LSC20 and Ni paste + Ni mesh as contact
7. Final seal at 900-930°C/2h and tested at 800°C with fuel H_2:N_2=1:1 (~4.75% H_2O) versus air at constant current mode (375 mA/cm²)
8. Wet air (~4.75% H_2O)
9. Impedance and IV sweep tests
10. Air side heat exchanger made of alumina (99%)

Generic Stack Test Fixture

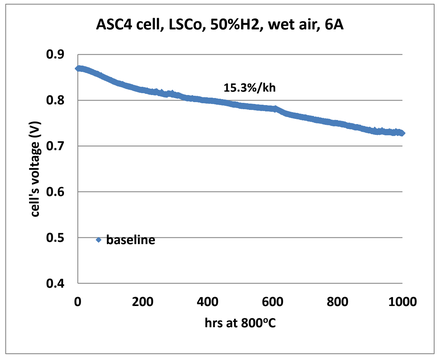


Sources of Cr

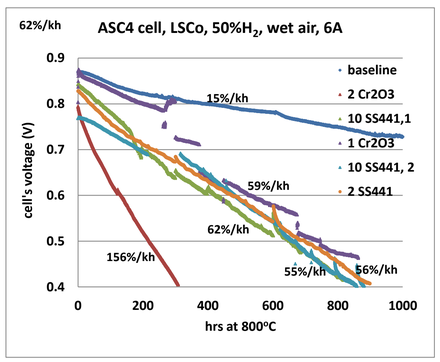
1. Partially sintered Cr_2O_3 rod (1300°C2h)
2. Pre-oxidized AISI metal stripes (1000°C 4h)

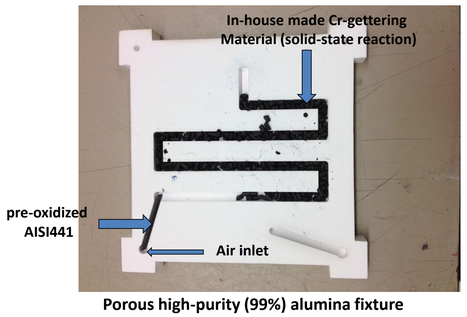


Baseline Test of LSCF-based Cell (No Cr Source and No Cr-gettering)



Cell with Different Types of Cr Sources and No Cr-Gettering

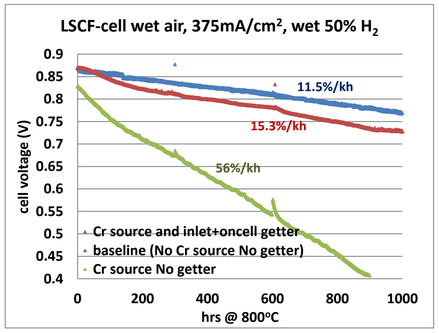




Porous high-purity (99%) alumina fixture

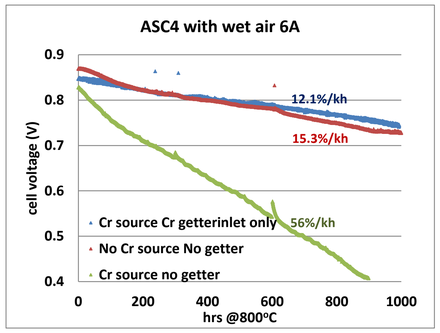
Cell with both Upstream and On-Cell Cr-Gettering

1. 2 pieces of pre-oxidized AISI441 stripes
2. Upstream placed Cr-gettering materials made at U. Conn. and PNNL
3. On-cell was applied by paste paint on cathode using LSCo+10%



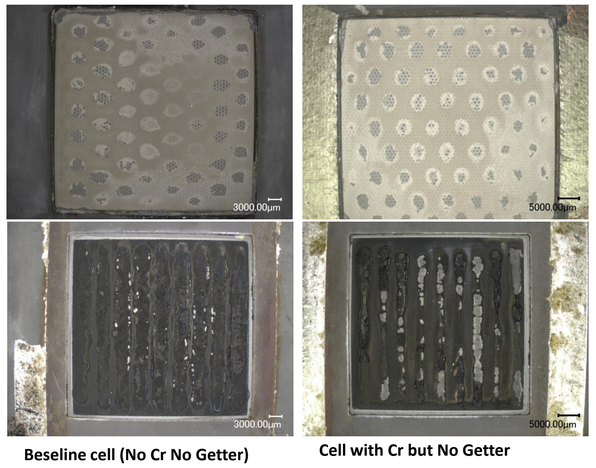
Cell with Upstream Cr-Gettering only

1. In-house made gettering material only with large porosity



Post-Mortem Optical Analysis

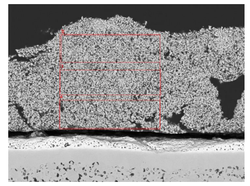
Substantial cathode delamination for cell tested with Cr source



Beseline cell (No Cr No Getter) | Cell with Cr but No Getter

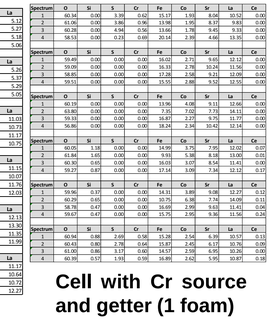
Post-Mortem Cathode Layer EDS Analysis

1. On baseline cell and cell with Cr source and 1 foam of Cr-getter at upstream
2. EDS of 6 random spots in cathode layer



Cathode layer

Spectrum	O	Na	Cr	Fe	Co	Sr	Zr	La
1	82.06	0.27	0.00	4.88	1.41	5.26	1.00	5.12
2	82.14	0.39	0.00	4.75	1.49	4.97	0.99	5.27
3	81.62	0.08	0.00	5.23	1.38	5.49	1.03	5.18
4	82.71	0.22	0.00	4.79	0.94	5.32	0.97	5.06
Spectrum	O	Na	Cr	Fe	Co	Sr	Zr	La
1	82.87	0.14	0.00	5.33	1.26	4.23	0.92	5.26
2	82.17	0.34	0.00	5.26	1.13	4.43	0.91	5.37
3	82.13	0.00	0.00	5.52	1.48	4.58	1.00	5.29
4	83.14	0.17	0.00	5.03	1.21	4.42	0.93	5.05
Spectrum	O	Na	Cr	Fe	Co	Sr	Zr	La
1	60.20	0.16	0.00	16.60	2.41	8.54	1.06	11.03
2	60.70	0.41	0.00	15.32	2.76	8.90	1.10	10.73
3	59.15	0.48	0.00	15.87	2.44	9.70	1.23	11.17
4	60.04	0.11	0.00	15.86	2.36	9.61	1.27	10.75
Spectrum	O	Na	Cr	S	Fe	Co	Sr	La
1	62.76	0.66	0.01	0.51	15.56	2.74	7.22	11.15
2	65.49	0.35	0.00	0.12	11.96	3.48	8.52	10.07
3	60.64	0.60	0.00	0.64	17.38	2.36	6.62	11.76
4	60.95	0.52	0.00	0.62	17.39	2.31	6.38	12.08
Spectrum	O	Na	Cr	S	Fe	Co	Sr	La
1	65.52	0.35	0.00	0.07	10.23	4.36	7.36	12.13
2	74.06	0.33	0.00	0.00	0.41	7.01	5.13	13.30
3	62.22	0.13	0.00	0.07	15.55	2.70	7.99	11.33
4	59.65	0.70	0.00	0.33	16.33	2.26	8.74	11.99
Spectrum	O	Na	Cr	S	Fe	Co	Sr	La
1	61.89	0.28	0.00	0.05	16.41	2.24	7.96	11.17
2	61.96	0.18	0.00	0.10	15.87	2.43	8.62	10.64
3	61.43	0.29	0.00	0.11	15.86	2.30	9.28	10.72
4	60.28	0.66	0.00	0.00	17.06	2.54	6.73	12.27



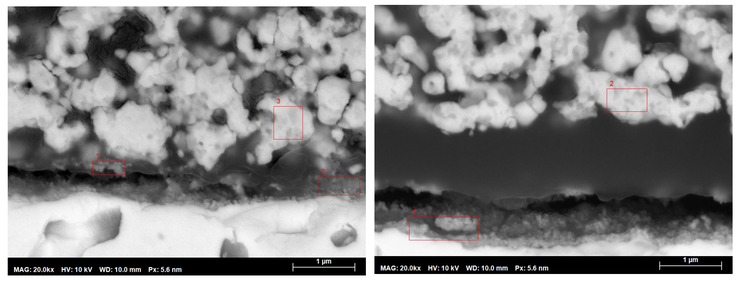
Cell with Cr source and getter (1 foam)

Baseline cell

No Cr was found in baseline cell, indicating good coatings on AISI441 metal parts, while sporadic and low concentration of Cr was found in cathode layer of cell tested with Cr source and 1 foam of Cr-getter

Post-Mortem Electrode/Electrolyte Interface EDS Analysis of Cell with Cr Source and 1 Foam of Cr getter

Cr segregated along electrode/electrolyte interface with Cr/Sr ratio far from 1, suggesting Cr_2O_3 instead of $SrCrO_4$ formation (likely by reduction process).



Spectrum	O	Si	Cr	Fe	Co	Sr	Y	Zr	La	Ce
1	38.17	13.92	4.30	12.89	0.61	0.71	2.84	1.91	3.46	21.18
2	39.41	9.55	3.37	7.02	0.82	1.40	6.02	0.19	2.52	29.70
3	58.68	1.00	0.00	17.89	2.86	6.55	0.50	0.18	11.33	1.01

Spectrum	O	Si	Cr	Fe	Co	Sr	Y	Zr	La	Ce
1	60.56	8.30	9.05	3.51	4.06	0.02	2.21	0.36	0.68	11.26
2	60.29	0.57	0.06	19.61	3.16	5.20			10.34	0.78

Summary and Conclusion

1. Cr-poisoning behavior was confirmed in LSCF-based cells with various types of Cr sources.
2. Electrochemical performance was established for baseline cell as well cells with Cr sources.
3. Validation of Cr-gettering materials was successfully demonstrated in two single cell tests: one with upstream only, and one with both upstream and on-cell application.
4. Cells with Cr-gettering materials showed much lower degradation rates as compared to cells without the getter.
5. Optical microscopy showed substantial electrode/electrolyte de-lamination for cells tested with Cr sources.
6. EDS at electrode/electrolyte interface revealed distinct Cr segregation while Cr was sporadically found in cathode layer with low concentrations.

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