Crystallographic structure and stability of Pt-substituted LSCo electrocatalyst for SOFC cathode

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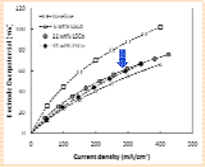
Introduction / Cell performance

Cathode Activation by Electrocatalyst Infiltration

⇒ **Dramatic reduction in electrode overpotential by composite cathode infiltration with LSCo, assumeably due to enhanced oxygen reduction reaction rate.**

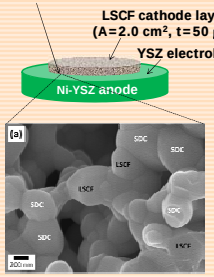


* S. Lee et al., J. Electrochem. Soc., 158 (2011) B735.

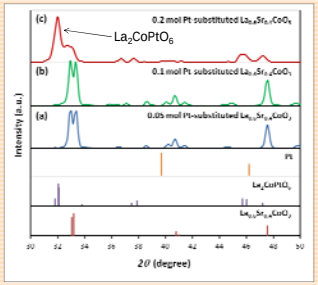
Novel electrocatalyst: $La_{0.6}Sr_{0.4}Co_{0.9}Pt_{0.1}O_{3-\delta}$

Solid-solution of noble metal with perovskite oxides is expected to
(1) prevent the metal's irreversible coarsening (agglomeration),
(2) reduce losses due to volatilization at high operating temperatures, and
(3) avoid reactions with other components that lead to catalyst deactivation.

SDC-LSCF functional layer
(A=2.0 cm², t=10 μm)

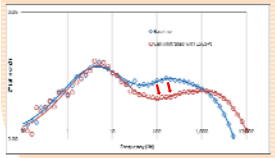


X-ray diffraction patterns of Pt-substituted LSCo calcined at 850°C for 4 h with different Pt doping level: (a) 0.05 (b) 0.1, and (c) 0.2 mol.



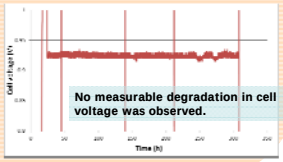
Cell performance

Bode plots of a baseline cell and the cells infiltrated with LSCoPt precursor



Impedance of the frequency range between **20-200 Hz is reduced** for the infiltrated cell.
⇒ **Evidence of cathode activation by LSCoPt infiltration**

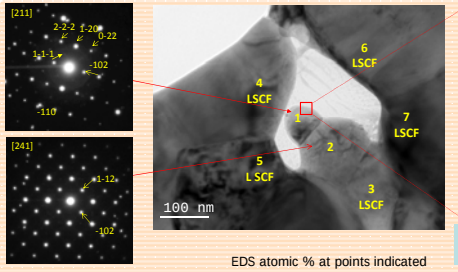
Cell voltage vs. time of the cell infiltrated with LSCoPt precursor under the constant current of 0.25 A/cm² at 750°C.



Cell voltage of the infiltrated cell is **stable** for around 280 h.

TEM feature 1: LSCoPt infiltrate particles

< 0 h operated cathode (850 ℃ calcined)>



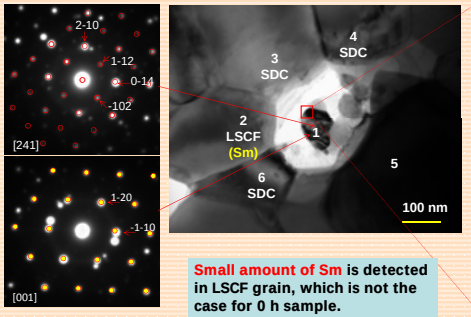
No secondary phases were found inside the LSCoPt particle.

EDS atomic % at points indicated

Atomic%	1	2	3	4	5	6	7
O	49.62	56.34	55.53	60.33	57.67	55.36	50.71
Fe	5.62	12	14.79	14.75	15.04	16.1	18.21
Co	12.48	6.56	5.21	3.32	3.69	3.53	4.8
Sr	3.47	7.19	9.6	8.01	9.28	9.86	10.28
La	25.74	17.29	14.88	13.59	14.33	15.15	16
Pt	3.07	0.62	-	-	-	-	-

The LSCoPt infiltrate is indexed as rhomohedral structure, which is same as LSCF, but different with LSCo which has cubic structure.

< 280 h operated cathode>



No secondary phases were found inside the LSCoPt particle.

Small amount of Sm is detected in LSCF grain, which is not the case for 0 h sample.

The LSCoPt infiltrate is indexed as rhomohedral structure.

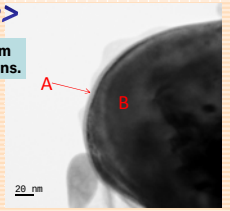
	O	Fe	Co	Sr	La	Pt	Sm	Ce	Zr
1	36.34	1.44	23.15	1.92	33.26	3.9			
2	57.96	15.95	3.77	7.15	11.54		3.63		
3	66.55						2.59	29.23	1.64
4	62.87						3.17	32.34	1.61
5	43.24	14.32	3.93	7.34	13.08		3.43	13.13	1.52
6	55.38						2.99	39.89	1.74

TEM feature 2: LSCoPt infiltrate layers

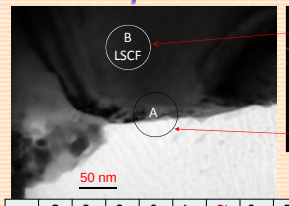
< 0 h operated cathode>

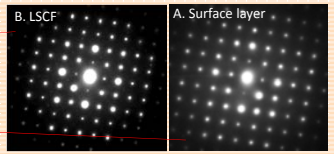
LSCoPt layers with the thickness of 5 – 10 nm are formed on the surfaces of backbone grains.

Atomic%	A	B
O	39.52	34.72
Fe	15.77	25.00
Co	12.35	5.55
Sr	7.00	13.92
La	23.81	20.82
Pt	1.57	-



< 280 h operated cathode>





	O	Fe	Co	Sr	La	Pt	Sm	Zr
A	62.4	5	10.35	3.19	15.08	3.98		
B	55.78	15.73	3.59	7.36	13.89		2.11	1.53

The surface layer is analyzed as LSCoPt, and contains small amount of Fe.

The surface layer and LSCF grain has the same crystal structure and orientation. (epitaxial relationship)

Conclusion

The cathode infiltrated with LSCoPt and tested for 280 h was compared with the as-infiltrated cathode (850°C-calcined and 0 h tested) using TEM:

1.0.1 mol of Pt is well dissolved in LSCo lattice after calcination at 850°C. There is no precipitate or secondary phase inside the infiltrate grains. Small amount of Fe is detected from the infiltrates of both cathodes.

2.LSCoPt phase is indexed as that with rhombohedral structure, which is as same as that from LSCF backbone, but different from cubic LSCo.

3.LSCoPt infiltrate is about 50 – 100 nm in size, and which is maintained during the 280 h operation.

4. In addition to the granular feature of LSCoPt infiltrate, thin, continuous layer structure of the infiltrate is also found for both cathodes. While the layer of the 0 h operated cell is amorphous for the cell without operation, it is crystal and epitaxial with LSCF backbone grains for the 280 h tested cathode.

5. Sm is detected in LSCF backbone grains for the 280 h operated cell, but not for the 0 h cell, implying cation interdiffusion during a cell operation.

Overall, TEM examination and cell performance clearly demonstrate the stability of this SOFC cathode infiltrated with nanostructured Pt-doped LSCo electrocatalyst.

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