Time-dependent stability of SOFC activated by nano-sized cathode electrocatalyst

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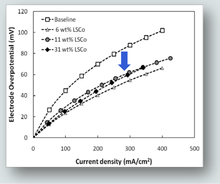
Introduction

Cathode Infiltration with electrocatalysts

⇒*Dramatic decrease in electrode overpotential due to enhanced oxygen reduction reaction.*

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



But, long-term stability is questionable…

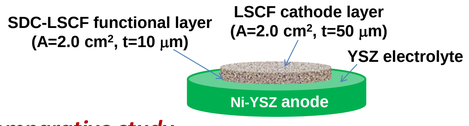
because of electrocatalysts'

1) *Nanometer size (= small curvature radius)*
2) *Instability (decomposition or interaction)*

Theme of this study

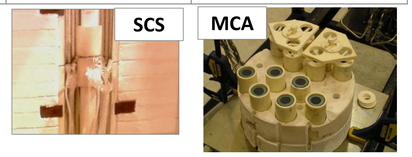
⇒ *Time-dependent stability of infiltrated cathode*

Features of this study



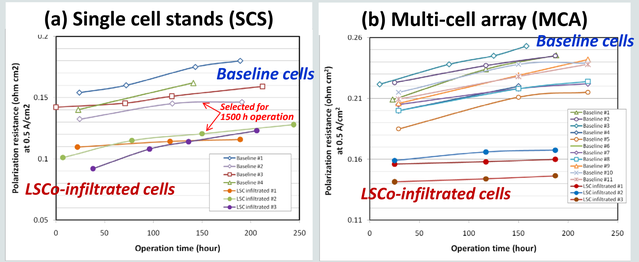
	Single cell stands (SCS)	Multi-cell array (MCA)
Fuel composition	97% H_2 + 3% H_2O	Pure H_2
Gas flow rate	400 sccm for cathode 400 sccm for anode	2000 sccm for cathode 2000 sccm for anode (12 cells)
Sealing material	Mica	Glass
Current collectors	Paste	Mesh
Heating schedule	Direct heating to 750C	850C (30 min) aging before 750C operation

1) *Comparative study*
   commercial baseline cells (MSRI Co.) vs. LSCo-infiltrated cells
2) *Cathode backbone*: composite of SDC-LSCF
3) *Multiple cell tests for statistical reliability*
   utilizing single cell test stands (SCS) or multi cell array (MCA)
4) *Impedance analysis* for degradation mechanism investigation



Multiple cell tests for 200 h

Fig. Polarization resistance (Rp) variation with time (DC 0.5 A/cm²)



(a) Rp obtained at SCS (average value at the operation of 24 h)
- Baseline cell = 0.14 ohmcm²
- Infiltrated cell = 0.10 ohmcm²

29% decrease in Rp by infiltration (= 35% increase in power density under 0.7V, assuming Ro=0.2 ohmcm²)

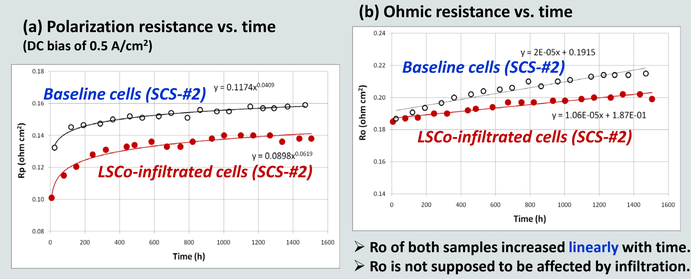
(b) Rp obtained at MCA, (average value at the operation of 24 h)
- Baseline cell = 0.20 ohmcm²
- Infiltrated cell = 0.15 ohmcm²

25% decrease in Rp by infiltration

Time-dependent stability for 200 h:
(1) Regardless of test stands, cathode was activated by LSCo infiltration.
(2) All the tested cells showed Rp increase with operation time.
(3) No accelerated degradation was shown for infiltrated cells.

1500 h test for selected cells

Fig. (a) Rp and (b) Ro variation of the selected cells tested 1500 h



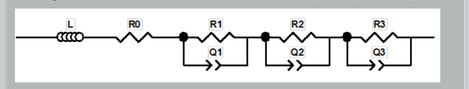
- Ro of both samples increased linearly with time.
- Ro is not supposed to be affected by infiltration.

- Rp vs. time (1500 h): power law relationship
  $y = 0.1174\ x^{0.0409}$ for Baseline cell (SCS-#2)
  $y = 0.0898\ x^{0.0619}$ for LSCo infiltrated cell (SCS-#2)

Time-dependent stability for 1500 h:
(1) No accelerated degradation by infiltration was confirmed.
(2) 70% of Rp increase over 1500 h occurs within initial 200 h operation.

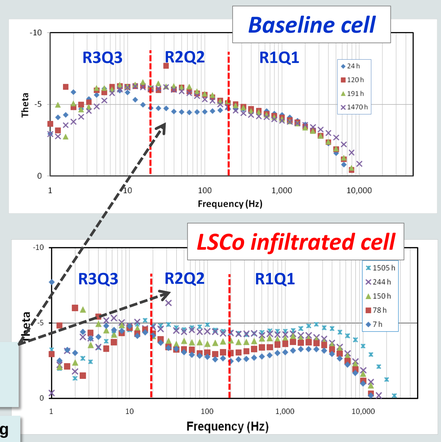
Impedance Study

Equivalent circuit used for fitting



(1) Ro: ohmic resistance
(2) R1Q1: High Frequency (HF, > $2x10^2$ Hz): charge transfer / bulk diffusion
(3) R2Q2: Intermediate Frequency (MF, $2x10^1$ - $2x10^2$ Hz): incorporation of oxygen molecule into cathode
(4) R3Q3: Low Frequency (LF, 10^0 – $2x10^1$ Hz): seems to be related to anode reactions
(5) < 10^0 Hz: gas diffusion polarization

Bode plot change over 1500 h



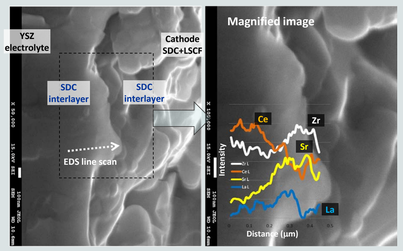
Characteristic appearance of a new feature in the MF range with a summit frequency of 20-200 Hz, while Ro, R1 and R3 were nearly constant.

Bode plots confirm that Rp change occurs mostly during initial 200 h.

Microstructure analysis

(1) $SrZrO_3$ formation

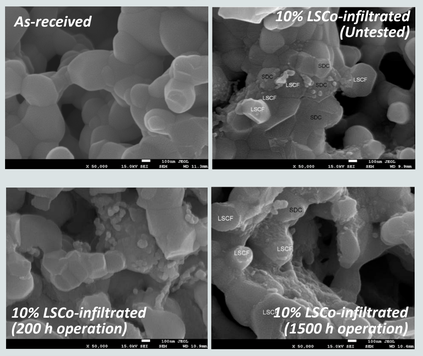
Baseline cell tested for 1500 h



Strontium (Sr) and zirconium (Zr) were detected as major elements at the interface of YSZ electrolyte and SDC interlayer.

$SrZrO_3$ formation may be one of the reasons of cathode degradation with time for both baseline cell and infiltrated cell.

(2) Coarsening



- Overall microstructural changes with operation time seem to be minimal.
- There is **no clear evidence of particle coarsening.** (loss of surface area).
- Particle **wetting behavior** on backbone cathode needs to be considered seriously because of its high contribution to cathode microstructure.

Conclusion

- ✓Long-term stability of infiltrated cells has been investigated systematically utilizing (1) commercial cells with composite cathode as baseline and (2) impedance spectrometry.
- ✓There was virtually no difference in Rp degradation behavior between the two cells, baseline cell and LSCo-infiltrated cell, tested for 1500 h.
- ✓Most of Rp degradation happened during initial a few hundred hours of operation.
- ✓Intermediate frequency (MF) arc has been mostly affected by time-dependent degradation for both cells tested for 1500 h.
- ✓$SrZrO_3$ formation in spite of SDC interlayer seems to be one of the reasons of cathode degradation.
- ✓**Conclusively, there was no accelerated degradation by nano-sized LSCo electrocatalyst.**

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