Mitigation of Degradation associated with Elevated Steam Content in SOFC cathode oxidant by Surface Modification

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Introduction

Moisture content in cathode feed air is postulated to lead to performance degradation in LSM and LSCF cathodes.

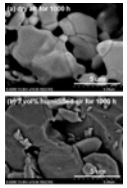
- PNNL: Humidity causes degradation in the performance of LSM/YSZ cathodes. It is more pronounced at lower temperature, partially reversible.
- Case Western Reserve Univ.: Abrupt rise in ASR was observed upon 3% steam introduction
- Kyushu Univ.: Steam decomposes LSM to form Mn_3O_4 on the LSM surface rather than at cathode / electrolyte interface (Liu et al., *J Power Sources*, 196 (2011) 7090)

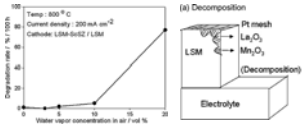
Proposed degradation mechanism:

$$LaMnO_3 + \frac{3}{2}H_2O \rightarrow La(OH)_3 + \frac{1}{2}Mn_2O_3$$

$$2\,La(OH)_3 \xrightarrow{>600^\circ C} La_2O_3 + 3H_2O$$

The group observed Mn_3O_4, possibly due to further reduction of Mn_2O_3





Purpose of the Study

- Determine the effects of high steam on cathode performance;
- Identify the underlying mechanisms responsible for cathode degradation;
- Improve long term stability of SOFC by modifying cathode structure (surface composition) based on mechanistic understanding of cathode degradation.

NETL Operating Parameters

Cells:

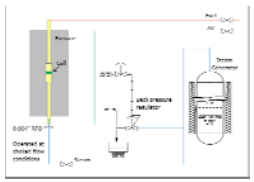
- Commercially available MSRI anode supported cells
- Cathode: LSM[$(La_{0.8}Sr_{0.2})_{0.98}MnO_3$] / LSM-YSZ active layer
- Electrolyte: YSZ; Anode: Ni-YSZ

Steam Generation:

- Saturated steam is pressure/temperature controlled and injected through a restrictive flow orifice at choked flow conditions.

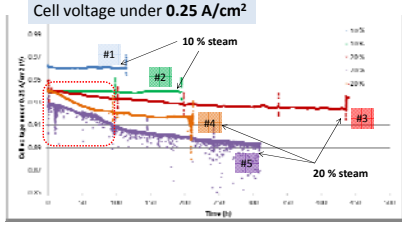
Operating Conditions:

- 800°C, 0.75 A/cm² or 0.25 A/cm²
- 10 or 20% steam content / balance air



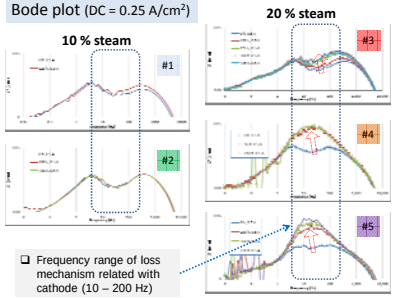
Steam Content (10 % vs. 20 %) Effect

Cell voltage under **0.25 A/cm²**



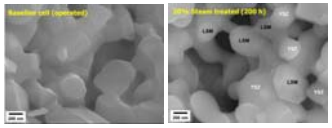
Steam content	sample	Degradation rate @ 0 - 100 h	Degradation rate @ 100 - 1000 h
10%	#1	1.2	0.1
	#2	0.1	0.1
20%	#3	**8.3**	2.0
	#4	**24.0**	2.9
	#5	**25.0**	4.6

Bode plot (DC = 0.25 A/cm²)



- Frequency range of loss mechanism related with cathode (10 – 200 Hz)

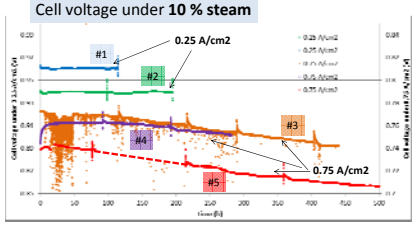
1. No noticeable degradation was observed for the cells tested under 10% steam.
2. Cell performance was severely degraded under 20% steam, particularly within 100 h after current loading.
3. The observed degradation is analyzed to be related with surface oxygen exchange and/or oxidant gas concentration at cathode.



4. The cathode tested under high steam content appears to have (1) more rounded grains, (2) grooved boundary at YSZ/LSM interfaces, and (3) some flake-like particles.
5. No evidence of decomposed LSM or Mn-rich phase was found within the analytical resolution limit.

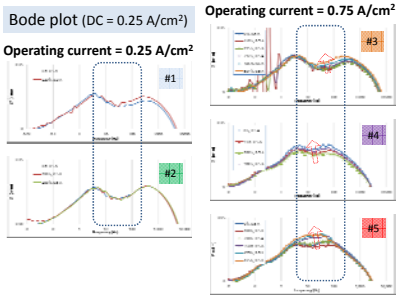
Operating Current (0.25 A/cm² vs. 0.75 A/cm²) Effect

Cell voltage under **10 % steam**



Current density	sample	Degradation rate @ 0 - 100 h	Degradation rate @ 100 - 1000 h
0.25 (A/cm²)	#1	1.2	0.1
	#2	0.1	0.1
0.75 (A/cm²)	#3	**9.9**	**9.9**
	#4	**9.6**	**9.6**
	#5	**11.7**	**11.7**

Bode plot (DC = 0.25 A/cm²)

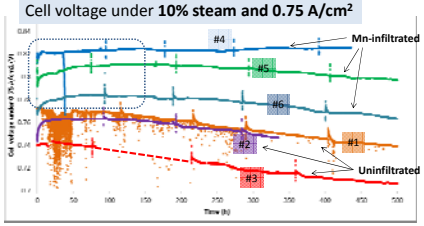


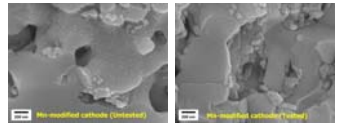
1. No noticeable degradation was observed for the cells tested under 0.25 A/cm2.
2. Cells were severely degraded when tested under higher current density (0.75 A/cm2).
3. Degradation rates were relatively independent on operation time (linear relationship) over all the test period.
4. The degradation under high current density was analyzed to be related with surface oxygen exchange and/or oxidant gas concentration at cathode.

Surface Modification with Mn

Possible degradation mechanisms under high steam content	Strategy	Method
Accelerated removal of Mn from LSM/YSZ interface and eventual decomposition of LSM	Prevent Mn deficiency (LSM decomposition)	**Surface modification with Mn**
Deactivation of surface near TPB due to absorption of steam-originated functional groups	Extend TPB length = low Rp (overpotential) = low degradation rate	

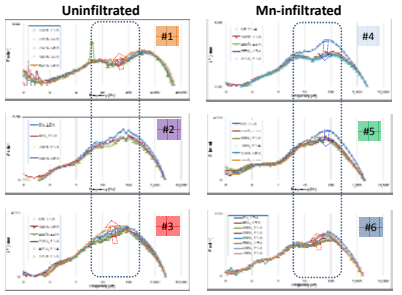
Cell voltage under **10% steam and 0.75 A/cm²**





	sample	Degradation rate @ 0 - 100 h	Degradation rate @ 100 - 1000 h
Uninfiltrated	#1	9.9	9.9
	#2	9.6	9.6
	#3	11.7	11.7
Mn-infiltrated	#4	N/A	N/A
	#5	N/A	5.2
	#6	N/A	8.5

Bode plot (DC = 0.75 A/cm²)



1. All the cells with cathode infiltrated with Mn revealed performance improvement over the first 100 h*. (*Operation time was counted from the point when steam was introduced, after 50 – 100 h of burn-in period.)
2. Long-term operation of the cells #5 and #6 showed initial performance increase followed by 5-8 %/1000 h degradation.
3. Both the initial performance improvement and the degradation with operation are related with cathode, based on the EIS analysis.
4. Mn infiltrate on LSM/YSZ cathode were coarsened with operation period.

Summary & Conclusion

- Steam content in air matters to cell degradation rate at low current density (0.25 A/cm²): (1) Essentially no degradation with 10% steam; and (2) Rapid initial degradation followed by a slower, more linear degradation at extended time with 20% steam.
- Current density matters to cell degradation rate at relatively low steam content (10%): Accelerated degradation was observed for the cells tested at the higher current density, 0.75 A/cm².
- **Mn** was introduced into LSM/YSZ cathode by solution infiltration method to modify surfaces of the composite cathode with the expectation that it prevents Mn deficiency from LSM/YSZ interface and extend effective three-phase boundary (TPB) under high steam condition.
- Mn-infiltrated cells showed performance improvement initially, and maintained lower degradation rates compared to uninfiltrated cells.
- This study demonstrates the effects of steam content and operating current density on cathode degradation rate, and suggests that surface modification by infiltration is a technique to mitigate electrode degradation.