Mechanistic Understanding of LSM Cathode Interaction with H_2O and CO_2

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Abstract: The stability of strontium (20%) doped lanthanum manganite (LSM) cathode has been studied in air containing different H_2O and CO_2 levels (0 - 10%) at 750-850ºC and 0.5 V bias using LSM/YSZ/LSM symmetric cells. Surface analyses of the post-test LSM cathodes reveal the formation of SrO and strontium and/or lanthanum carbonates, respectively, in air containing H_2O and CO_2. The formation of these compounds contributes to the electrochemical performance degradation of the symmetric cells; more pronounced in H_2O containing air. It is observed, supported by thermodynamic calculation, that ≤0.5% CO_2 in air does not affect the electrochemical performance of LSM. Mechanisms for the LSM cathode interaction with H_2O and CO_2 have been proposed.

Introduction

LSM cathode in a SOFC stack are exposed to H_2O, CO_2, and other trace impurities in inlet air at ≥ 750°C. The nominal intrinsic impurities in air contain ~3% H_2O, ~400 ppm CO_2 and 0.05 - 0.15 ppm SO_2. Inlet air may also contain chromium vapor species from the balance of plant components (BOP) and metallic interconnects. The impurities in air poisons the LSM cathode in the order of chromium vapor species>H_2O>CO_2 and subsequently degrades the electrochemical performance. In-depth understanding of LSM cathode interaction with the impurities present in air is necessary to develop design and materials modifications.

Objective

- To understand and identify the reaction processes for LSM interaction with H_2O and CO_2 in air
- To determine the mechanisms for LSM degradation due to interaction with H_2O and CO_2 in air

Experimental

Fabrication of LSM/YSZ/LSM symmetric cell at 1200°C in air

Electrochemical testing

Post test characterization: SEM, XPS, FTIR

Input parameters: *750-850ºC, Atmospheric air containing 0-10% H_2O and 0-10% CO_2, and 0.5 V*

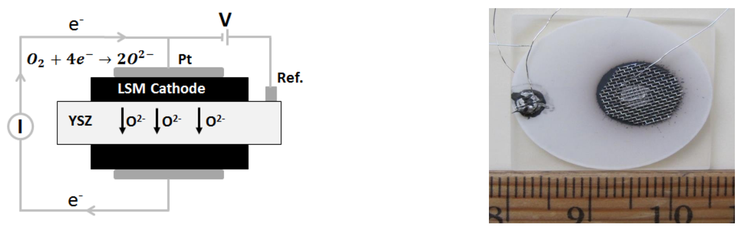


Figure 1. Configuration of a LSM/YSZ/LSM symmetric cell for electrochemical testing

Results and Discussion

Electrochemical performance

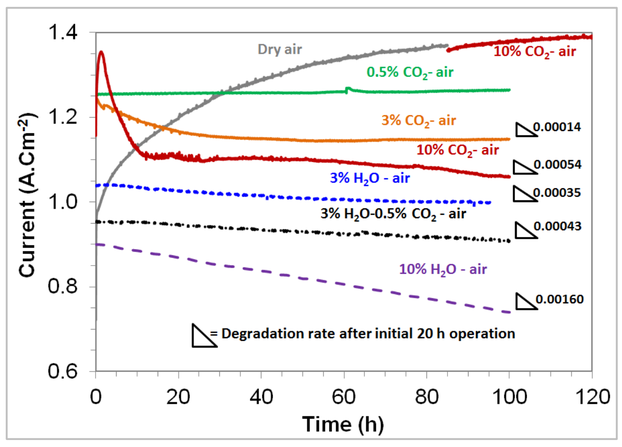


Figure 2. I-t plots of LSM/YSZ/LSM cells at 850°C and 0.5 V bias in different atmosphere

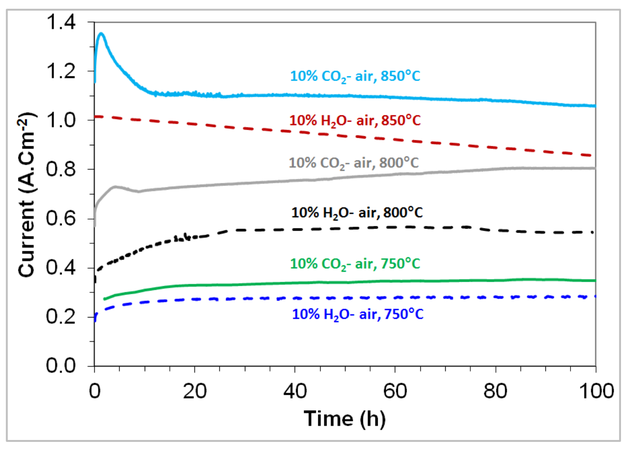


Figure 3. I-t plots of LSM/YSZ/LSM cells at 0.5 V bias in 10%CO_2-air and 10% H_2O-air at different temperatures

- Presence of H_2O in air decreases the cell performance
- CO_2 ≤0.5% in air does not affect cell performance
- Degradation rates for cell performance is higher in H_2O than CO_2
- Simultaneous presence of H_2O and CO_2 in air enhances degradation
- Current density (Figure 2) increases with increase in operating temperature

Surface Analysis of LSM cathode

Elemental analysis by XPS: [a] Cell fabricated at 1200°C in air for 2 h; [b] Cell tested in 10%H_2O-air at 850°C and 0.5 V

Sample	$\frac{Sr}{La}$	$\frac{Sr}{Mn+La}$	Binding energy (eV)		
	Molar ratio	Molar ratio	Sr 3d5/2	La 3d5/2	Mn 2p3/2
Pre-test LSM[a]	0.23 ± 0.01	0.13 ± 0.01	132.3 ± 0.2	833.9 ± 1.1	641.1 ± 0.5
Post-test LSM[b]	0.34 ± 0.02	0.21 ± 0.01	132.8 ± 0.2	834.3 ± 1.1	641.6 ± 0.5

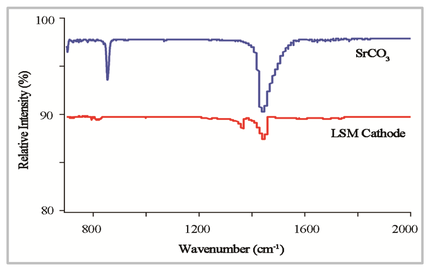


Figure 4. ATR-FTIR spectra of standard $SrCO_3$ and post-test LSM cathode (at 1123 K in 10% CO_2-air with 0.5 V bias)

Surface morphology of LSM cathodes

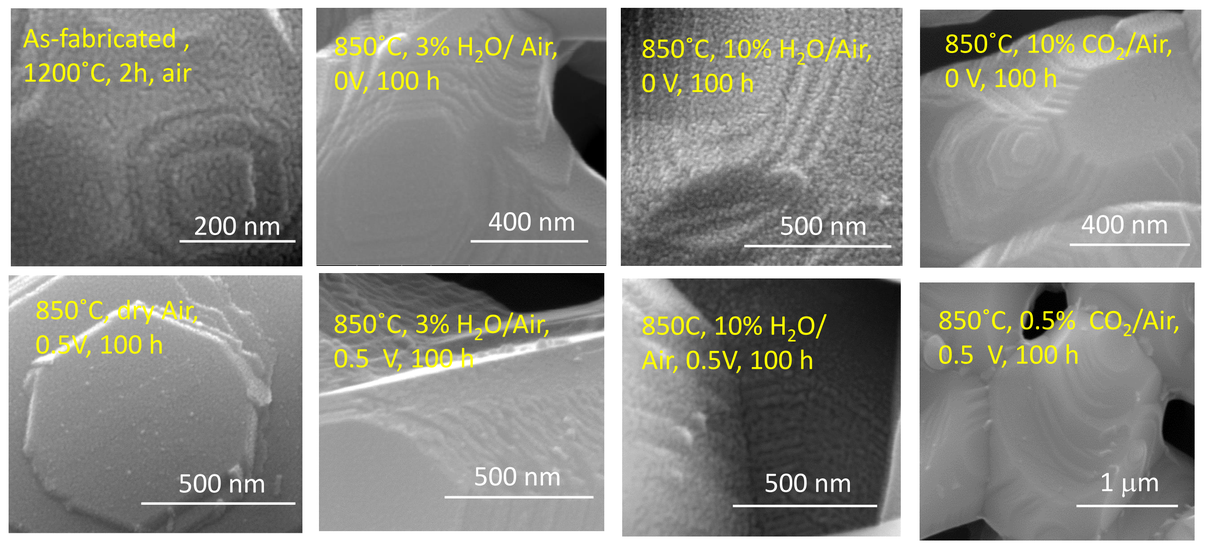
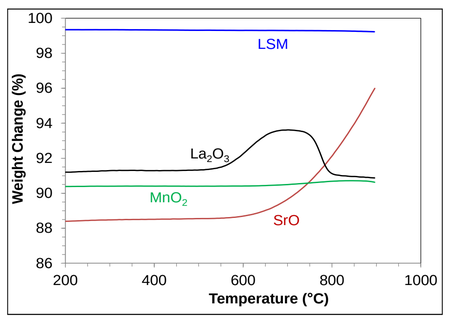


Figure 5. SEM images of LSM surfaces

- **H_2O in air favors segregation of Sr-enriched particles at the LSM cathodes. Applied bias tends to intensify surface segregation.**
- **CO_2 in air also favors surface segregation but the segregation extent is much less than that in presence of H_2O. Surface segregation is not distinct in ≤0.5% CO_2 in air.**

Gibbs free energy (kJ/mol) of $SrCO_3$ and $La_2O_2CO_3$



Temp (K)	CO_2 content	298	1000	1100	1200
ΔG_{SrCO_3}	100%	-189.2	-71.9	-55.9	-40.1
ΔG_{SrCO_3}	10% in air	-183.5	-52.8	-34.9	-17.1
ΔG_{SrCO_3}	400 ppm in air	-163.0	16.2	41.0	65.6
$\Delta G_{La_2O_2CO_3}$	100%	-147.3	-31.6	-15.9	-0.5
$\Delta G_{La_2O_2CO_3}$	10% in air	-141.6	-12.5	5.1	22.5
$\Delta G_{La_2O_2CO_3}$	400 ppm in air	-121.1	56.5	81.0	105.2

Reactions:

$SrO(s) + CO_2(g) \leftrightarrow SrCO_3$

$La_2O_3(s) + CO_2(g) \leftrightarrow La_2O_2CO_3$

CO_2 in ambient air is not detrimental for LSM cathode

Degradation mechanisms

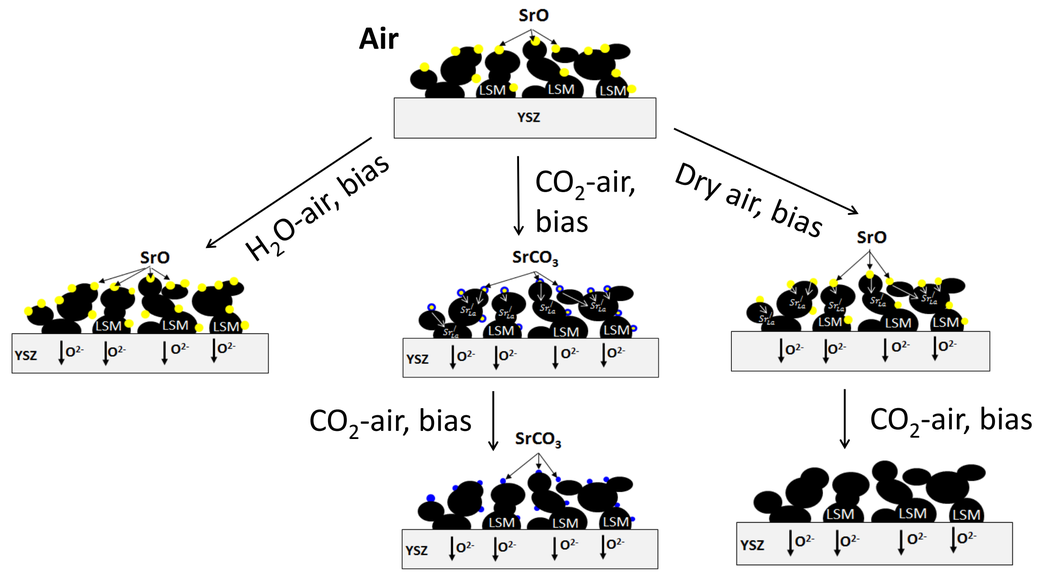


Figure 6. Schematic of the LSM cathode degradation mechanisms in air containing H_2O and CO_2.

Conclusions

- ✓ **Role of the presence of CO_2 and H_2O on LSM cathode performance in air has been investigated.**
- ✓ **Presence of H_2O in air is more detrimental to cell performance than CO_2.**
- ✓ **Nominal CO_2 content (~400 ppm) in ambient air has no measurable effect on LSM.**
- ✓ **Structural and chemical degradation mechanisms have been developed.**

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Acknowledgements

Financial support from USDOE Office of Fossil Energy under grant DE-FE–0009682 is gratefully acknowledged. The authors thank Dr. Jeffery Stevenson (PNNL), Mr. Rich Goettler (LGFC) and Dr. Joe Stoffa (NETL) for helpful discussion.

Presented at the 15th SECA CTP Meeting, Pittsburgh July 22-23, 2014