Performance regeneration in lanthanum strontium manganite cathode during exposure to H₂O and CO₂ containing ambient air atmospheres

Boxun HU, Manoj K. MAHAPATRA[†] and Prabhakar SINGH

Center for Clean Energy Engineering, Department of Materials Science and Engineering, University of Connecticut,
44 Weaver Road, Storrs Mansfield, CT 06269-5233, USA

The regenerability and stability of lanthanum strontium manganite (LSM)/yttria doped zirconia (YSZ)/LSM symmetrical cells have been examined after the cells were exposed to real-world air environment containing H₂O and CO₂. An alternate exposure experiment in 20% H₂O-air and dry air has been conducted to test the reversibility of the cell degradation in H₂O/air. Long-term experiment in 3% H₂O-0.5% CO₂-air, dry air, 0.5% CO₂-air, and 10% CO₂-air has shown the stability and regenerability of the cell performance. Additional experiments show that periodic water content fluctuation causes the cell performance fluctuation. Electrochemical performance measurements and post-test microstructure analysis indicate that the segregation of SrO on the LSM surface and formation of La₂Zr₂O₇ at the LSM/YSZ interface degraded the electrochemical performance by increasing the polarization resistance. The cell performance degradation can be partially recovered by exposure to dry air. Thermogravimetric analysis (TGA) has been conducted for the LSM as well as its constituent oxides to elucidate degradation mechanisms. Mechanisms related to the performance degradation and regenerability have been proposed.

©2015 The Ceramic Society of Japan. All rights reserved.

Key-words : Solid oxide fuel cell, Lanthanum strontium manganite cathode, Degradation, Polarization resistance, Segregation, Performance regenerability

[Received December 31, 2014; Accepted January 29, 2015]

1. Introduction

Solid oxide fuel cell (SOFC) technology offers high chemical to electrical energy conversion efficiency, potential for fuel flexibility, and applications in areas ranging from stationary centralized and distributed generation to mobile auxiliary power plants.^{1,2)} The SOFCs have the potential to be cost-competitive due to the use of low cost ceramic materials as cathode, anode, and electrolyte unlike devices utilizing noble group metal catalysts and requiring elaborate balance of plant for the processing and cleanup of fuel and oxidants.³⁾ A typical tubular or planar SOFC is composed of multilayer ceramic materials. A high operating temperature (973–1273 K) is required for anode fuel reforming, increase of electrolyte conductivity, and oxygen reduction. Perovskite-type oxide La_{0.8}Sr_{0.2}MnO₃ (LSM) has been extensively used as cathode materials.⁴⁾ Although LSM/YSZ containing SOFC has exhibited long-term chemical and mechanical stability during full cell/stack testing under normal cathode exposure environment, slight increase of polarization resistance has led to minor performance degradation.⁵⁾ Cathodic polarization considerably contributes to the energy loss, more at low operating temperatures.⁶⁾

Compressed environment air with water (~3% representing 100% relative humidity at room temperature) and carbon dioxide (~350 ppm) is used as cathode gas. H₂O and CO₂ compete with O₂ at LSM cathodes for adsorption and oxygen reduction reaction (ORR). The ORR proceeds at cathode surface and triple phase

boundary (TPB, cathode, electrolyte, and gas) at cathode/electrolyte interface.⁷⁾ Extensive studies have shown that the cell performance degradation is caused by oxide segregation,^{8,9)} chromium deposition,¹⁰⁾ material deterioration,¹¹⁾ and La₂Zr₂O₇ formation at LSM/YSZ interface.^{12,13)} We have recently reported the stability of LSM cathode in humidified air¹⁴⁾ and carbon dioxide containing air.¹⁵⁾ In humidified air, SrO segregation on LSM cathode was enhanced by water content, electric bias, and low oxygen partial pressure;¹⁴⁾ in CO₂-containing air, SrO converts to SrCO₃ at the LSM surface, resulting in initial performance degradation. Thus, an initial LSM activation in air incorporates surface SrO into LSM lattice and minimize the degradation.¹⁵⁾ Oxide segregation is determined by thermal stability of Sr(OH)₂ and SrCO₃. Increase of temperature improves cell electrical performance by reducing non-polarization resistance (R_{np}) and polarization resistance (R_p). However, high temperature leads to La₂Zr₂O₇ formation at LSM/YSZ interface.^{12,16)} Intermediate temperatures are optimal for energy efficiency and long-term operation. The humidity in ambient air fluctuates daily and seasonally. However, few studies have been reported the cell performance recovery under such real-world conditions.

This paper presents experimental findings of the performance degradation and its regenerability obtained during the electrochemical tests performed using LSM/YSZ/LSM symmetrical cells in different H₂O and/or CO₂ containing air. Higher CO₂ content (5000 ppm) was used for accelerated cell degradation to observe surface morphology and chemical changes within a reasonable testing time. Alternate exposure experiments in H₂O/CO₂/air and in dry air have been conducted to test the reversibility of the degradation in H₂O/CO₂/air. An experiment with periodic water content fluctuation shows the performance fluctuation.

[†] Corresponding author: M. K. Mahapatra; E-mail: mkmanoj@engr.uconn.edu

[‡] Preface for this article: DOI <http://dx.doi.org/10.2109/jcersj2.123.P4-1>

tuation. Mechanisms related to the performance degradation and regenerability have been proposed.

2. Experimental

2.1 Materials and experimental setup

The procedures for the cell fabrication and electrical testing have been described in previous studies.¹⁴⁾ LSM [(La_{0.8}Sr_{0.2})_{0.98}MnO₃] ink were screen-printed on both side of YSZ [(Y₂O₃)_{0.08}-(ZrO₂)_{0.92}] electrolyte (Fuel Cell Materials) to fabricate LSM/YSZ/LSM symmetrical cells. The LSM electrodes have a diameter of 1.0 cm with a thickness of about 15 μm. Platinum mesh and wires (Alfa Aesar, wire diameter: 0.2 mm) and platinum paste (Engelhard) were used as electrode materials.

Figure 1 shows the schematic of the experimental set up for electrochemical testing. As-fabricated LSM/YSZ/LSM cells were loaded in an alumina tube. The cathode gases (150 cm³/min) were introduced to the symmetrical cells by a mass flow controller. The three platinum electrodes of the symmetrical cell were connected to the leads of a potentiostat. The as-assembled setup was heated in a vertical furnace to the testing temperatures with a ramp rate of 3 K/min. For long-term stability tests, cells were tested in air containing 0.5% CO₂ and 3% H₂O (using a water bubbler), at 1023–1123 K temperature range in 0 and 0.5 V cathodic biases up to 1500 h. The temperature of the water bubbler was at 298 K but fluctuated with outside temperature in hot summer. The voltage was applied between cathode and reference electrode. After testing, the cells were cooling down to ambient temperature and were used for post-test characterization.

2.2 Characterization

Electrochemical performance was measured using a multi-channel potentiostat (VMP2, Bio-Logic). The current was recorded every minute. The electrochemical impedance spectra (EIS) were measured in the frequency range from 0.5 Hz to 200 kHz with a 15 mV sinus amplitude at an interval of 2 h.

The microstructural and elemental compositional analyses

were performed using an FEI Quanta 250 FEG scanning electron microscope attached with an energy dispersive X-ray spectroscopy (EDS). Thermo-gravimetric analysis (TGA) of SrO (99.5%), and La₂O₃ (99.9%) (Alfa Aesar) was performed in 3% water-air using a NETZSCH Jupiter instrument (STA 449 F3) to identify the plausible mechanisms of LSM degradation. Humidified air (80 cm³/min) with 3% water was introduced to the chamber via a water bubbler and the samples were heated at 3 K/min up to 1173 K. 20% H₂O-air (balance) was injected by a water syringe pump using dry air as carrier gas and the injection tube was kept at ≥393 K to avoid condensation.

3. Results

3.1 Electrochemical performance

3.1.1 Performance recovery in dry air after degradation in H₂O-air

The symmetrical cell was activated in 3% H₂O-air for 34 h. Then, the inlet gas was switched from 3% H₂O-air to dry air, and the current density of the LSM/YSZ/LSM symmetrical cell quickly increased 0.07 A·cm⁻² (15% of increase) (**Fig. 2**). After the cell current reached constant in dry air, the inlet gas was switched to 20% H₂O-air at 67 h. The cell current suddenly decreased from 0.53 to 0.07 A·cm⁻² (~87% degradation). After the inlet gas was switched back to dry air, the cell current recovered and showed only 2% of current loss. The similar degradation patterns in 20% H₂O-air and recovery patterns in dry air have been repeated for two more times.

The R_{np} (non-polarization resistance) of the symmetrical cell showed no apparent change during the test, while the R_p (polarization resistance) decreased in the activation process; The R_p increased from 0.66 to 4.4 Ω·cm after the inlet gas was switched from dry air to 20% H₂O-air; then the R_p decreased to 0.67 Ω·cm after the cell was activated in dry air. After each cycle, the peak value of R_p in 20% H₂O-air increased.

3.1.2 Performance degradation in 3% H₂O-0.5% CO₂-air and regenerability in dry air

Figure 3(A) shows the electrical performance of the LSM/YSZ/LSM symmetrical cells in (i) dry air, (ii) 0.5% CO₂-air, (iii) 3% H₂O-0.5% CO₂-air, and (iv) 3% H₂O-10% CO₂-air at 1073 and 1123 K during the long term test. The current density initially increases from 0.35 to 0.95 A·cm⁻² with a bias due to the activation process (0–150 h). The I-t curve indicates that:

1) The cell performance has no significant change (within 0.5%) in 20–50 h when the exposure atmosphere was switched from dry air to 0.5% CO₂ containing air,¹⁵⁾ as shown in both steps b and e.

Fig. 1. The experimental setup for the electrochemical test of LSM/YSZ/LSM cell (bottom) in H₂O/CO₂ containing air.

Fig. 2. I-t and R-t curves of the LSM/YSZ/LSM symmetrical cells tested in 3% H₂O-air (c), dry air (a), and 20% H₂O-air (b) at 1123 K with 0.5 V bias. R_p: polarization resistance, R_{np}: non-polarization resistance.

Fig. 3. I-t (A, C-E) and R-t (B) curves of the LSM/YSZ/LSM symmetrical cells tested in dry air and 3% H₂O-0.5% CO₂-air at 1073 and 1123 K with 0.5 V bias for 1500 h. Steps a, d, and i is in dry air, Steps b and e is in 0.5% CO₂-air; Steps c, f, g, and h is in 3% H₂O-0.5% CO₂-air; Step j is in 3% H₂O-10% CO₂-air. Figures 3(C)–3(E) is enlarged plots of Fig. 3(A).

2) The cell performance shows apparent degradation in 3% H₂O-0.5% CO₂-air at 1073 K. In the step c, the cell current density decreased from 0.98 to 0.76 A·cm⁻² in 550 h (3.9×10^{-2} A·cm⁻² per 100 h, 22% degradation). In the step f, the cell current density decreased from 0.81 to 0.73 A·cm⁻² in 320 h (2.6×10^{-2} A·cm⁻² per 100 h, 10% degradation). Steps c and f are superimposed in Fig. 3(C) for comparison.

3) The cell performance improves as the temperature increases from 1073 to 1123 K [Step g in Figs. 3(A) and 3(D)]. The improvement may be attributed to the increased electrochemical kinetics and the dissociation of strontium (lanthanum) carbonate at above 1073 K.

4) The cell performance also improves on changing the cathode atmosphere from 3% H₂O-0.5% CO₂-air to dry air as revealed in the steps d and i [Figs. 3(A) and 3(E)]. The figure also shows that the presence of 0.5% CO₂ in dry air does not negatively affect the performance. This result also suggests that the cathode degradation is partially reversible with cathode atmosphere composition.

5) The difference in cathode degradation rate in 3% H₂O-0.5% CO₂-air and 3% H₂O-10% CO₂-air is not distinct as reflected in steps h and j [Fig. 3(E)].

Area specific resistance (ASR), Rnp, and Rp were calcu-

lated from electrochemical impedance spectroscopy as shown in Fig. 3(B). Rnp did not show apparent change during the long-term test except during the operating temperature change at 1150 h. Rp contributed to the ASR change. During the activation (0–150 h), the ASR decreased fast in the beginning and then Rp slowly reach stable. When adding 3% water in the air, Rp slightly decreased. In 3% H₂O-0.5% CO₂-air, the Rp continuously increased. After switched to dry air, the Rp gradually decreased and then became stable. After exposure in 3% H₂O-0.5% CO₂-air again, the Rp slightly increased again.

3.1.3 Performance fluctuation with humidity changes in air

Except the activation period (0–40 h), the I-t curve (Fig. 4) of the LSM/YSZ/LSM symmetrical cell has shown a periodic change with a 24 h interval due to fluctuation in room temperature when the cell was tested in 3–6% H₂O-0.5% CO₂-air at 1123 K with 0.5 V bias for 120 h. The saturated water content in water bubbler changed with the environment temperature (280–310 K). The polarization resistance-time (Rp-t) curve also shows periodic change while Rnp shows no apparent change. When the Rp increased with increasing water content in air, the current density of the cell decreased, therefore, the cell electrochemical

Fig. 4. Fluctuation of water content in summer (A) caused a periodic fluctuation of the performance (B) of the LSM/YSZ/LSM symmetrical cells in 3–6% H₂O-0.5% CO₂-air at 1123 K with 0.5 V bias for 120 h.

performance degraded. Except the periodic change, Fig. 4 also shows performance degradation (decreased I) with time.

3.2 Morphologies

A symmetrical cell tested in dry air at 1123 K for 100 h shows no particle on the cathode surface [Fig. 5(A)]. An experiment in 3% H₂O-air at 1023 K for 100 h with 0.5 V bias has been performed, sparse particles were observed on LSM cathode surface [Fig. 5(B)]. Large amounts of nanoparticles have been observed in the SEM images after the cathode was finally tested in 20% H₂O-air [Fig. 5(C)]. For the cathode tested for 1500 h [Fig. 5(D)], the surface particles grow larger than those of Fig. 5(B), but much less particles than those on the cathode in 20% H₂O-air. No apparent delamination has been observed at the LSM/YSZ interface [Fig. 5(E)]. However, small particles formed at the LSM/YSZ interface (marked between two lines) in Fig. 5(F). The EDS analysis of these particles shows the ratio of Zr/La is about 1:1, indicating the formation of La₂Zr₂O₇.

3.3 Thermogravimetric analysis

LSM and its constituent oxides react with water and carbon dioxide. Thermogravimetric analysis of the LSM and its constituent oxides in carbon dioxide has been reported in our previous reports.¹⁵⁾ Figure 6 shows the TGA plot of SrO, La₂O₃, and LSM in 3% H₂O-air. At the temperature range of 298–673 K, SrO shows a weight increase due to water adsorption and reaction.¹⁷⁾

With the temperature increasing to 873 K, Sr(OH)₂ · xH₂O lost water. Until 1053 K, Sr(OH)₂ is completely decomposed to SrO in 3% H₂O-air. La₂O₃ shows a similar pattern to SrO. La₂O₃ adsorbs water and have the following reaction:¹⁸⁾

La(OH)₃ · xH₂O start to lose water at ~523 K. La(OH)₃ is completely decomposed to La₂O₃ in 3% H₂O-air at ~873 K. The weight of LSM remained constant when heated from 673 to 1173 K in 3% H₂O-air.

4. Discussions

Oxygen reduction reaction proceeds at the LSM surface and LSM/YSZ interface although there is no consensus which sites are dominated.⁷⁾ Secondary phases forming at the LSM/YSZ interface or the LSM surface will affect the cathode performance. There are two different types of reactions at the cathode sites. One type of reaction is impurities or components in air with cathode materials. Another type of reaction is between LSM cathode and YSZ electrolyte. The effect of CO₂ and H₂O in air will be discussed.

Thermogravimetric analysis of the LSM and its constituent oxides in carbon dioxide and water containing air shows that LSM is stable in CO₂-air or H₂O-air but its constituent oxides (La₂O₃ and SrO) are reactive to CO₂ or H₂O. Segregation of SrO

Fig. 5. SEM images of the post-test LSM cathodes. A: in dry air at 1123 K for 100 h, B: in 3% H₂O-air at 1123 K for 100 h, C: in 20% H₂O-air at 1123 K for 100 h, D: 1500 h test of the sample in Fig. 3, E and F: cross-section of the same sample with D. New particles formed at LSM/YSZ interface are marked between two red lines. “+” indicates SEM-EDS analysis area. All cathode here is applied a bias of 0.5 V bias.

Fig. 6. TGA plot of LSM, SrO, and La₂O₃ in 3% H₂O/air.

on the LSM surface has been reported during the calcination of LSM at high temperatures (>1473 K).^{7),12)} At operating temperatures (1023–1273 K), segregation of SrO has been reported in our previous studies.¹⁴⁾ Sr(OH)₂ and La(OH)₃ forms in H₂O-air; SrCO₃ and La₂O₂CO₃ forms in CO₂-air. The concentrations of H₂O and CO₂ determine which compound, among SrCO₃, La₂O₂CO₃, Sr(OH)₂, and La(OH)₃, predominates at the SOFC operating temperature.

Based on our electrochemical performance results and surface morphology studies, an illustration summarizes surface SrO/SrCO₃ segregation in different environment (Fig. 7). With applying a cathodic bias, SrO is incorporated into LSM surface during activation process in dry air. Without SrO on the cathode surface, no SrCO₃ forms when adding CO₂. Increasing 0.5% CO₂ to 10%

Fig. 7. Illustration of particle formation and removal with bias in dry air and H₂O/CO₂ containing air.

CO₂ did not degrade the cell performance [Fig. 3(a)].¹⁵⁾ Water adsorption and dissociation cause lanthanum vacancies and lead to SrO segregation on the LSM cathode.¹⁴⁾ Higher water content leads to more SrO segregation. In 3% H₂O-air, sparse SrO particles formed on the surface. In 20% H₂O-air, the LSM cathode surface was fully covered by SrO nanoparticles [Fig. 5(C)], and the electrochemical performance is very low (Fig. 2). In Figs. 2 and 3(A), water has immediate effect on current decrease and long term effect.¹⁹⁾ After the inlet gas switched to dry air, SrO nanoparticles were incorporated into LSM lattice again. When the water content slowly changed between 3–6% [Fig. 4(A)], more SrO segregation on the cathode changes with an increase of water content and lead to electrochemical performance degradation, and vice versa. Figure 4 demonstrated the electrochemical performance fluctuation with a change of water content in air. Fortunately, even in hot and humid summer, the water content in atmospheric air usually has much smaller change and the performance fluctuation will be much smaller.

The polarization resistance is affected by particle size, electrode thickness and porosity, surface reaction coefficient, ionic conductivity, and active sites.^{20),21)} For this study, the LSM particle size, cathode thickness and electrode porosity are constant, and R_p changes are mainly related to surface reaction coefficient, ionic conductivity, and active sites. Segregated SrO particles block the active sites for oxygen reduction, and reduce the surface reaction coefficient. The R_p of Figs. 2 and 3(B), and reflects the SrO/SrCO₃ segregation on the LSM cathode. These R_p changes reflect that the effect of water is much stronger than that of CO₂. A thin layer of secondary phases (La₂Zr₂O₇ + Mn₂O₃) formed at the LSM/YSZ interface via the reaction:¹⁴⁾

These insulated compounds also contribute to high polarization resistance.

5. Conclusions

We have studied the regenerability and reversibility of the performance degradation of LSM/YSZ/LSM symmetrical cells in H₂O and/or CO₂ containing air. The electrochemical performance degradation of the LSM cathode has been studied along with the post-test characterization of the LSM surface and the LSM/YSZ interface using SEM-EDS.

The performance degradation in H₂O-CO₂-air environment can be mostly recovered by exposure to dry air. Segregation of SrO on the cathode surface decreases the electrochemical performance by increasing the polarization resistance. Segregated SrO nanoparticles can be incorporated into LSM lattices by cathodic

activation in dry air. Water plays a major role in the degradation in H₂O-CO₂-air environment. Water content fluctuation leads to the electrochemical performance fluctuation while an increase of CO₂ content has no observable change in the electrochemical performance after electrode activation. Formation of secondary phase such as La₂Zr₂O₇ has been observed at the LSM/YSZ interface. Surface segregation and interface compound formation lead to the increase of polarization resistance and subsequently degrade the electrochemical performance.

Acknowledgements This study was performed under a grant from the Office of Fossil Energy, US Department of Energy (grant number: DE-FE-0009682). Technical discussion with Dr. Jeff Stevenson (Pacific Northwest National Laboratory), Dr. Joe Stoffa (National Energy Technology Laboratory) and Mr. Rich Goettler (LG Fuel cells) is gratefully acknowledged.

References

- 1) P. Singh and N. Q. Minh, *Int. J. Appl. Ceram. Technol.*, **1**, 5–15 (2004).
- 2) N. Q. Minh, *Solid State Ionics*, **174**, 271–277 (2004).
- 3) O. Z. Sharaf and M. F. Orhan, *Renew. Sustain. Energy Rev.*, **32**, 810–853 (2014).
- 4) S. P. Jiang, *J. Mater. Sci.*, **43**, 6799–6833 (2008).
- 5) L. Blum, U. Packbier, I. C. Vinke and L. G. J. de Haart, *Fuel Cells (Weinheim, Ger.)*, **13**, 646–653 (2013).
- 6) M. Liu, M. E. Lynch, K. Blinn, F. M. Alamgir and Y. Choi, *Mater. Today*, **14**, 534–546 (2011).
- 7) N. Caillol, M. Pijolat and E. Siebert, *Appl. Surf. Sci.*, **253**, 4641–4648 (2007).
- 8) R. R. Liu, S. H. Kim, S. Taniguchi, T. Oshima, Y. Shiratori, K. Ito and K. Sasaki, *J. Power Sources*, **196**, 7090–7096 (2011).
- 9) A. Huber, M. Falk, M. Rohnke, B. Luerssen, M. Amati, L. Gregoratti, D. Hesse and J. Janek, *J. Catal.*, **294**, 79–88 (2012).
- 10) S. C. Paulson and V. I. Birss, *J. Electrochem. Soc.*, **151**, A1961–A1968 (2004).
- 11) H. Yokokawa, T. Horita, K. Yamaji, H. Kishimoto and M. E. Brito, *J. Korean Ceram. Soc.*, **49**, 11–18 (2012).
- 12) M. Keane, M. K. Mahapatra, A. Verma and P. Singh, *Int. J. Hydrogen Energy*, **37**, 16776–16785 (2012).
- 13) A. Chen, J. R. Smith, K. L. Duncan, R. T. DeHoff, K. S. Jones and E. D. Wachsman, *J. Electrochem. Soc.*, **157**, B1624–B1628 (2010).
- 14) B. Hu, M. Keane, M. K. Mahapatra and P. Singh, *J. Power Sources*, **248**, 196–204 (2014).
- 15) B. Hu, M. J. K. Mahapatra, M. Keane, H. Zhang and P. Singh, *J. Power Sources*, **268**, 404–413 (2014).
- 16) N. Li, M. K. Mahapatra and P. Singh, *J. Power Sources*, **221**, 57–63 (2013).
- 17) E. T. Carlson, *J. Res. Natl. Bur. Stand.*, **53**, 371–372 (1954).
- 18) A. Neumann and D. Walter, *Thermochim. Acta*, **445**, 200–204 (2006).
- 19) A. Hagen, K. Neufeld and Y. L. Liu, *J. Electrochem. Soc.*, **157**, B1343–B1348 (2010).
- 20) S. Farhad and F. Hamdullahpur, *Electrochim. Acta*, **61**, 1–12 (2012).
- 21) J. Fleig and J. Maier, *J. Eur. Ceram. Soc.*, **24**, 1343–1347 (2004).