Manganese Oxide Formation in Lanthanum Strontium Manganite-Yttria-Stabilized Zirconia SOFC Cathodes

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Microstructural changes in the cathode adjacent to the cathode–electrolyte interface were studied in SOFCs with lanthanum strontium manganite (LSM)/Y₂O₃-stabilized ZrO₂ (YSZ) composite cathodes after long-term operation (1.3 to 2.0 kh) with steam (1 to 3 pct H₂O) added to the cathode gas. We specifically sought to understand why the degradation rate (the increase of area specific resistance with time) was markedly higher at lower temperatures (*e.g.*, 1073 K (800 °C)) than at higher temperatures (*e.g.*, 1198 K (925 °C)). Transmission electron microscopy, combined with X-ray energy-dispersive spectroscopy and electron energy-loss spectroscopy, was used to detect and identify submicron Mn_xO_y precipitates. The particles were shown to be Mn₃O₄ in cells operated at 1198 K (925 °C), and both Mn₃O₄ and Mn₂O₃ in cells operated at 1073 K (800 °C). In a cell exposed for 5 kh at 1198 K (925 °C) to a cathode atmosphere of 1.1 pct H₂O at 4 bara, Mn_xO_y precipitates were uniformly distributed across the cathode. On the other hand, in an identical cell exposed to the same conditions but operated continuously at 380 mA cm⁻², Mn_xO_y precipitates were observed almost exclusively within about 3 μm of the electrolyte/cathode interface. Whether Mn_xO_y formation is causative or simply correlative with the steam effect remains an important question for future work.

DOI: 10.1007/s40553-014-0026-5
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I. INTRODUCTION

FUEL cells offer the following advantages compared to conventional power sources: higher efficiencies, lower emissions, modular installation scalable from milliwatts to megawatts, and distributed power generation to reduce transmission losses.^[1,2] Fuel cells have produced billions of kilowatt-hours of electrical energy in stationary and mobile applications all over the world.

Among fuel cell technologies, solid oxide fuel cells (SOFCs) offer unique benefits:^[3] they run not only on hydrogen but also on widely available hydrocarbon fuel; they need little or no precious metal catalysts; they provide high-quality utility-grade heat, which, in combination with electrical efficiencies of up to 60 pct, leads to total system efficiencies of 80 to 85 pct; and they can be run in reverse as electrolysis cells—*i.e.*, using electricity to produce hydrogen from water—making them both an energy-conversion and an energy-storage technology.

Electrical losses at the cathode in SOFCs with LSM-based ([La_{1-x}Sr_x]_{1-y}MnO_{3±z}, perovskite structure)

cathodes operating at the lower end of the useful temperature range are a significant technical limitation,^[4] as indicated by measurements of area specific resistance (ASR) in single “button” cells (Figure 1).^[5] The cathode reaction requires an electronic conductor (LSM), an ionic conductor, often Y₂O₃-stabilized or Sc₂O₃-stabilized ZrO₂ (YSZ or ScSZ), and oxygen gas to meet at the so-called three-phase boundaries (TPB). In the current work, cells consisted of porous LSM/zirconia composite cathodes, a stabilized zirconia electrolyte, and Ni/zirconia anodes.

LSM exhibits negligible ionic conductivity.^[3,6] This confines the TPB within the composite cathode to a thin surface region near the physical boundary between the LSM, the ionic ZrO₂-based conductor, and the pore. For SOFC systems close to commercial deployment, LSM-based cathodes have received considerable attention for their thermo-mechanical and chemical compatibility with other cell components, and for their long-term stability in the intended operating environment.

A significant mode of degradation of LSM/YSZ composite cathodes occurs when the hot exhaust from the cell stacks, which can include several percent by weight of water vapor, is used to pre-heat the incoming reactants and increase the overall system efficiency.^[7–12] Under these conditions, an increase in ASR occurs below 1173 K (900 °C)^[8–12] but not above this temperature.^[8,12] The ASR rise on introduction of humidity consists of an initial fast transient followed by a slower increase.^[8,9,11,12] The effect is seen in cathodes of LSM with Gd-doped CeO₂ (GDC)^[11] but not in cathodes of (La,Sr,Co) ferrite (LSCF) with GDC.^[9] This difference

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Manuscript submitted January 31, 2014.

Article published online August 9, 2014

Fig. 1—(color figure online). Contributions to electrical losses (area specific resistance, ASR) from various active layers in LG Fuel Cell Systems (LGFCs) single “button” SOFCs at 1073 K, 1133 K, and 1193 K (800 °C, 860 °C, and 920 °C).^[5] CCC: cathode current collector, ACC: anode current collector. ©2014 LG Fuel Cell Systems Inc. Used with permission.

might be associated with the surface oxygen exchange rate, which has been reported to be temperature dependent for LSM, but relatively independent of temperature for LSCF.^[13]

The rate of ASR rise increases with increasing current density ($0.25\text{--}0.75\text{ A cm}^{-2}$).^[9] Lower ASR can be restored by operating the cell in dry cathode air,^[7,9–11] but the extent of this reversibility varies with specific test conditions. For example, it has been reported^[9] that the ASR rise was only partially reversed on removal of H_2O from the cathode gas at 1023 K (750 °C), and that at levels of humidity below ~ 5 pct, the effect appeared to depend on current density and temperature. In that study,^[9] the ASR increased linearly at 1023 K (750 °C) for 0 to 12.8 pct humidity at 0.41 A cm^{-2} , whereas others^[8] reported no ASR rise with 3 pct humidity at 1073 K (800 °C) and 0.200 A cm^{-2} . The details of the “steam effect” (and cathode losses in general) also depend on the composition of the LSM.

Two of the salient characteristics of the steam effect thus are that in humid atmospheres, a fast and then a slow rise in ASR is observed at lower temperatures (e.g., 1048 K (775 °C)), but not at higher temperatures (e.g., 1173 K (900 °C)), and that the pre-steam values of ASR can be restored by running the cell at these higher temperatures.

One mechanism inferred for the steam effect was based on electrical impedance spectroscopy (EIS) studies.^[12] Mn normally diffuses (as Mn^{2+}) in dry air from LSM into adjacent YSZ, whereas in moist air, a reaction product is formed between the LSM and the YSZ (the “fast” effect). During prolonged humidification (the “slow” effect), the Mn volatilizes, causing decomposition at the LSM surface and hindering both the adsorption of oxygen on the LSM and the charge transfer at the interface. Microstructural evidence for such a mechanism was obtained by etching the LSM out of the cathode, revealing craters in the electrolyte surface that were attributed to formation of a reaction product at the LSM-electrolyte interface.

The current work explores the possibility that the rise in ASR of LSM-YSZ SOFC cathodes during long-term operation under practical conditions is connected to

microstructural changes, specifically to the phase stability of the LSM. The imaging and microanalysis techniques used here leave the critical YSZ-LSM interface intact and provide more detailed views of the chemical changes that took place there during cell operation.

The ASR of SOFCs was monitored during practical operating conditions that either did, or did not, elicit the steam effect. After cell operation, the microstructural changes in these cathodes were studied using transmission electron microscopy (TEM), X-ray energy-dispersive spectroscopy (XEDS), and electron energy-loss spectroscopy (EELS). In a previous study, the use of EELS to determine the valence state of Mn in the LSM phase of SOFC cathodes was validated by X-ray photoelectron spectroscopy (XPS).^[14] In the present study, EELS was used as a “fingerprint” method to identify the specific manganese oxide phases observed in the cathodes after operation.

II. EXPERIMENTAL PROCEDURES

A. SOFC Fabrication and Testing

The LSM–3YSZ composite cathodes in the cells described in Figures 2 through 7 contained LSM of the same nominal A-site-deficient composition (proprietary to LG Fuel Cell Systems Inc.) and acquired from a major US fuel cell materials supplier. Electrolyte-supported button cells were made using ZrO_2 with 3 mol pct Y_2O_3 (3YSZ) or 6 mol pct Sc_2O_3 (6ScSZ) as electrolyte. For cathode-symmetric cells, LSM-YSZ electrodes and LSM current collector layers were screen-printed onto both sides of pre-fired electrolyte disks, and then co-fired at 1418 K (1145 °C). Subscale cells (one cell, or five cells connected in series) with segmented-in-series design were fabricated by screen printing the anode (NiO–YSZ), electrolyte, and cathode onto porous inert ceramic tubes. (The NiO was subsequently reduced to Ni.) Anode and cathode current collector layers were also deposited onto anode and cathode sides, respectively, to reduce in-plane resistance. Subscale cells were operated in air or diluted air with H_2O contents ranging from 0 to 3 pct under constant current (380 to 480 mA cm^{-2}) at constant temperature (1048 K to 1198 K (775 °C to 925 °C), controlled by the testing furnace). Cell ASR was calculated as the difference between open cell voltage and the operating voltage, divided by current density.

Total electrode polarization was obtained from subscale cells. The cathode contribution to the total electrode polarization was deduced through AC impedance measurements on cathode-symmetric cells tested under similar conditions. AC impedance was measured using a Solartron 1470 multi-channel potentiostat and 1255B frequency response analyzer.

B. Microstructural Characterization

TEM thin foils were taken from the cathode/electrolyte interface using a focused ion beam (FIB) milling technique and standard *in situ* lift-out procedure in a

segment	T , K (T , °C)	cathode %O ₂	cathode %H ₂ O
A	1173 (900)	12	dry
B	1123 (850)	12	dry
C	1048 (775)	12	dry
D	1048 (775)	12	3
E	shutdown for cell repair		
F	1173 (900)	12	3
G	1048 (775)	12	dry

Fig. 2—(color figure online). ASR changes during testing at 450 mA cm^{-2} at the indicated temperatures and atmospheres. ©2014 LG Fuel Cell Systems Inc. Used with permission.

FEI Quanta 3D scanning electron microscope (SEM). A probe of 100 pA beam current at 30 kV accelerating voltage was used for final polishing.

The microstructures of the SOFC specimens were examined in a high-resolution (S)TEM (Zeiss Libra 200 (S)TEM), operated at 200 keV with a heated Schottky field-emission cathode and equipped with an in-column Omega electron energy filter. Elemental analysis was performed with XEDS using both point- and line-scanning mode. All concentration profiles were plotted using cation percentage by excluding the oxygen content. Elemental distribution maps were acquired in the spectrum imaging (SI) mode. Phase maps were constructed by superimposing individual Zr (red), La (blue), and Mn (green) maps. EELS spectra of the O-K and Mn- $L_{2,3}$ edges were used to identify specific manganese oxide phases. All the EELS spectra were acquired with the in-column Omega filter in spectrum mode using a CCD camera with $2k \times 2k$ resolution. The same background-subtracted window was applied to all spectra^[15,16] using the Pearson method.^[17]

III. RESULTS AND DISCUSSION

Figure 2 shows typical results of the steam effect in a test on a single cell operated at 450 mA cm^{-2} . In dry cathode gas, ASR jumped within minutes when temperature was decreased from 1173 K (900 °C, segment A) to 1123 K (850 °C, segment B) and then again from 1123 K to 1048 K (850 °C to 775 °C, segment C). This reflects the normal effects of both slower reaction kinetics and lower ionic conductivity (higher activation and ohmic polarizations, respectively) at lower temperatures. Between temperature changes, the ASR rose slowly at constant operating temperature, even without added humidity. When 3 pct H₂O was added to the cathode atmosphere at 1048 K (775 °C, segment D), an additional almost instantaneous rise in ASR occurred, followed by a slower rise (though faster than the slow rise seen in dry air). In segment E, the test was shut down for repair of the cell. On raising the temperature again to 1173 K (900 °C), but keeping the H₂O content at 3 pct (segment F), the ASR rapidly returned almost to its previous 1173 K (900 °C)/dry air value (segment

A) and was nearly constant thereafter. On lowering the temperature to 1048 K (775 °C) in dry air (segment G), the ASR behavior was almost identical to that exhibited prior to H₂O exposure (segment C). That is, under these conditions, the steam effect was essentially completely reversible.

To further examine the role of temperature in the steam effect, two subscale cells (five cells connected in series) were tested at 400 mA cm^{-2} under constant current control mode, one at 1198 K (925 °C) and one at 1073 K (800 °C), with cathode gas containing 1 to 3 pct H₂O. Plots of ASR vs time (Figure 3) revealed that the degradation rate at 1198 K (925 °C) ($0.004 \Omega \text{ cm}^2 \text{ kh}^{-1}$) was an order of magnitude lower than at 1073 K (800 °C) ($0.04 \Omega \text{ cm}^2 \text{ kh}^{-1}$). During a 48-h excursion at 1048 K (775 °C), the ASR rose at an even higher rate ($0.2 \Omega \text{ cm}^2 \text{ kh}^{-1}$). This finding is consistent with prior reports that, relative to dry cathode air, the increase in degradation rate in humid cathode atmospheres is significant at temperatures below 1173 K (900 °C)^[8–12] but essentially absent at higher temperatures.^[8,12]

Figure 4 shows TEM images of two cathodes after operation in humid air, one at 1198 K (925 °C) (top) and one at 1073 K (800 °C) (bottom). The dark-field scanning transmission electron microscopy (DF-STEM) images of the cathode/electrolyte interface are at the left, and the corresponding XEDS elemental maps at the right. The porous LSM/YSZ composite cathode (the major portion of the images) and the dense YSZ electrolyte (far left) are clearly observed. XEDS elemental mapping showed several submicron Mn-rich precipitates (green areas) in the cathodes of both cells, especially near the cathode–electrolyte interface.

The STEM-EDS technique yielded detailed chemical information about these Mn-containing precipitates. Figure 5 shows a representative DF-STEM image, its corresponding superimposed elemental map depicting the line scan location, and the cation concentration profile of the 1198 K (925 °C) cell of Figures 3(a) and 4. These precipitates primarily contain Mn and O with only a minor concentration of other elements; they are essentially Mn_xO_y precipitates. Similar results were obtained from other precipitates in the cells described here.

Figure 6 shows the background-subtracted EELS O-K and Mn- $L_{2,3}$ spectra acquired from two Mn_xO_y

Fig. 3—(color figure online). Cell ASR with H_2O in cathode environment as a function of operating temperature: (a) 1198 K (925 °C), 480 mA cm^{-2} ; (b) 1073 K (800 °C), 400 mA cm^{-2} . Both cells tested with reformat at the anode. ©2014 LG Fuel Cell Systems Inc. Used with permission.

precipitates (identified as grain 1 and grain 2) in the cell operated at 1073 K (800 °C). The O–K edge was selected for electronic fine structure analysis because its variation among different Mn_xO_y phases is well documented.^[18] Also, the Mn– $L_{2,3}$ edge can be used to confirm the identity of the Mn_xO_y phase. The resemblances of the shape of the O–K edge between grain 1 and Mn_2O_3 , and between grain 2 and Mn_3O_4 , are clear. Similarly, the acquired Mn– $L_{2,3}$ edges of grain 1 and grain 2 resemble the ones reported for Mn_2O_3 and Mn_3O_4 . Finally, Table I shows the measured edge positions and calculated L_3/L_2 ratio of the Mn– $L_{2,3}$ edge^[19] and confirms the identification of the Mn_xO_y phases present in grains 1 and 2 of Figure 6. Clearly, both Mn_3O_4 and Mn_2O_3 formed in the cells tested at 1073 K (800 °C).

The EELS study was further carried out on all the Mn_xO_y precipitates in TEM foils in both cells. In the cell of Figures 3(a), 4 (top), and 5, which was tested under

conditions that showed no steam effect (1198 K (925 °C), 1.2 pct H_2O , only $0.004 \text{ } \Omega \text{ cm}^2$ rise in ASR per kh), only Mn_3O_4 was present (Figure 7a), whereas both Mn_3O_4 and Mn_2O_3 were observed (Figure 7b) in the cell of Figure 6, which was tested under conditions that showed a significant steam effect (1073 K (800 °C), 1.2 pct H_2O , $0.05 \text{ } \Omega \text{ cm}^2$ rise in ASR in the first 500 hours, followed by a rise of $0.03 \text{ } \Omega \text{ cm}^2$ from 1000 to 2000 hours).

The appearance of Mn_2O_3 in the cell tested at lower temperature in Figure 7(b) is consistent with general trends towards higher oxidation states with decreasing temperature in transition metal oxides.^[20] Further, our earlier work^[14] showed that the average valence of Mn in the LSM phase near the cathode–electrolyte interface increased from 3.38 ± 0.11 in the as-fabricated cell (fired at 1418 K (1145 °C)) to 3.59 ± 0.07 after operation at 1048 K (775 °C) for 214 hours in air with 3 to 4 pct H_2O . The specific Mn_xO_y phases observed in

Fig. 4—(color figure online). Left: DF-STEM images across electrolyte (YSZ)/cathode (LSM + YSZ) interface of SOFCs operated at 1198 K (925 °C) (top) and 1073 K (800 °C) (bottom) in humid air on the cathode side. Right: Corresponding elemental maps, constructed by superimposing Zr (blue), La (red), and Mn (green) maps (so that the LSM phase appears yellow). (The vertical stripes in the 1073 K (800 °C) images are “curtaining” artifacts originating from porosity during FIB foil preparation.).

Fig. 5—(color figure online). DF-STEM image (upper left), XEDS elemental map (lower left), and the elemental concentration profiles (right) acquired across YSZ/Mn-oxide/LSM phases along the indicated arrow, in the cell in Figs. 3 and 4 that was operated at 1198 K (925 °C).

Figure 7 are also consistent with reported Zr–Y–Mn–O phase equilibria^[21] and with detailed thermodynamic calculations^[22] on LSM over the relevant range of temperatures and p_{O_2} .

Mn-rich LSM compositions are used in SOFCs to decrease the tendency of LSM to react with the zirconia (either in the electrolyte or in the LSM-YSZ cathode) to form insulating $La_2Zr_2O_7$ pyrochlore or $SrZrO_3$

Fig. 6—(color figure online). EELS fine structure of O- K edge (top center) and Mn- $L_{2,3}$ edge (bottom center) from two Mn-oxide grains (top left and bottom left) at the cathode–electrolyte interface of an SOFC operated at 1073 K (800 °C) for 2000 h at 388 mA cm⁻² and 6.4 bara. Anode atmosphere: reformat; cathode atmosphere: 12 pct O₂, 1.2 pct H₂O, balance air. Comparison to reference spectra^[18] (far right) indicates that grain 1 is Mn₂O₃ and grain 2 is Mn₃O₄.

Fig. 7—(color figure online). XEDS maps taken near the cathode–electrolyte interface (left edge in each image). (a) Cell of Fig. 3(a), 4 (top), and 5 tested for 1340 h at 1198 K (925 °C) in 1.2 pct H₂O; EELS identified Mn₃O₄ precipitates (arrows). (b) Cell of Fig. 4 (bottom) and 6 tested for 2000 h at 1073 K (800 °C) in 1.2 pct H₂O at 0.388 A cm⁻²; EELS identified both Mn₃O₄ (blue arrows) and Mn₂O₃ (red arrows). False-color EDS elemental mapping: yellow (LSM); blue (YSZ); and green (Mn_xO_x).

Table I. Quantitative EELS Data of Mn- $L_{2,3}$ Edge From Grain 1 and Grain 2 (Fig. 6) Compared To Reference Values^[19] for Mn₂O₃ and Mn₃O₄

	Precipitate 1 (Mn ₂ O ₃)	Mn ₂ O ₃	Precipitate 2 (Mn ₃ O ₄)	Mn ₃ O ₄
L_3 (eV)	639.7		639.4	
L_2 (eV)	650.5		650.5	
ΔE (L_2-L_3) (eV)	10.8	10.8	11.1	11.2
L_3/L_2	2.5	2.4 (0.1)	3.0	2.8 (0.2)
Valence state	+3		+3, +2	

perovskite phases.^[23,24] Accordingly, with the Mn-rich composition used here, these phases were absent in the cells studied. Above certain values of the Mn/(La + Sr) ratio, depending on temperature and oxygen activity, the solubility limit of Mn in LSM would be exceeded, and exsolution of Mn_xO_y polymorphs can be expected, as observed here.

In their study of the steam effect, Nielsen and Mogensen^[11] combined microstructural evidence and AC impedance results to infer that a reaction product forms between the LSM and YSZ in moist cathode atmospheres, hindering the adsorption of oxygen on the LSM and the charge transfer at the interface. Many—but not all—of the Mn_2O_3 and Mn_3O_4 particles seen in Figure 6 do coincide with LSM-YSZ interfaces and with TPBs, suggesting that the reaction product inferred by Nielsen and Mogensen may have been the Mn_xO_y seen here. On the other hand, Figure 7(a) (the cell operated at 1198 K (925 °C), which exhibited a negligible steam effect) shows more individual Mn_xO_y precipitates than does Figure 7(b) (the cell operated at 1073 K (800 °C), which exhibited a significant steam effect). It appears that it is not the total number of Mn_3O_4 particles, but the appearance of Mn_2O_3 , that correlates with the steam effect. If there is a mechanistic relationship between Mn_xO_y formation and the steam effect, it does not appear to involve a simple decrease in TPB density: the cell operated at 1073 K (800 °C) had a rate of ASR increase 10 times greater than that of the cell operated at 1198 K (925 °C), and it would be hard to argue that Figure 7(b) shows ten times as much loss of TPB due to Mn_xO_y formation as Figure 7(a).

The fact that the steam effect in LSM cathodes is more pronounced at lower temperatures may be related to temperature- and atmosphere-related changes in the defect chemistry and electronic structure of LSM. At lower temperatures, the concentration of oxygen vacancies will be reduced, because of both the mass-balance nature of defect equilibria and the tendency of multi-valent cations like Mn to exhibit higher oxidation states at low temperatures. Oxygen vacancies are known to be important for oxygen surface exchange on cathode surfaces. The adsorption of moisture from the cathode gas stream to the LSM surface may further increase the

Mn valence state and reduce oxygen vacancy concentrations (especially at the LSM surface) in LSM.

Another factor that would affect the tendency for Mn_xO_y to form is the solubility of Mn in the zirconia phase. (ZrO_2 acts as another sink for Mn beyond the solubility limit in LSM.) The Mn-Y-Zr-O phase diagrams determined by Chen *et al.*^[21] show that Mn has a much lower solubility in tetragonal zirconia (such as the 3YSZ used here) than in cubic zirconia (*e.g.*, 8YSZ).

Backhaus-Ricoult has reported TEM/EELS and XPS analyses of Mn valences in LSM and in zirconia at LSM/YSZ interfaces.^[25,26] Those studies associated the diffusion of Mn (as Mn^{2+}) into YSZ with faster incorporation of oxygen into the electrolyte and improvements in cell performance. Although those studies were conducted in dry cathode atmospheres, it is possible that conditions that stabilize Mn as Mn^{3+} in Mn_2O_3 (*e.g.*, Figure 7(b)) rather than as Mn^{2+} in YSZ lead to slower cathode kinetics and higher cathode ASR, thus contributing to the steam effect. Other work by our group (to be reported elsewhere) indicates noticeably lower incidence of Mn_xO_y precipitates in LSM-8YSZ cathodes, even with Mn-rich LSM formulations such as the one reported on here.

To further understand free Mn_xO_y formation in LSM cathodes during fuel cell operation and its effect on cathode performance, two identical cells with LSM/zirconia cathodes were exposed at 4 bara to a cathode atmosphere of 1.1 pct H_2O at 1198 K (925 °C) for 5 kh (2.5 times longer than the tests illustrated in Figures 4 through 7). One cell (referred to as the reference cell) had no voltage or current applied, while the other cell (referred as the active cell) was operated continuously at 380 mA cm^{-2} (*i.e.*, conditions similar to those of Figure 7(a) except at a 21 pct lower current density and a much longer time). Post-test XEDS maps (Figure 8) show that Mn_xO_y precipitates are distributed uniformly across the entire cathode of the reference cell (Figure 8a), but these precipitates were concentrated almost exclusively within about $3 \mu\text{m}$ of the electrolyte/cathode interface of the active cell (Figure 8b), *i.e.*, they are more localized than the Mn_xO_y precipitates seen in Figure 7(a). Clearly, with or without electrochemical activity, the temperature and atmosphere permit

Fig. 8—(color figure online). XEDS maps (same colors as Figs. 4 through 7) of the cathodes of identical cells exposed at 4 bara to a cathode atmosphere of 1.1 pct H_2O at 1198 K (925 °C) for 5 kh. (a) No applied current or voltage. (The single-phase LSM cathode current collector is visible at the far right.) (b) Cell operated continuously at 380 mA cm^{-2} .

existence of Mn_xO_y precipitates. Under long-term cell operation, however, Mn may migrate towards the cathode/electrolyte interface, or a gradient in oxygen activity across the cathode may favor Mn_xO_y formation near the cathode/electrolyte interface. The accumulation of free Mn_xO_y precipitates near the electrolyte/cathode interface could fill up some of the pores, potentially blocking active TPB sites and reducing cathode performance.

The question of whether Mn_xO_y formation and the steam effect are related to cathode kinetics must also consider the report by Armstrong *et al.*^[13] that the surface oxygen exchange rate in LSM increases with decreasing temperature—i.e., counter to the role of temperature in the steam effect. Furthermore, Yasumoto *et al.*^[27] reported that the activity of LSM cathodes decreases as their oxygen nonstoichiometry increases, which is directly related to the local p_{O_2} and temperature. Clearly, differences in test conditions, cathode atmosphere, and cathode formulations between studies will lead to differences in Mn_xO_y formation. However, the electrical conductivity of the cathode, the cathode reaction kinetics, and the local electrochemistry, complicate attempts to elucidate the mechanisms behind the steam effect. An important question for future work is whether these Mn_xO_y precipitates, and their specific oxidation states, are related (directly or indirectly) to the steam effect, and if so, how the phase stability can be controlled to mitigate the effect.

IV. CONCLUSIONS

During operation of SOFCs with LSM-based cathodes for up to 2,000 h with H_2O in the cathode environment, the ASR increases more rapidly at 1073 K (800 °C) than at 1198 K (925 °C) (the “steam effect”). XEDS mapping after cell operation revealed formation of Mn_xO_y precipitates in the LSM-YSZ cathode, especially near the cathode–electrolyte interface. STEM-EDS line scans showed that the Mn_xO_y precipitates contained only trace amounts of other cations. Comparison of the O–K and Mn– $L_{2,3}$ edges in the EELS spectra further showed that for the cell operated at 1198 K (925 °C), only Mn_3O_4 was present. In contrast, both Mn_3O_4 and Mn_2O_3 were present in the cell operated at 1073 K (800 °C). After operation for 5,000 h at 1198 K (925 °C), Mn_3O_4 formation was confined almost exclusively to within about 3 μm of the cathode–electrolyte interface. While the formation of Mn_2O_3 is certainly implicated in the steam effect, definitive evidence that this is the origin of the effect is still lacking.

ACKNOWLEDGMENT

This material is based upon work supported by the US Department of Energy, National Energy Technology Laboratory under Award Number DE-FE0000303.

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