CHROMIUM POISONING OF SOFC CATHODES: INFLUENCE OF THE LSM-YSZ STRUCTURE

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ABSTRACT
The structure of the cathode strongly influences the degree and rate at which a (La0.8Sr0.2)0.98MnO3 (LSM) - 8% YSZ ceramic cathode assembly will exhibit “chromium poisoning” effects. Under cathodic polarization at 600°C (under flowing, “dry” air), porous films of LSM on dense YSZ in contact with a 430 stainless steel (430SS) contact will lose a significant degree of activity, especially at a high overpotential of -0.5 V vs. Pt/air. Under the same conditions, similar film thicknesses, and using the same materials, structurally graded cathodes composed of 50:50 LSM:YSZ topped with a 100% LSM contact layer exhibit high activity whether a Pt or 430SS contact is employed. Under the same conditions, patterned, fully dense, ca. 80 nm thick LSM films on dense YSZ also show relatively stable activity in the presence of either a Pt or 430SS contact. Electron microprobe analyses of the surfaces of the samples clearly show that Cr2O3 is deposited at and around the perimeter of the cathode film for all samples polarized using a 430SS contact. However, little if any Cr species were found beneath the porous 50:50 LSM:YSZ film, in contrast to the porous LSM film samples, where large concentrations of Cr species were observed at what ostensibly is the buried LSM-YSZ-air triple-phase boundary (TPB). Thus, the stability of the 50:50 LSM:YSZ composite samples seems to be linked to the absence of Cr species at the buried TPB. The same cannot be said for the dense LSM sample, as other factors must be contributing to its resistance to Cr poisoning.

INTRODUCTION
A number of research groups have suggested that the long-term loss of cathode activity in commercial planar SOFC configurations that employ chromia-forming metal interconnects is related to the preferential deposition of chromium oxide (Cr2O3) and Cr-Mn spinels in the general vicinity of the triple-phase boundary (TPB) (1-16). Generally referred to as “chromium poisoning”, this process is proposed to occur during cathodic polarization of porous strontium-doped lanthanum manganite (LSM) cathodes in yttria-doped zirconia (YSZ)-based solid oxide fuel cells. In particular, results presented by several researchers (1-9,11,12) showed that their half-cell performances decayed substantially during polarization over a period of hours to days, and this decay was explained in terms of the observed Cr species deposited at the TPB. Interestingly,
significantly lower rates and magnitudes of performance decay have been observed by several SOFC manufacturers who employ stainless steel interconnects.

Nevertheless, chromia-related cathode performance losses over time are real. Thus, our goal is to understand the factors that contribute to this loss of cathode activity by systematically investigating the effects of polarization, temperature, and cathode-electrolyte structure on polarization losses, as well as on the observed deposition of solid Cr species at the LSM-YSZ-air TPB interfaces. Towards this end, we have found that: 1) the deposition of Cr$_2$O$_3$ from vapor phase species is potential controlled and unique in its ability to form a new electroactive interface based on the Cr$_2$O$_3$-YSZ-air TPB (17), 2) the Cr$_2$O$_3$ phase can be reversibly removed at 800 °C with concomitant “semi”-restoration of the electrochemical activity of the cathode, and 3) the irreversible growth of (Cr,Mn)$_3$O$_4$ spinel phases readily occurs under cathodic polarization at 800°C, but not at open circuit, or if polarized at 600°C (18). In terms of the cathode-electrolyte structure, preliminary research by our group showed that certain LSM-YSZ structures in direct contact with a chromia-forming stainless steel are not susceptible to cathode activity losses when polarized at 800°C (19). The present work explores the structural contributions to cathode stability at 600°C and presents complementary electrochemical and electron microprobe WDX data for a porous 100% LSM cathode, a 50:50 LSM:YSZ composite cathode, and a dense, RF sputtered LSM film, each sintered onto dense YSZ supports.

EXPERIMENTAL METHODS

**Porous 100% LSM on YSZ.** Samples of porous (La$_{0.8}$Sr$_{0.2}$)$_{0.98}$MnO$_3$ (LSM, Praxair Ceramics Inc.), coated on densified 8 mol% Y$_2$O$_3$-ZrO$_2$ wafers (YSZ, Ceraflex®), were prepared in the unfired state by Versa Power Systems Ltd. The ca. 15 μm thick LSM films on these wafers were prepared by suspending the LSM powder ($d_{50}$ ≈ 0.5 μm for the avg. particle size) as an organic solvent-ceramic slurry and screen-printing the mixture (twice, to form two film layers) onto a 5 x 5 cm square wafer of 200 μm thick, densified YSZ (4 x 4 cm film area). The large area LSM film was then subdivided into 49 individual, ca. 4 x 4 mm squares of LSM film by physically removing film between each square using a razorblade. Wafers were then fired at 1150°C for 2 hours (in air, as is the case for all fabrication steps), with heating and cooling ramp rates of ca. 200°C/hour at the higher temperature ranges. The backside of the YSZ wafer was patterned with tape, sputter coated with Pt metal (ca. 150 nm thick) to form the initial portions of the counter electrodes (CE) and reference electrodes (RE), and then fired at 1000°C for 5 to 10 hours. For individual experiments, each wafer was subdivided into 16 pieces, ca. 12 x 12 mm, such that at least one full ca. 4 x 4 mm square of LSM film, as the working electrode (WE), rested on the middle each piece. All samples contained at least one additional portion of LSM film, disconnected from the main WE film, so that side-by-side comparisons could be made between adjacent films. Each ca. 6 x 6 mm Pt film CE was located on the backside of the YSZ, directly opposite to the LSM WE. The Pt film RE was located off to one side of the CE contact.

**Porous 50:50 LSM:YSZ on YSZ.** Samples were prepared in a similar manner as described above. For the composite LSM:YSZ mixture, the average particle size ($d_{50}$) of the YSZ was ca. 0.6 μm. Analysis of a cross section by SEM revealed the LSM:YSZ composite film to be ca. 15 μm thick. As a last step, to increase the conductivity of the...
cathode, a slurry of LSM powder in glycerol was painted onto the 50:50 LSM:YSZ WE (but leaving clearly exposed edges), and the entire piece was fired at 1150°C for ca. 2 hours. This action greatly increased the porosity of the Pt CE contact film, but did not seem to impact the electrochemical performance of the final assembled half-cell.

**Dense LSM on YSZ.** A custom-designed Sputter Deposition system with 2" Magnetron Sputter Guns (Torr International, USA) was used for RF sputtering of dense LSM thin film on YSZ. Using a simple mask, a ca. 6 x 6 mm by ca. 80 nm thick LSM film was deposited on a ca. 12 x 12 mm x 200 μm thick densified piece of YSZ via RF magnetron sputtering of a (La0.8Sr0.2)0.98MnO3 target (99.9% purity, Praxair Ceramics Inc.). The pressure of argon during deposition was 5 mTorr and LSM film was deposited at an Ar:O2 gas flow ratio of 8:2. Sputtering was performed at 4 W/cm² rf power on the target and at ca. 90 mm distance between substrate and target. Substrates were heated to 500°C by halogen lamps. The sample was then post-annealed in O2 at 800°C for 1 hr. The electrical conductivity of LSM thin film on sapphire measured by Van der Pauw method was 230 S/cm at 800°C in air. The backside was then patterned with tape, sputter coated with Pt metal (ca. 150 nm thick) to form the locations for the counter and reference electrodes, and then fired at 1000°C for 2.5 hours. To increase the conductivity of the cathode, the edges of the LSM film were masked off and a thin film of Au metal (ca. 5.5 x 5.5 mm) was sputter coated in the center of the square LSM film. During the electrochemical experiments, where the sample was held at 600°C, the Au film segregated into coalesced islands roughly ¾ μm apart.

**Electrochemical and Surface Studies.** In-house designed, electrochemical half-cell holders were used for the electrochemical studies. A spring loaded, broad-point WE contact, composed of either Pt metal or 430 stainless steel (Bal. Fe, 16.2% Cr, 0.31% Mn, 0.26% Si, 0.18% Ni, 0.04% C, 0.03% Cu, 0.03% Mo, 0.018% P, <0.003% S), was located on one side of a ceramic cell holder. A ca. 1 mm hole was located in the middle of the point contact so that air flow (medical grade air with <50 ppm water) could be directed through the middle of the point contact onto the WE (flow rates were roughly 20 ml/min). The WE of each LSM-YSZ sample was then centered on this contact. The sputtered Pt CE and RE contacts on the other side were then each coated with a thick film of Pt paste (Ferro Pt 4082, 74.3% Pt metal) and contacted to large, 100 mesh Pt gauzes (spot-welded to 0.37 mm dia. Pt wire). Likewise, the backside of the WE contact was attached to a Pt gauze/Pt wire with Pt paste. The sample and Pt gauze contacts were then sandwiched between 19 mm dia. ceramic disks (contact surfaces grooved with 1 mm deep gas diffusion channels) and held in place by a spring-loaded Ni wire. A spring-loaded quartz tube (up the center of the cell holder) was used to apply very light pressure to the Pt/LSM or 430SS/LSM contact, as well as to carry the air supply to the WE.

A computer controlled, EG&G 173 potentiostat/276 interface module was programmed to perform a series of electrochemical experiments that alternated between occasional cyclic voltammogram (CV) scans (5 mV/s) between −0.5 and 0.1 V vs. Pt/air, and a series of 19,900 s (ca. 5.5 hour) amperometry experiments acquired at either −0.1, −0.2, or −0.5 V. The cell went to open circuit for ca. 11 seconds between each experiment step. In terms of surface studies, samples were vapor-coated with carbon and imaged under high vacuum using either a Philips/FEI ESEM at the University of Calgary Microscopy and Imaging Facility (high resolution SEM images), or the JEOL JXA-8200 electron microprobe (UCLEMA) (low resolution SEM images and WDX element maps/spot
analyses), typically using a 10 kV excitation voltage. Often, the electrochemistry of these samples was then directly re-examined after imaging.

**RESULTS & DISCUSSION**

**Electrochemical Results**

**Porous 100% LSM on YSZ.** The activity over time of cathode composed of porous films of LSM on dense YSZ is dramatically different, depending on whether the cathode is contacted by Pt metal or 430SS. The first 100 hours in Fig. 1 follow the current as a function of time as the LSM is polarized at overpotentials of -0.2 and -0.5 V vs. Pt/air using a Pt contact. CVs run between 0.1 and -0.5 V at 5 mV/s are shown as vertical gray lines in this long duration study. Generally, currents increase with time when the cell is polarized at -0.2 and -0.5 V, although there is more variation in stability at -0.5 V. In particular, when polarizing the cell at -0.5 V, cathode activity is at its highest immediately after holding the sample at open circuit for a few seconds (the ca. 11 s time gap between terminating one experiment and initiating the next), after which the current output at -0.5 V slowly decays. This is observed as multiple spikes in current for the black curves in Fig. 1. When the sample is place in a cell holder containing 430SS as the WE contact (120 to 250 hrs in Fig. 1), measured currents quickly decay during polarization, with far higher decay rates observed at -0.5 V. Again, cathode activities briefly recover each time the polarization is stopped for ca. 11 s between experiments, but just as quickly decay again during polarization. Eventually, measured currents decay to levels ranging from ca. 5% (-0.2 V) to 1% (-0.5 V) of the original activity.

**Porous 50:50 LSM:YSZ on YSZ.** Compared to porous LSM samples, the activity of composite cathodes tends to be more stable with polarization over time, especially in the presence of 430SS. Figure 2a shows the effects of overpotential versus time at 600°C when a Pt contact is used, where the black curves show the current at -0.1, -0.2, and -0.5 V, and the gray curves correspond to CVs run between 0.1 and -0.5 V at 5 mV/s. Over the 150 hr time period, currents measured at a given overpotential tend to slowly decay, a trend that has been observed at these particular samples. However, when comparing 100% LSM and 50:50 LSM:YSZ composite samples prepared under the same conditions from the same batch of starting materials (Fig. 1 vs. Fig. 2a), the composite sample is found to be ca. 4 to 5 times more active.

Figure 2b shows the effect of cathodic polarization on the current output of the 50:50 LSM:YSZ sample when a 430SS contact is employed. Although initial current levels at a given potential are somewhat lower than those in Fig. 2a, the currents do not decay further in the presence of a chromia source, and for the -0.5 V overpotential, actually improve over time. This is in direct contrast to the behavior of 100% LSM samples, where the activity is mostly lost under these conditions (for example, see Fig. 1).

**Dense LSM on YSZ.** Although exhibiting far less stability over time as compared to the 50:50 LSM:YSZ sample, dense films of LSM do exhibit relatively stable current responses in the presence of a chromia source. The first ca. 130 hrs of data in Fig. 3a show the results of polarizing the dense LSM sample, in the presence of a Pt contact, at either -0.1, -0.2, or -0.5 V (black curves), or during a CV run between 0.1 and -0.5 V at
5 mV/s (gray curve). The next ca. 130 hrs in Fig. 3a follow the results when a 430SS contact is employed. Figure 3b shows an enlarged current scale plot of Fig. 3a. For this sample, stability of the current with time is clearly an issue, especially when polarized at −0.5 V, whether a Pt or 430SS contact is employed. However, the degrees of short and long term decay in current are relatively independent of the type of electrical contact used, suggesting that Cr-poisoning at 600°C is not a problem for this type of sample.

Microscopy Results

Direct evidence of transfer of Cr species from the 430SS to electrochemically active TPB regions on the LSM-YSZ samples can be found from detailed WDX analyses of the sample surfaces. Such studies show that deposition of Cr$_2$O$_3$ at/around active TPB sites is ubiquitous at 600°C, whether a sample exhibits electrochemical symptoms of Cr-poisoning or not. However, beneath the porous cathode films, a variety of results are observed.

Porous 100% LSM on YSZ. Figure 4 shows secondary (SE) and backscattered electron (BSE) SEM images of a portion of the 100% LSM sample acquired after the electrochemical study shown in Fig. 1. Although not seen in the SE image, the BSE image clearly shows a gray band with multiple band structures (roughly 4 overlapping bands) on the YSZ immediately adjacent to the LSM film. This band is only observed around LSM films that were electrically contacted and negatively polarized. All other uncontacted LSM films near the WE did not exhibit this band. At the same time, the shape and size of this band around the perimeter of the LSM WE is not uniform in appearance, and even missing in some locations (not shown). It is not clear at this time as to what factors may contribute to this effect, although it would seem that the location of 430SS point contact on the LSM film is not a factor, as we have found no correlation between the location of the point and the band breadth. On the other hand, it may be related to uneven air flow across the WE surface (9), which is much harder to control or verify in our studies.

Figure 5a shows an enlarged BSE image, and corresponding WDX Zr, Cr, and Mn element maps, of a small portion of the LSM perimeter. It can be clearly seen that a relatively high concentration of Cr is found as a structured band on the YSZ surface immediately adjacent to the LSM film perimeter. Figure 5b shows a WDX line scan of Cr, Mn, and La taken along the marked white lines in Fig. 5a, starting in the LSM zone. It can be seen that, at the point where the concentration of Mn and La drop to baseline levels (i.e., at the edge of the LSM film), the concentration of Cr increases from levels just above baseline, reaches a plateau, and then drops off to baseline levels. Because only Cr and elements associated with the YSZ were identified in the Cr band, and because the relative concentration of Zr was similar to that found beyond the Cr band, it was concluded that the Cr band is composed of a Cr$_2$O$_3$ film well under a micrometer in thickness. In a previous paper, the growth of this band out from the LSM-YSZ perimeter onto the YSZ surface was examined. It was shown that the Cr$_2$O$_3$ species created a new TPB, based on a Cr$_2$O$_3$-YSZ-air phase boundary, where the Cr$_2$O$_3$ is adequately electronically conductive to allow the TPB to propagate across the YSZ surface, thus contributing to the spread of the Cr$_2$O$_3$ band out from the LSM film perimeter (17). Periodic changes in the applied potential then lead to differing rates of film growth, which are sometimes observed as structures within the Cr band. It was further concluded
that, since Cr$_2$O$_3$ deposition could occur quite far from the LSM-YSZ-air TPB, it was highly likely that Cr$_2$O$_3$ deposition would also occur on all YSZ surfaces buried under the porous LSM film, as evident from WDX cross-sectional analyses of the samples.

Due to the thickness of the LSM film, WDX surface analyses cannot detect Cr at the buried TPB regions beneath the porous LSM film. However, WDX images of the cross-section of other samples poisoned under similar conditions clearly show a continuous band of Cr at the dense YSZ-porous LSM interface where the buried TPB ostensibly resides. By physically removing small portions of the LSM film, we have observed similar distributions of Cr species under the LSM film in this sample.

It should be noted that all Cr$_2$O$_3$ deposits generated thus far at 600°C can be reversibly removed. Electrochemical half-cell studies of similar samples have shown that the cathode activity can be restored to original levels, albeit with greatly lowered short-term stability, simply by first heating the Cr-poisoned sample to 800°C in air at open circuit. WDX analyses show that all detectable amounts of Cr species are removed from the sample surface, as well as all regions beneath the LSM.

**Porous 50:50 LSM:YSZ on YSZ.** Figure 6 shows SEM images of the 50:50 LSM:YSZ sample, acquired after the electrochemical study in Fig. 2. Again, the BSE image clearly shows a gray band on the YSZ immediately adjacent to the LSM film. This band follows much of the LSM film perimeter, although it is spotty or missing in certain sections. Figure 7a shows an enlarged BSE image, and corresponding WDX Zr, Cr, and Mn element maps of a small portion of the composite LSM:YSZ film perimeter. It can be clearly seen that a relatively high concentration of Cr is found on the YSZ surface immediately adjacent to the edge of the LSM:YSZ film perimeter, and that even more is found as a poorly organized band on the LSM:YSZ composite film. Figure 7b shows a WDX line scan of Cr, Mn, and La taken along the marked white lines in Fig. 7a, starting in the LSM:YSZ zone. Concentrations of Cr increase from levels just above baseline to a high plateau on the LSM:YSZ film, drops to a lower plateau on the YSZ surface, and then drops off to baseline levels. At the same time, concentrations of Mn and La crudely mirror each other (within the error generated by imaging a rough LSM:YSZ surface).

The presence of Cr species on/within the cathode film in this case is in direct contrast to 100% LSM samples that had been Cr-poisoned at 600°C, where Cr species are not associated with the LSM film. (Note that other Cr species such as (Cr,Mn)$_2$O$_4$ spinel crystals were not observed in this zone by high resolution SEM imaging, and thus it is inferred that the predominant Cr species is still Cr$_2$O$_3$.) Such behavior would be expected because the TPB zones in a composite cathode are thought to extend throughout the composite structure, being most active at the [dense YSZ]-[LSM:YSZ composite film] interface, and tapering off in activity further away from this interface due to a drop in ionic conductivity. To observe such a segregated zone of Cr$_2$O$_3$ is somewhat surprising, and may indicate that the growth of Cr$_2$O$_3$ films occurs preferentially at the Cr$_2$O$_3$-YSZ-air TPB rather than at the LSM-YSZ-air TPB.

Another major difference can be found beneath the cathode film. WDX images of removed portions of the LSM:YSZ film, as well as cross-section analyses, show that high concentrations of Cr reside primarily at the perimeter of the porous composite film, rather than throughout the composite cathode, and that only trace amounts can be found...
intermittently at the buried cathode-dense YSZ interface. The lack of Cr at the deeply buried TPB regions is consistent with the observed stable activity of the composite cathode, assuming that the majority of the cathode activity occurs at the buried TPB. At this point, we cannot explain why Cr₂O₃ would preferentially deposit at the edges of the composite cathode, rather than beneath the entire cathode, as is the case for the porous LSM film.

**Dense LSM on YSZ.** A dense LSM sample was chosen for comparison because the LSM-YSZ-air TPB is completely open to the surrounding atmosphere, and thus does not have the same mass transfer limitations that might be expected for the porous 100% LSM and 50:50 LSM:YSZ samples. Figure 8 shows SEM images of the dense LSM sample acquired after the electrochemical study in Figs. 3 and 4. The BSE image clearly shows a gray band immediately adjacent to the LSM film on the YSZ surface. This band was broadest in the region shown, and, similar to the other samples, varied in size around the LSM film perimeter. In addition, multiple band structures can be seen in this band (3 total bands in this image, although as many as 4 bands were found at other locations). Figure 9a shows the BSE image, and the corresponding WDX Zr, Cr, and Mn element maps of the dense LSM film perimeter. The Cr map, in particular, shows that the gray band is composed of three different surface densities of Cr species. Such structure in the Cr₂O₃ band is similar to that observed for the Cr-poisoned porous LSM sample in Fig. 5a and is explained in ref. 17. In addition to the bands, localized concentrations of Cr, found throughout the LSM film zone, probably mark defects in the LSM film, although analysis of SEM images suggests that a few of the sites may be metal oxide debris from the 430SS. The relatively high concentration of Cr in the Au film zone (lower left corner of each map) has not been explained as yet.

Figure 9b shows a WDX line scan of Cr, Mn, and La, taken along the marked white lines in Fig. 9a, starting in the LSM zone. In this case, the edge of the LSM film is rather diffuse, as evident by the lack of a sharp transition for the concentrations of Mn and La in the line scan when followed from the LSM film onto the YSZ surface. As a consequence, the highest concentration of Cr is not found on the YSZ surface, but rather in a zone that includes the edge of the LSM film perimeter. Such behavior is qualitatively similar to that observed for the 50:50 LSM:YSZ sample, and probably reflects a highly active LSM-YSZ-air TPB zone at the edge of the LSM film. Where concentrations of Mn and La reach baseline levels, the concentration of Cr also decreases to a new plateau level, before eventually dropping suddenly again to baseline levels well out on the YSZ surface. Interestingly, it would seem that all TPB sites, conveniently located on the surface of the sample, have been covered with a film of Cr₂O₃, and yet little if any effects of Cr-poisoning are observed in the electrochemistry of this sample.

**CONCLUSIONS**

The data presented here supports the notion that LSM cathodes can rapidly lose their activity towards oxygen reduction when polarized in the presence of a chromia source at 600°C. This loss of activity, however, is highly dependent on the structure of the cathode relative to the YSZ electrolyte support. Samples composed of porous cathode films of LSM lose activity far more rapidly and completely than samples composed of either porous 50:50 LSM:YSZ composite films, or dense films of LSM. When examining their
surfaces using an electron microprobe, all samples exhibit signs of Cr$_2$O$_3$ transfer and preferential deposition at active electrochemical interfaces. However, closer inspection revealed that the 50:50 LSM:YSZ samples lacked Cr contaminants at interfaces buried beneath the composite cathode film. This lack of Cr species at buried TPB regions would partially explain why the 50:50 LSM:YSZ samples do not lose activity, even when they are Cr contaminated. The same argument cannot be used for the dense LSM film samples, where all of the TPB regions seem to have been covered by Cr$_2$O$_3$ (down to the micrometer to sub-micrometer resolution of the WDX technique.)

Considering that the same materials and heating routines were used to prepare both the porous 100% LSM and 50:50 LSM:YSZ samples, and that the major difference between all of these samples is the cathode structuring in and around the TPB, it would also seem logical to conclude that structure plays a leading role in determining whether a sample is Cr-poisoned or not. At this juncture, we lack a simple explanation as to why the cathode structure influences where Cr species are deposited, or how it influences the Cr-poisoning susceptibility of a sample, but this problem will be addressed in future research.

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Figure 1. Plot of current vs. time during polarization of the porous 100% LSM cathode at 600°C in flowing air in the presence of either a Pt or 430SS electrical contact. Sample polarized at -0.2 and -0.5 V (black lines), and during CVs run between 0.1 and -0.5 V at 5 mV/s (gray lines). All potentials vs. Pt/air.

Figure 2. Plot of current vs. time during polarization of the porous 50:50 LSM:YSZ cathode at 600°C in flowing air in the presence of either a Pt or 430SS electrical contact. Sample polarized at -0.1, -0.2, and -0.5 V (black lines), and during CVs run between 0.1 and -0.5 V at 5 mV/s (gray lines).
Figure 3a. Plot of current vs. time during polarization of the dense LSM cathode at 600°C in flowing air in the presence of either a Pt or 430SS electrical contact. Sample polarized at -0.1, -0.2, and -0.5 V (black lines), and during CVs run between 0.1 and -0.5 V at 5 mV/s (gray lines).

Figure 3b. Enlarged plot of the data in Fig. 3a.
secondary electron (SE) backscattered electron (BSE)

Figure 4. SE and BSE SEM images of the porous 100% LSM sample (carbon coated) acquired after the electrochemical study in Fig. 1. 10 kV excitation voltage. The LSM film contacted as the working electrode is marked "WE". Dark objects on the YSZ surface in the BSE image are mostly composed of isolated LSM debris resulting from subdividing the green LSM film with a razorblade prior to sintering.

(a) 

(b) 

Figure 5. 5a) BSE and WDX Zr, Mn, and Cr element maps of a magnified portion of the porous 100% LSM sample shown in Fig. 4 (located just above the image in Fig. 4 along the right WE edge, and rotated 90° ccw). 10 kV excitation voltage, 25 ms dwell time per pixel, data point acquired every 0.3 μm. 5b) WDX line scan of Cr, Mn, and La taken along the marked white lines in Fig. 5a, starting in the LSM zone. 10 kV excitation voltage, 1000 ms dwell time per pixel, data point acquired every 0.5 μm.
Figure 6. SE and BSE SEM images of the 50:50 LSM:YSZ sample (carbon coated) acquired after the electrochemical study in Fig. 2. 10 kV excitation voltage.

Figure 7. 7a) BSE and WDX Zr, Mn, and Cr element maps of the 50:50 LSM:YSZ sample shown in Fig. 6. 10 kV excitation voltage, 25 ms dwell time per pixel, data point acquired every 0.3 μm. 7b) WDX line scan of Cr, Mn, and La taken along the marked white lines in Fig. 7a, starting in the LSM zone. 10 kV excitation voltage, 1000 ms dwell time per pixel, data point acquired every 0.5 μm.
Figure 8. SE and BSE SEM images of the dense LSM sample (carbon coated) acquired after the electrochemical study in Fig. 3. 10 kV excitation voltage.

Figure 9. 9a) BSE and WDX Zr, Mn, and Cr element maps of the dense LSM sample shown in Fig. 8. 10 kV excitation voltage, 35 ms dwell time per pixel, data point acquired every 0.3 μm. 9b) WDX line scan of Cr, Mn, and La taken along the marked white lines in Fig. 9a, starting in the LSM zone. 10 kV excitation voltage, 1000 ms dwell time per pixel, data point acquired every 0.5 μm.