

Use of an “Open” Triple-Phase Boundary to Demonstrate Where Chromium Contaminants Initially Deposit at the LSM-YSZ Interface.

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Background & Method: A number of research groups have demonstrated that pure and mixed metal chromium oxides preferentially deposit around the general vicinity of the triple-phase boundary (TPB) during cathodic polarization of porous strontium-doped lanthanum manganite (LSM) cathodes in yttria-doped zirconia (YSZ)-based solid oxide fuel cells. This deposition directly leads to increased polarization losses by blocking diffusion of oxygen to the active sites (1-4). It is also well understood that the chromium originated from the chromium oxides found on the surface of the metal alloys used as the electrical contact to the cathode. Likewise, there are many factors that influence the rate of chromium species deposition at the cathode-electrolyte interface region. These include the nature of the interconnect material, temperature, oxygen partial pressure, water partial pressure, gas flow rate, applied current density, and the nature of the species present on the surface of the electrolyte and cathode materials (1-7).

In this study, we wanted to identify where the solid chromium species initially deposited, and at what point their deposition around the TPB region directly influences the electrochemical properties of the cathode-electrolyte half-cell. Towards this end, we have fabricated an 8%-YSZ electrolyte wafer into which a densified piece of $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$ (LSM) is embedded into its surface prior to sintering at 1250 °C. After polishing, a well-defined LSM/YSZ TPB can be obtained on the surface of the ceramic wafer. Pt paste counter and reference contacts were added to the backside of the YSZ wafer, and a 17-4 stainless steel disk was pressure contacted to the LSM only. The wafer was then subjected to a series of cathodically polarized experiments at 800 °C in air. Post experiment surface analyses were performed using SEM and electron microprobe techniques.

Results: Under the conditions noted above, we have found that Cr-containing species, in particular $(\text{Cr,Mn})_3\text{O}_4$ spinel crystals, are preferentially deposited on the YSZ side of the triple-phase boundary. This is demonstrated in Figure 1, where the SEM images of a typical location along the LSM/YSZ interface show crystals (seen as bright objects in Fig. 2A) on the YSZ side of the interface. Figure 2 shows the -0.5 V fixed potential, current versus time curve used to generate the resulting surface changes seen in figure 1. The formation of these spinel crystals only occur under cathodic polarization, and not at open circuit conditions. Because the $(\text{Cr,Mn})_3\text{O}_4$ spinel phase was the predominant product to be observed, it is believed that Cr_2O_3 , another solid typically reported in the literature to be deposited at the TPB, rapidly equilibrates with the surrounding gaseous environment. The results presented here show that under chromium poisoning conditions, little if any degradation of the cell's performance is observed if the TPB does not become blocked.

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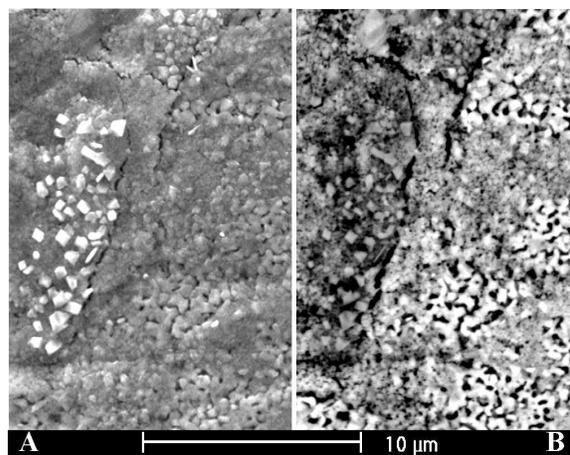


Figure 1. SEM secondary (A) and back-scattered (B) electron image of the face of a composite YSZ/LSM chip after exposure to a chromia-forming steel alloy in air under cathodic polarization. The YSZ can be identified in B as the darker zone is on the left side, and LSM as the lighter zone on the right. The grey areas on the LSM side were found to be a thin layer of YSZ, possibly imbedded into the LSM during the initial polishing step.

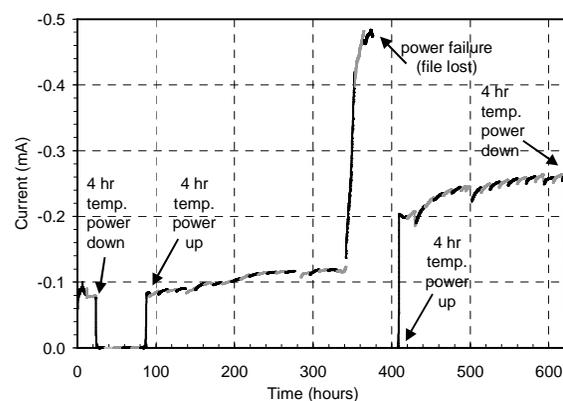


Figure 2. Plot of current vs. time for a series of -0.5 V fixed potential experiments applied to the 1250 °C co-sintered LSM/YSZ wafer. Each run lasted 11 1/3 hrs and was preceded by a 5 scan CV cycled between 0.1 and -0.5 V at 5 mV/s (not shown). Except during the CV's and the power failure noted above, a -0.5 V bias was continuously applied to the cell. Except at those points noted in the plot, the temperature was kept at a constant 800 °C. The temperature ramp for temperature power up and down was 194 °C/hr.