

Electrochemically Assisted Growth of Chromium Contaminants and Concomitant Loss of Activity in LSM-based SOFC Cathodes.

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Background & Method: Understanding the electrochemical reactions that occur at gas-solid interfaces is of particular importance in solid oxide fuel cell (SOFC) research. In this regard, 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 negative polarization of porous strontium-doped lanthanum manganite (LSM) cathodes on yttria-doped zirconia (YSZ) electrolytes (1-4). This deposition directly leads to increased polarization losses either by blocking diffusion of oxygen to the active sites, or by interfering with one or more steps occurring in the O_2 reduction reaction. It is 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, many factors influence the rate of Cr species deposition at the cathode-electrolyte interface region, including: the type of the interconnect material, temperature, O_2 partial pressure, water partial pressure, gas flow rate, applied current density, and the type of electrolyte and cathode materials employed (1-6).

In this study, we show that the deposition of certain solid chromium species is electrochemically driven, and that they directly influence the activity of the cathode-electrolyte half-cell towards O_2 reduction. Towards this end, 8% YSZ electrolyte wafers were mass fabricated with porous, ca. 15 μm thick films of $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$ (LSM) with controlled dimensions. After sintering at 1150 $^\circ\text{C}$, sputtered Pt film counter and reference electrodes were added to the backside of the YSZ wafer and re-sintered at 1000 $^\circ\text{C}$. For electrical contact to the LSM film, spring loaded point contacts made either of Pt metal or 430 stainless steel (SS) were used, the latter also acting as the volatile chromium oxide source. The wafers were then subjected to a series of negatively polarized half-cell experiments between 600 to 800 $^\circ\text{C}$ in flowing air (< 50 ppm H_2O). Post experiment surface analyses were performed using an SEM and electron microprobe.

Results: When polarized at -0.5 V vs. Pt/air in the presence of 430 SS, activity losses for the LSM cathode was readily observed, whether at 600 $^\circ\text{C}$ (Fig.1) or 800 $^\circ\text{C}$. This is in marked contrast to when the Pt contact was used, where relatively stable currents with time were recorded at 600 $^\circ\text{C}$ (Fig.1). Activity losses at 600 $^\circ\text{C}$ could be reversed by removing the 430 SS, replacing it with the Pt contact, heating the sample to 800 $^\circ\text{C}$ in flowing air, prior to re-running the electrochemistry. It was far more difficult to recover initial activity if the sample was polarized at 800 $^\circ\text{C}$. Surface analyses showed two different results. When only polarized at 600 $^\circ\text{C}$, Cr_2O_3 was observed as a deposit around all LSM-YSZ interfaces, and as a thin film on the YSZ surface adjacent to the LSM working electrode (Fig.2). Adjacent regions with uncontacted LSM films were not affected. The Cr_2O_3 could be removed by a 800 $^\circ\text{C}$ heat treatment. However, for those samples polarized at 800 $^\circ\text{C}$ in the presence of the 430 SS contact, $(Cr,Mn)_3O_4$ spinel crystals were also observed at the LSM-YSZ interface, particularly on the YSZ surface. Attempts at recovering

the electrode activity at 800 $^\circ\text{C}$ resulted in removing the Cr_2O_3 , but not the spinel phase. Our published results showed that the growth of the Cr_2O_3 film across the YSZ surface is electrochemically driven (7). This presentation addresses how the electrochemistry influences the formation of the $(Cr,Mn)_3O_4$ spinel phase, ultimately leading to SOFC power losses.

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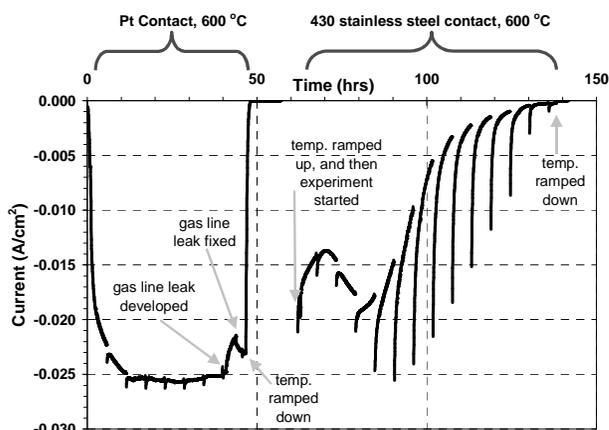


Figure 1. Current vs. time plot for a series of -0.5 V fixed potential experiments run at 600 $^\circ\text{C}$ in flowing air. Each run lasted 5.7 hrs and was preceded by a 2 scan CV cycled between 0.1 and -0.5 V at 5 mV/s (not shown). A third of the way through the experiment, the cell was returned to 25 $^\circ\text{C}$, the Pt contact was replaced with a 430 SS contact, and reheated to 600 $^\circ\text{C}$.

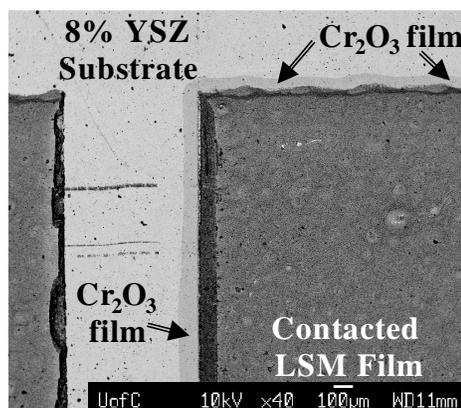


Figure 2. SEM back-scattered electron image of the surface of the LSM-YSZ sample after the Cr-poisoning experiment in Fig. 1.