Effect of harsh anneals on the LSM/YSZ interfacial impedance profile

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Abstract

AC impedance spectroscopy was used to investigate the effects of microstructural and interfacial changes on the cathodic reaction occurring at the LSM/YSZ interface. These effects were induced by using harsh anneals of temperatures ranging from 1250 to 1400 °C and times ranging from 1 to 48 h. Additional characterization of the effects of the anneal was performed through the use of SEM and EDS. A separate semicircle with a distinct time constant was observed in the Nyquist plot of samples that have been exposed to anneals of 1400 °C. The magnitude of the resistance of this semicircle was shown to be dependent on the time and temperature of the applied anneal. Extended interfacial pores were also shown to occur in 1400 °C annealed samples.
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1. Introduction

In recent years, a drive towards high efficiency, low emissions, power sources has created a great deal of interest in fuel cells. Solid oxide fuel cells (SOFCs) have potential to meet these requirements and run on a readily available fuel supply [1]. The quality of the electrode–electrolyte interface is important to the performance of any cell. Of particular interest is the triple phase boundary (TPB), the area where the cathode, electrolyte, and oxidant meet. For pure electronic conducting electrodes, the electrochemical reaction driving fuel cell operation is restricted to this area [2]. Additionally, it has been shown that increasing the TPB area results in reduced electrode resistance for LSM/YSZ systems [3,4]. To maximize the TPB requires high porosity in the electrode and good adhesion between the electrode and electrolyte.

A lanthanum strontium manganite ($La_{1−x}Sr_xMnO_3$, LSM) cathode on yttria-stabilized zirconia (ZrO_2–Y_2O_3, YSZ) electrolyte system is currently the state of the art; however, the performance stability of such devices is an issue [1,5,6]. Much of the power loss in SOFCs is due to polarization loss at the cathode–electrolyte interface,

one source of which is degradation of this interface due to the formation of tertiary phases. During fabrication or long term high temperature operation, the cathode and electrolyte may react to form insulating tertiary phases at the cathode–electrolyte interface that are detrimental to performance in LSM on YSZ devices [7]. Additionally, coarsening of the cathode and delamination at the interface inhibit the cathodic reaction by reducing the TPB. These and other effects can be induced in a timely fashion through the use of high temperature anneals. The impact of microstructural and interfacial changes on the electrochemical steps contributing to the overall cathodic reaction is studied herein.

2. Experimental

Symmetrical LSM/YSZ/LSM test samples were produced for the work. The electrolyte used in the work was prepared by a tape cast method by Marketech International, Inc. The YSZ contained 8 mol% yttria and had dimensions of 10.0 mm × 20.0 mm × 0.1 mm. LSM ink was provided by Nextech Materials, Ltd. and consisted of a 1:4 Sr:La ratio. Two layers of LSM were screen printed on each side of the YSZ electrolyte resulting in a symmetric sample. A drying
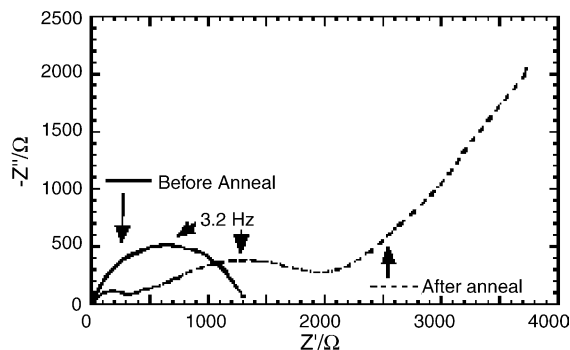
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Fig. 1. Z^* plots measured at 600 °C of symmetrical LSM on YSZ samples as sintered and after a 1400 °C, 48 h anneal.

step was performed after the screen-printing of each layer in a Fisher Isotemp drying oven at 100 °C for 1 h. After drying, sintering was performed at 1100 °C for 1 h in a Lindberg high temperature box furnace (molybdenum disilicide heating element). The resulting symmetrical samples had LSM thickness of about 10 µm and YSZ thickness of 100 µm.

The samples were mounted in a quartz tube inside a Barnstead/Thermolyne furnace with pressure contact leads to the frequency response analyzer. The quartz tube consisted of an inlet and outlet for gas flow, gold leads shielded by alumina rods with platinum paint, and a pressure contact sample holder, which eliminates the need to sinter contacts on the samples. Oxygen, nitrogen, and air gases were flowed over the samples in measurement conditions. Flow rates were 21.0 cm³/min as measured by mass flow controllers.

A Solartron 1260 impedance gain analyzer was used to measure the frequency response of the prepared samples. Auto-integration was used under "I, long" measurement conditions with an integration time of 60 s. I, long is a Z plot option in which the current is measured for noise and an attempt is made to get consistency in the measurements with a maximum standard deviation of 1% when possible. The active frequency range was 1.0×10^{-1} to 3.2×10^{7} Hz. A Solartron 1287 potentiostat was used for measurements involving application of a bias. Z plot and Z view were used to acquire and display the impedance data.

A JEOL 1400 SEM equipped with EDS was used to investigate the microstructure of the LSM/YSZ interface before and after the application of a 1400 °C, 48 h anneal. SEM and EDS measurements were performed at the Major Analytical Instrument Center (MAIC) at the University of Florida.

3. Results and discussion

The effect of a 1400 °C 48 h anneal on the electrochemical behavior of the symmetric sample is displayed in Fig. 1. In this figure, a 600 °C measurement temperature was used in the frequency response analysis. Upon comparison of the profile before and after the anneal, it is apparent that one process with a characteristic frequency of 3.2 Hz is present in both

spectra. Examining the low frequency regime reveals drastic change as the system exhibits linear behavior with an angle close to 45°. Such behavior has been reported in [8] and is described as a Warburg impedance. In the high frequency regime, a process appears in the post-annealed sample that was not apparent in the as sintered sample. The causes and significance of these changes are discussed below.

Included in Fig. 2a–c are high and low magnification Nyquist plots and a Bode plot of the as sintered sample at various measurement temperatures. Apparent in the Nyquist plots are high and intermediate frequency semicircles and part of a low frequency tail. A comparison of Fig. 2a and b display the similarities in the high frequency processes for the various temperature profiles. The aspect ratio of the high and intermediate processes is relatively consistent upon comparison of the 250 °C profile in Fig. 2a with the 400 °C profile in Fig. 2b. Utilization of the imaginary impedance versus frequency (Bode plot) allows viewing of the evolution of all process contributions at all measurement temperatures in one figure. At lower measurement temperatures, the resolution of low frequency phenomenon is limited by measurement time, while the high frequency phenomenon becomes unresolvable for the higher measurement temperatures due to systematic limitations including inductive effects of the leads.

Fig. 3a and b exhibit the dependence of the as sintered sample on oxygen partial pressure. Examination of Fig. 3a reveals the dependence of the low frequency process on oxygen partial pressure. In the absence of oxygen the profile resembles that of a Warburg impedance. This is an expected result considering that in a nitrogen ambient, the transport of oxygen molecules to the surface is extremely slow compared to the processes which consume oxygen, occurring on and in the sample. In the presence of oxygen the low frequency semicircle becomes resolvable. Increasing the oxygen partial pressure decreases the magnitude of this semicircle. The process step corresponding to this semicircle is either directly or indirectly dependent on molecular oxygen. In contrast, immediately apparent in Fig. 3b is the independence of the system response on oxygen partial pressure in the high frequency regime. The segments of the spectra causing the mid and high frequency process steps do not involve molecular oxygen.

Bias voltages of 0.0–0.6 V were applied to the as sintered test sample at a 400 °C measurement temperature. The results are shown in Fig. 4a and b. It was found that the high and intermediate frequency arcs were unaffected by the application of the bias, while the low frequency arc magnitude decreased as bias was increased. This dependence is an indication that the low frequency process step involves directly or indirectly ionic or electronic species. Coupling this knowledge with the information extracted from the oxygen partial pressure dependence leads to the conclusion that the low frequency process is attributed to a step involving molecular or atomic oxygen and ionic oxygen, such as dissociative adsorption. This finding is in agreement with previous works [9–11].