EFFECT OF POLARIZATION ON THE ACTIVATION PROCESS OF (La, Sr)MnO₃ ELECTRODES OF SOLID OXIDE FUEL CELLS

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ABSTRACT

The effect of polarization on the electrode behavior and microstructure of freshly-prepared (La₀.₈Sr₀.₂)₀.₉Mn₀₃ (LSM) electrodes was investigated. The electrode polarization (i.e., interface) resistance \( R_e \) decreased significantly with the cathodic polarization while in the case of the anodic polarization \( R_e \) increased initially, followed by a gradual decrease. In addition, the polarization treatment has significant effect on the microstructure of the LSM electrode. The original and large agglomerates in freshly-prepared LSM electrodes were broken down into sphere-shaped grains when exposed to cathodic or anodic current passage of 200 mA cm⁻² at 800°C in air for 3 hr. The grain growth of the LSM electrodes was inhibited under cathodic polarization as compared to that under open circuit. This explains the observed high stability of the LSM cathode under solid oxide fuel cell operation conditions. The cathodic or anodic polarization treatment also has significant effect on the morphology and topography of the LSM electrode/Y₂O₃-ZrO₂ (YSZ) electrolyte interface.

INTRODUCTION

It is well known that the electrochemical activity of Sr-doped LaMnO₃ (LSM) electrode of solid oxide fuel cells improves significantly with the cathodic polarization. However, as shown recently [1], there is a complex relationship between microstructure and electrochemical polarization performance for the O₂ reduction reaction on LSM electrodes. The best example is the initial polarization behavior of the freshly-prepared LSM electrodes. For the O₂ reduction reaction on the freshly prepared LSM electrodes, the initial polarization losses are very high and decrease significantly with cathodic polarization/current passage [2]. Such activation effect of the cathodic polarization/current passage on the polarization performance of the LSM electrodes has been attributed to the generation of oxygen vacancies [3,4], the enlargement of three-phase boundary (TPB) area [5], and the breaking of surface passive layers associated with SrO segregation [6]. In this study, we report some new results on the electrode behavior and microstructure changes of LSM electrodes under various polarization/current passage treatments. The results indicate that polarization treatments not only result in significant improvement in the electrochemical activity of the LSM electrodes but also lead to significant microstructure change in the bulk LSM electrode and at the electrode/electrolyte interface.
EXPERIMENTAL

Zirconia electrolyte discs were prepared from 8 mol% Y₂O₃-ZrO₂ (YSZ, Tosoh, Japan) by die-pressing, followed by sintering at 1500°C in air for 4 hrs. The thickness and diameter of sintered YSZ electrolyte discs were ~1 mm and 18 mm, respectively. A-site nonstoichiometric (La₀.₈Sr₀.₂)₀.₉MnO₃ (LSM) powders were prepared by co-precipitation and calcined at 900°C in air. X-ray diffraction (XRD) spectra of the as-fired powder showed the perovskite structure only. LSM electrode ink was applied to the electrolyte substrate by screen-printing and sintered at 1150°C in air for 2 hrs. Electrode coating thickness was ~15 µm and electrode coating area was 0.5 cm². Pt paste was painted to the other side of the YSZ electrolyte substrate as the counter and reference electrodes. The counter electrode was symmetrically positioned at the center, opposite to the working electrode. The reference electrode was painted as a ring around the counter electrode. The gap between the counter and reference electrodes was ~4 mm.

All polarization treatments were performed under a current density of 200 mA cm⁻² at 800°C in air. Polarization treatments selected in this study were (a) cathodic for 3 hrs, (b) cathodic and anodic for 6 hrs, (c) anodic for 3 hrs, and (d) cathodic, anodic and cathodic for 9 hrs. Duration for each individual polarization section was kept as 3 hrs. The polarization was interrupted from time to time to conduct electrochemical impedance spectroscopy (EIS) measurement using a Solartron 1260 frequency response analyzer in combination with a Solartron 1287 electrochemical interface. The frequency range of EIS was from 0.1 Hz to 100 kHz and signal amplitude was 10 mV. EIS measurements were performed at open circuit. Electrode ohmic resistance (Rₑ) was measured from the high frequency intercept and electrode interface (polarization) resistance (Rₑ) was obtained directly from the difference between the high-frequency and low frequency intercepts on impedance curves.

The effect of polarization was also studied on the LSM electrodes under a constant cathodic current load of 500 mA cm⁻² at 1000°C in air for 1600 hrs. Microstructure of the LSM electrode and the LSM electrode/YSZ electrolyte interface before and after the polarization treatments were examined by scanning electron microscopy (SEM, Leica S360) and atomic force microscopy (AFM, Nanoscope IIIA, Digital Instruments). To examine the LSM/YSZ interface, the LSM electrode was removed by HCl acid treatment in an ultrasonic bath at room temperature. Thereafter the specimen was cleaned and dried before the SEM and AFM examination.

RESULTS AND DISCUSSION

Figure 1 shows the typical impedance responses of a freshly-prepared LSM electrode as a function of cathodic current passage time at 200 mA cm⁻² and 800°C in air. The absolute value of Rₑ depended on the individual LSM electrodes. However, the trend of the change of Rₑ with the cathodic current passage was the same. Rₑ showed very sharp decrease at the first 5 min of cathodic polarization, followed by a much slower decrease in Rₑ. The initial Rₑ value was 18.5 Ω cm⁻² before cathodic current passage and was reduced rapidly to 3.5 Ω cm⁻² after 5 min of current passage. At the end of 3 hr cathodic polarization treatment Rₑ was reduced to 0.75 Ω cm⁻². This indicates that the activation process of the cathodic polarization on the polarization performance of LSM electrodes is rather rapid.
Figure 1. Initial impedance responses of a freshly-prepared LSM electrode as a function of cathodic current passage at 200 mAcm\(^{-2}\) and 800°C in air.

Figure 2 shows the electrode polarization resistance (R\(_e\)) of the freshly-prepared LSM electrodes under various polarization treatment programs at 200 mAcm\(^{-2}\) and 800°C. For O\(_2\) reduction on a freshly-prepared LSM electrode, the electrode polarization resistance (R\(_e\)) decreased rapidly with the cathodic polarization treatment (Fig. 2a). On the other hand, R\(_e\) increased monotonically with subsequent anodic current passage and the rate of increase in R\(_e\) with the anodic polarization treatment was much slower than the corresponding rate of decrease of R\(_e\) with the cathodic polarization treatment (Fig. 2b). Nevertheless, the increase in R\(_e\) is an indication of deactivation effect of anodic polarization on the O\(_2\) reaction at LSM electrodes. Similar to that observed on the freshly-prepared LSM electrode, R\(_e\) decreased very rapidly with the subsequent cathodic current passage though the initial decrease in the R\(_e\) appears to be not as sharp as that observed on the freshly-prepared LSM electrodes (Fig. 2c).

Figure 2. Electrode polarization resistance (R\(_e\)) of freshly-prepared LSM electrodes under various polarization treatment programs.
The effect of anodic current polarization on the $R_E$ of freshly-prepared LSM electrodes is very different from that observed on previously polarized LSM electrodes (Fig. 2d). The change of $R_E$ with the anodic current passage time can be characterized by two distinct regions: an initial increase with anodic current passage followed by a region where $R_E$ showed a gradual decrease. At the end of 3 hrs of anodic polarization, $R_E$ was 32 $\Omega$ cm$^2$ and was still higher than the initial value of 20 $\Omega$ cm$^2$ before the anodic polarization. The significant difference in the effect of the anodic polarization treatment on the electrode behavior of LSM before and after cathodic polarization treatment indicates that the electrode processes occurring in the polarization treatment are not completely reversible [2]. It was also noted that the ohmic resistances of the electrode as measured from the intercept at high frequencies on the impedance curves were not changed after various polarization treatments. This indicates that either anodic polarization or the subsequent anodic polarization treatments after cathodic polarization have no effect on the physical contact between the LSM electrode and the YSZ electrolyte. This was also confirmed by the good adhesion of the LSM electrodes after testing.

Figure 3 shows the SEM pictures of the fractured cross-sections of LSM electrodes after cathodic current passage for 3 hrs, cathodic and anodic current passage for 6 hrs, anodic current passage for 3 hrs, and cathodic, anodic and cathodic current passage for 9 hrs at 200 mA cm$^{-2}$ and 800°C in air. The LSM electrode before any current treatment is shown in Fig. 3a. For the purpose of simplicity, only the SEM pictures of the LSM bulk phase were shown in the figure. However, the microstructural change at the LSM/YSZ interface is similar to that observed in the bulk [7]. The microstructure of the freshly-prepared LSM electrode is characterized by large agglomerates with no clear grain boundaries between LSM particles (Fig. 3a). After cathodic current passage treatment, large agglomerates of LSM electrodes disappeared and microstructure of the LSM electrode was characterized by much smaller and well-defined granular-shaped particles with clear grain boundaries (Fig. 3b). This is similar to the microstructure change induced by cathodic polarization on LSM electrodes with different composition [8]. However, such change in the microstructure of LSM electrode does not seem to affect the good bonding between LSM particles and YSZ electrolyte. This is indicated by the continuity at the LSM and YSZ interface [7]. There is also significant increase in small pores due to the microstructural change of the LSM cathode after cathodic current passage. Similarly, the microstructure of the freshly-prepared LSM electrode after cathodic and anodic polarization was characterized by well-defined sphere-shaped particles (Fig. 3c). This indicates that the morphology change caused by the cathodic current passage treatment cannot be reversed with subsequent anodic current passage treatment. The microstructural change was also observed on the freshly-prepared LSM electrode after anodic current passage (Fig. 3d). The morphology change induced by the anodic current passage was similar to that by the cathodic current passage treatment on the freshly-prepared LSM electrode. This shows that the morphology and microstructure change of freshly-prepared LSM electrode can take place either under cathodic or under anodic polarization conditions. Similar morphological change was also observed after sequential cathodic, anodic and finally cathodic current passage for total 9 hrs (Fig. 3e). However, it appears that LSM particles grow after such sequential polarization treatment. Table 1 gives the average grain size of the LSM electrodes after various current passages at 200 mA cm$^{-2}$ and 800°C in air.
Figure 3. SEM pictures of freshly-prepared LSM electrodes (a) before the polarization, (b) after cathodic polarization for 3 hrs, (c) cathodic and anodic for 6 hrs, (d) anodic for 3 hrs and (e) cathodic, anodic and cathodic for 9 hrs.

Table 1. LSM grain size after various current passage treatments.

| Treatment                        | Cathodic, 3 hrs | Anodic, 3 hrs | Cathodic and anodic, 6 hrs | Cathodic, anodic and cathodic, 9 hrs |
|----------------------------------|-----------------|---------------|---------------------------|-------------------------------------|
| Size, μm                         | 0.76±0.18       | 0.67±0.19     | 0.89±0.29                 | 1.04±0.29                           |

Figure 4 is the SEM pictures of the LSM electrode sintered with and without a current load of 500 mA cm\(^{-2}\) at 1000°C in air for 1600 hrs. In comparison the surface of the LSM electrode before the test is shown in Fig. 4a. The initial grain size of the LSM electrode was 0.78±0.286 μm. The grains of LSM electrodes grew when sintered at 1000°C as compared to that of the freshly prepared LSM electrodes before the test. However, the grains of the LSM electrodes sintered under a cathodic polarization were in fact smaller than that sintered under no current load (i.e., at open circuit). The grain size of the LSM electrode was 0.88±0.302 μm after sintering at 1000°C under a current load of 500 mA cm\(^{-2}\) for 1600 h. In the case of the LSM electrode sintered at open circuit under the same conditions, the LSM grains grew to 1.174±0.251 μm, which is 33% larger than that sintered under current load. The same trend was observed for the LSM electrodes with different stoichiometrical compositions [9]. The grain size measurements from the SEM analysis revealed the significant grain growth of LSM electrodes sintered at open circuit under no current load as compared to that under cathodic polarization conditions at 1000°C.
Figure 4. SEM pictures of the LSM electrode (a) before the test, (b) after sintered at 1000°C in air for 1600 hrs and (c) after sintered under a current load of 500 mA cm⁻² at 1000°C in air for 1600 hrs.

Figure 5 shows the AFM images of the YSZ surface in contact with the LSM electrode before and after various polarization treatments. After removing the LSM electrode coating by HCl acid treatment, rings or dents approximately 0.5-1.0 μm in diameter can be clearly seen on the YSZ surface (Fig. 5a). They grew out of the YSZ electrolyte, forming convex-shaped rings on the YSZ surface. The rings had sharp boundaries and the depth of the rings was in the range of 90 to 140 nm. The location of these rings on the YSZ surface shows a random distribution, either on the smooth surface of YSZ grains or at the grain boundary area [10]. This indicated that the rings are the contact points between LSM particles and the YSZ surface. There were no square islands formed on the convex rings, indicating that there is no formation of a secondary phase such as lanthanum zirconate between A-site deficient LSM and YSZ under the experimental conditions in this study [11]. Despite the difference in the polarization treatment programs, the changes in the morphology and topography of the convex rings are similar. After various polarization treatments, the sharp edge of the YSZ rings disappeared and the rings grew outwards. The circumference of the rings became a two-dimensional boundary area. The width of the rings was in the range 0.08 to 0.23 μm and the average ring width was 0.15 ± 0.05 μm. The significant change in the topography of the convex rings indicates that microstructure and morphology changes occur not only in the bulk of the LSM electrode [7] but also at the LSM/YSZ interface. It is noted that such interfacial changes induced by the cathodic polarization are not reversible under subsequent anodic polarization, as shown in Fig. 5c. Moreover, the anodic current treatment on a freshly-prepared LSM electrode also induced the change in LSM/YSZ interface topography in a similar manner to the cathodic current treatment (Fig. 5d). This indicates that the initial LSM/YSZ interface formed by the thermal treatment of the system is morphologically unstable. Either cathodic or anodic current passage has a significant effect on the morphology and topography between the LSM electrode/YSZ electrolyte interface.
CONCLUSIONS

This study clearly shows that polarization treatments not only have significant effect on the electrochemical activity of the LSM electrodes for the oxygen reduction reactions but also have significant effect on the microstructure and morphology of the LSM electrode and at the LSM electrode/YSZ electrolyte interface. Under cathodic polarization, the generation and migration of oxygen vacancies and Mn ions and lattice expansion and crystallographic distortion could all contribute to the microstructural changes. Similar to that observed under cathodic current passage, anodic current passage also induced microstructure and morphology improvement on freshly-prepared LSM electrode, which is most likely due to the lattice shrinkage under oxidation environment. The reduced sintering under cathodic polarization could be related to the elimination of the cation vacancies at the A-sites, thus reducing the driving force for the sintering and grain growth of the LSM electrodes [12]. The formation of a convex ring on the YSZ electrolyte surface and its subsequent broadening under various polarization treatments indicate that oxygen reduction and oxidation reactions most likely occur at the O\textsubscript{2}/LSM/YSZ three phase boundary areas.

Figure 5. AFM images of the YSZ surface in contact with LSM electrode; (a) before the polarization treatments, (b) after cathodic polarization for 3 hrs, (c) cathodic and anodic polarization for 6 hrs, and (d) after anodic polarization for 3 hrs.
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