FABRICATION OF HIGH PERFORMANCE (La,Sr)MnO₃ CATHODES BY ION IMPREGNATION

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ABSTRACT

The electrode performance of (La,Sr)MnO₃ (LSM) cathodes modified by ion impregnation methods was investigated. By impregnation of nanosized electrocatalytic oxide particles into LSM structure, electrode performance of modified LSM cathodes for the O₂ reduction reaction was substantially increased. At 700°C, the electrode interface conductivity of impregnated LSM electrodes increased to 1.4 Scm⁻² compared with 0.038 Scm⁻² for LSM electrodes without impregnation. The electrode interface conductivity was enhanced by 36 times. Ion-impregnated LSM electrodes showed better polarization performance than LSM/Y₂O₃-ZrO₂ and LSM/(GdCe)O₂ composite electrodes reported in the literature. The results showed that LSM electrodes modified by ion impregnation are promising candidate cathode materials for intermediate-temperature solid oxide fuel cells.

INTRODUCTION

Strontium-doped LaMnO₃ (LSM) perovskite is the most investigated cathode material for solid oxide fuel cells (SOFCs) due to its high electrochemical activity for the O₂ reduction reaction and good stability and compatibility with Y₂O₃-ZrO₂ (YSZ) electrolytes (1-8). With proper processing and optimization of the microstructure and stoichiometric composition, LSM electrodes can deliver high performance and stability for the O₂ reduction reaction at high temperatures (1, 9-11). However, it is increasingly clear that for a commercially viable SOFC technology, the operating temperature of SOFC needs to be reduced to around 600 to 800°C in order to achieve long-term performance stability and to use cost-effective materials for the cell, interconnect and manifold components (12). Due to its low oxygen ion conductivity and high activation energy, LSM is limited in the application of cathodes for low-temperature SOFC. Attempts have been made to improve the performance of LSM-based materials, notably in the development of LSM/YSZ composite cathodes (13-16). Herbstritt et al. (17) showed that by formation of a three-dimensional interface of screen-printed YSZ particles on the YSZ electrolyte, the cell polarization resistance and overpotential were significantly decreased. Another alternative is the development of mixed ionic and electronic conducting (MIEC) materials as cathodes such as (La,Sr)(Co,Fe)O₃ perovskites (12, 18-20). However, use of such MIEC materials requires the introduction of thin interlayer such as ceria to inhibit the formation of resistive reaction products.
between zirconia electrolyte and LSCF cathodes (21). The introduction of additional electrolyte layer increases the complexity of the cell structure, the fabrication cost and instability in the stack due to the difference in the thermal expansion coefficient.

We have shown recently that by impregnation of electrocatalytic oxide particles such as Sm-doped CeO₂ into the Ni/YSZ cermet structure, the microstructure and electrode performance of Ni/YSZ cermet anodes were significantly improved (22). Watanabe et al. (23) used an impregnation method to incorporate metal catalysts such as Pt and Ru to Sm-doped CeO₂ anodes and Sr-doped LaMnO₃ cathodes, leading to the significant reduction of the polarization losses of the electrodes. Similar effects of impregnation of Pt and Pd particles on the electrode performance have been reported by Sahibzada et al (24) on La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃ cathode. This showed that the impregnation method can be used to deposit electrocatalytic oxide phase into the LSM porous electrode structure to enhance the electrochemical performance of the cathodes without diminishing the advantages of the stability and compatibility of LSM electrode materials with YSZ electrolyte in SOFC. In this paper the electrode performance of conventional LSM electrodes with ion impregnation will be reported. The results demonstrate the feasibility of the ion impregnation method in the fabrication and development of high performance LSM-based cathodes for intermediate temperature SOFC.

EXPERIMENTAL

Electrolyte substrates were prepared from 8 mol% Y₂O₃ doped ZrO₂ powder (TZ8Y, Tosoh, Japan) by pressing, followed by firing at 1500°C for 4 hr in air. The electrolyte substrates were polished and cleaned. The substrates were ~19 mm in diameter and 0.75 mm thick.

La₀.₇₂Sr₀.₁₈MnO₃ (LSM) powder was synthesized by coprecipitation wet chemical process and coarsened at 1000°C. LSM electrode coating was applied to TZ8Y electrolytes by screen printing, followed by sintering at 1150°C for 2 hr in air. Electrode coating thickness was 30 to 50 μm, and electrode area was 0.5 cm².

The impregnation solution of 20 mol% Gd(NO₃)₃ + 80 mol% Ce(NO₃)₃ (Gd₀.₂Ce₀.₈(NO₃)₃) was prepared from Gd(NO₃)₃·6H₂O (99.9%, Aldrich) and Ce(NO₃)₃·6H₂O (99.9%, Aldrich). The metal ion concentration of the solution was 3 M. Nano-YSZ suspension solution (Nextech, USA) was also used as impregnation solution. The pH of the 3M Gd₀.₂Ce₀.₈(NO₃)₃ solutions was ~3. In general, ion impregnation of the electrode coating was carried out by placing a drop of the solution on top of the coating and letting the solution soak into the cathode coating in open air. Then, the surface of the electrode coating was wiped with soft tissue and dried in open air. The sample was fired at 850°C in air for 1 hr before the testing. After the heat treatment the above nitrate salt solutions would be expected to decompose to Gd₀.₂Ce₀.₈O₂ oxide phase. The weight of the electrode coating before and after the impregnation treatment was measured to estimate the impregnated oxide loading. The Gd₀.₂Ce₀.₈O₂ oxide loading of the electrode coating was estimated to be 1–2 mg cm⁻² after one impregnation and 3-5 mg cm⁻² after three consecutive impregnation processes. Figure 1 shows schematic diagram of the ion impregnation process.

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Pt paste (Ferro Corporation, USA) was painted on to the opposite side of the working electrode to make counter and reference electrodes. The counter electrode was symmetrical to the working electrode, and a reference electrode was painted as a ring around the counter electrode. The gap between the counter and reference electrodes was ~4 mm. Pt mesh was used as a current collector for both working and counter electrodes, and two Pt wires were spot-welded to the current collector separately as current and voltage probes. The electrode performance of LSM with and without ion impregnation was measured in air at temperatures of 700°C to 850°C in a three-electrode arrangement, using galvanostatic current interruption (GCI) and electrochemical impedance spectroscopy (EIS). Overpotential ($\eta$) and electrode ohmic resistance ($R_O$) values were obtained from the current interruption transient curves. EIS was performed at open circuit using an Autolab electrochemical impedance analyzer (PGSTAT30). The impedance measurement was in the frequency range of 0.1 Hz to 100 kHz with signal amplitude of 10 mV. The electrode interface (polarization) resistance ($R_E$) was directly measured from the impedance curves.

RESULTS AND DISCUSSION

Figure 2 shows the initial impedance curves of LSM electrode with and without ion impregnation treatment of 3-M Gd0.2Ce0.8(NO3)4 under a cathodic current density of 200 mAcm$^{-2}$ at 850°C in air. The LSM electrode without ion impregnation treatment shows the same initial behavior as those observed on the freshly prepared LSM electrodes (5,25). Before passing cathodic current, the initial electrode behavior was characterized by high-electrode polarization resistance ($R_E$ was 7.7 $\Omega$cm$^2$) and $R_E$ decreased rapidly with the cathodic current passage. The activation effect of the cathodic current passage on the initial polarization behavior of the LSM electrode is most likely related to the presence of surface species such as SrO$_2$ and MnO$_2$ enriched at the LSM electrode surface and the morphological change induced by the cathodic polarization (4,25).

Very different than pure LSM electrode, impedance responses of the LSM electrode for the O$_2$ reduction after the ion impregnation with 3-M Gd0.2Ce0.8(NO3)4 were essentially independent of the cathodic current passage. Such initial electrode behavior was in fact very similar to that observed on mixed ionic and electronic conducting (La,Sr)(Co,Fe)O$_3$ (LSCF) electrodes (18). Clearly, the activation effect of the cathodic current passage is no longer effective on the LSM electrodes after the ion impregnation with 3-M Gd0.2Ce0.8(NO3)4 solutions. Electrode polarization resistance for the impregnated LSM was 0.5$\Omega$cm$^2$, which is much smaller than 7.7 $\Omega$cm$^2$ of the LSM with no impregnation.
This indicates significant improvement in the electrode performance of LSM with 3-M Gd$_{0.2}$Ce$_{0.8}$(NO$_3$)$_x$ impregnation treatment.

Figure 2. Initial impedance responses of LSM electrode (a) without and (b) with 3M Gd$_{0.2}$Ce$_{0.8}$(NO$_3$)$_x$ impregnation.

Figure 3 shows the impedance Bode plots of the O$_2$ reduction on LSM electrodes with and without 3-M Gd$_{0.2}$Ce$_{0.8}$(NO$_3$)$_x$ ion impregnation treatment at different temperatures. It appears that the characteristics of the electrode behavior also change. For pure LSM electrode, two impedance peaks were clearly visible, indicating that the electrode process of O$_2$ reduction is at least limited by two steps (8, 26). After the ion impregnation with 3-M Gd$_{0.2}$Ce$_{0.8}$(NO$_3$)$_x$ only one impedance peak was visible, which shifted with the temperature (b). The impedance behavior is similar to that observed for the mixed ionic and electronic conducting (LaSr)(CoFe)O$_3$ (LSCF) electrodes (18). From the activation energy plots of the electrode interface conductance ($\sigma$ is the reciprocal of electrode interface resistance R$_\sigma$) of the LSM cathodes with and without 3-M Gd$_{0.2}$Ce$_{0.8}$(NO$_3$)$_x$ ion impregnation treatment, the activation energy for the reaction on pure LSM electrode was 180 kJ mol$^{-1}$, while for the LSM electrode with ion impregnation it was 156 kJ mol$^{-1}$ close to 154 kJ mol$^{-1}$ reported for LSCF electrodes (18). The results indicate that ion impregnation with an ionic conducting phase such as Gd$_{0.2}$Ce$_{0.8}$(NO$_3$)$_x$ not only enhanced the electrocatalytic activity of LSM electrode but also affected the reaction process.

Figure 4 shows initial impedance curves measured on an LSM electrode after ion impregnation treatment of nano-sized YSZ suspension solution at 850°C under cathodic current density of 200 mA cm$^{-2}$. The behavior of the electrode fell somewhere between that of the pure LSM electrode and the LSM electrode impregnated with 3-M Gd$_{0.1}$Ce$_{0.9}$(NO$_3$)$_x$ solution. There were still some improvements in the electrode polarization resistance and polarization potentials with the cathodic current passage. However, the improvement in the electrode performance is much smaller than that of the
pure LSM electrode, indicating that the activation effect of the cathodic current passage on the electrode performance of LSM with nano-sized YSZ suspension solution is very small. The change in the high frequency intercept of the impedance curves may be due to the change in the contact in the cell testing. The activation energy for the reaction on

![Figure 3. Bode plots of impedance spectra of O_2 reduction on LSM electrodes with and without ion impregnation at different temperatures and open circuit.](image)

![Figure 4. Initial impedance curves of an LSM electrode after impregnation with nano-YSZ solution measured at 850°C in air.](image)
LSM electrode after ion impregnation with nano-sized YSZ suspension solution was 167 kJmol\(^{-1}\), which is between that for the reaction on pure LSM and on LSM impregnated with 3M \(\text{Gd}_{0.1}\text{Ce}_{0.9}(\text{NO}_3)_x\).

Figure 5 shows the polarization performance of LSM without and with ion impregnation at 700°C in air. In the figure, LSM-1GDC represents LSM electrode after one 3-M \(\text{Gd}_{0.1}\text{Ce}_{0.9}(\text{NO}_3)_x\) impregnation treatment and LSM-3GDC represents LSM electrode after three consecutive 3-M \(\text{Gd}_{0.1}\text{Ce}_{0.9}(\text{NO}_3)_x\) impregnation treatments. For comparison, the polarization performance of LSM/YSZ composite electrodes and LSCF electrodes taken from literature (13,15,18,27) is also given in the figure. The improvement of the electrode performance of LSM after ion impregnation is substantial. At 700°C, electrode interface conductivity \(\sigma_E\) of pure LSM electrode was 0.038 S cm\(^{-2}\), while for LSM electrode with three consecutive 3-M \(\text{Gd}_{0.1}\text{Ce}_{0.9}(\text{NO}_3)_x\) impregnation treatments (LSM-3GDC) \(\sigma_E\) was 1.4 S cm\(^{-2}\), an 36X increase in electrode interface conductivity. For LSM electrode with no ion impregnation, the overpotential \(\eta\) was 0.791 V at 700°C and 300 mA cm\(^{-2}\). On LSM-1GDC electrode, \(\eta\) was reduced to 0.35 V and on LSM-3GDC electrode \(\eta\) was decreased to 0.2 V at 700°C and 300 mA cm\(^{-2}\), a reduction of overpotential by a factor of 4 compared with pure LSM electrodes. The polarization performance of LSM with ion impregnation of nano-sized YSZ suspension solution was similar to that treated with 3-M \(\text{Gd}_{0.1}\text{Ce}_{0.9}(\text{NO}_3)_x\) solution.

For LSM/YSZ composite electrodes, the electrode conductivity \((\sigma_E = 1/R_E)\) at 700°C was reported in the range of 0.06 to 0.43 S cm\(^{-2}\), depending on the fabrication process and composition of the composites (13, 15, 27). Murray and Barnett (28) studied the impedance behavior of LSM/(Gd,Ce)O\(_2\) composite electrodes and the best performance was obtained for LSM (50 wt%)/GDC (50 wt%) composite electrodes on YSZ electrolyte with \(\sigma_E\) value of 0.94 S cm\(^{-2}\) at 700°C and \(\eta\) of 0.33 V at 100 mA cm\(^{-2}\) and 750°C. In comparison, \(\eta\) was 0.102 V at 100 mA cm\(^{-2}\) and 700°C, and \(\sigma_E\) was 1.4 S cm\(^{-2}\) at 700°C for LSM electrode with three consecutive 3-M \(\text{Gd}_{0.1}\text{Ce}_{0.9}(\text{NO}_3)_x\) ion impregnation treatments.
(LSM-3GDC). This indicates that Gd_{0.1}Ce_{0.9}(NO_3)_x-impregnated LSM electrodes have much higher polarization performance than LSM/YSZ and LSM/GDC composite electrodes at intermediate temperatures. The high performance of the ion impregnated LSM electrodes is most likely due to the effectiveness of the impregnation method in the distribution of the GDC particles in the LSM structure and at the electrode/electrolyte interface region. Detailed investigation of the microstructure of the ion impregnated LSM electrodes is under way. However, the performance of the ion-impregnated LSM electrodes still lower than that of LSCF electrodes, as shown in Figure 5. Nevertheless, it should be possible to improve the performance of ion impregnated LSM electrodes by optimizing the microstructure of the LSM electrodes and ion impregnation process.

CONCLUSIONS

It has been shown that ion impregnation method is very effective in enhancing the performance of LSM electrodes. In this method, very fine oxide particles such as (Y,Zr)O_2 and (Gd,Ce)O_2 were deposited and uniformly distributed into the structure of pre-fired LSM electrodes. For an LSM electrode with three consecutive 3-M Gd_{0.2}Ce_{0.8}(NO_3)_x impregnation treatments, electrode interface conductivity was increased by 36 times, and \eta at 300 mAcni^2 was reduced by 4 times compared with that of pure LSM electrodes at 700°C. LSM electrodes with 3-M Gd_{0.2}Ce_{0.8}(NO_3)_x impregnation treatment showed much higher electrode performance compared with LSM/YSZ and LSM/GDC composite electrodes reported in the literature. The similar electrode impedance behavior of ion-impregnated LSM and LSCF electrodes indicates the feasibility of forming MIEC-type electrode by modification of LSM microstructure through ion impregnation.

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