Preparation and Characteristics of LaMnO3 Thin Film Electrode on YSZ by a Vapor-Phase Process

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Dense and thin $LaMnO_3/YSZ/La_{0.85}Sr_{0.15}MnO_3$ cell was prepared by CVD-EVD process. The prepared $LaMnO_3$ film was sufficiently uniform and dense, no pore or crack was observed in the $LaMnO_3$ film. AC impedance measurements indicated that the electrode interface conductivity was linearly dependent on the electrode surface area. For dense and thin film electrode of $LaMnO_3$, oxygen electrochemical reaction proceeded predominantly at the electrode surface region.

Mixed conducting perovskite-type oxides, $LnMO_3$ (Ln : rare metal, M : transition metal) have attracted much attention in view of their applicability to cathode materials for high temperature electrochemical cells. Among them, a series of $La_{1-x}Sr_xMnO_3$ oxides ($0.0 < x < 1.0$) are currently used as cathode materials for solid oxide fuel cells (SOFCs) because of their relatively high catalytic activity for oxygen reduction and chemical stability.[1] In the mixed conducting $La_{1-x}Sr_xMnO_3$, holes and oxide ions are charge carriers.[2,3] It was reported by several researchers, however, that the oxide ion conductivity of $La_{1-x}Sr_xMnO_3$ is smaller by several orders of magnitude than its electronic conductivity.[2,3] Thus it is obscure whether oxide ion conduction in $La_{1-x}Sr_xMnO_3$ contributes to the electrode reactions or not. In order to clarify the electrochemical reaction site at $La_{1-x}Sr_xMnO_3$ cathodes, dense and thin film electrode of $La_{1-x}Sr_xMnO_3$ is very usefui as a model electrode system because of the following reasons: 1) area of the electrode surface and length of three-phase-boundary (interface of electrode, gas and electrolyte) is clearly defined; 2) diffusion length of oxide ions is also clearly defined. However preparation of dense and thin $La_{1-x}Sr_xMnO_3$ film is difficult by conventional technique such as sputter deposition,[1] slurry-coating[4] and flame-spraying[5]. As reported by A. O. Isenberg before, chemical vapor deposition (CVD) - electrochemical vapor deposition (EVD) process using metal chlorides as metal sources is a useful method for preparing dense and thin mixed conducting oxides film.[6,7] In the present study, as the first step for preparation of $La_{1-x}Sr_xMnO_3$ film electrode, we report preparation of dense and thin $LaMnO_3$ film electrode on YSZ film by the CVD-EVD process and electrochemical characteristics of the thin film electrode of $LaMnO_3$.

The schematic diagram of a cross-section of the multi-layer structure prepared in this study is shown in Figure 1. In order to prepare thin and dense $LaMnO_3$ film on YSZ by the EVD method, the YSZ has to be made into dense and thin film, because electron diffusion in the YSZ or oxide ion diffusion in the growing $LaMnO_3$ is rate limiting step in the EVD process of $LaMnO_3$ film deposition.

The porous $La_{0.85}Sr_{0.15}MnO_3$ substrates was prepared by a conventional solid state reaction method. The $La_{0.85}Sr_{0.15}MnO_3$ powder and polyethylene glycol (2 wt%) were mixed and pressed into a pellet which was then sintered in air at 1573 K for 48 h. The apparent densities of the porous substrates were in the range of 75 to 80% of the theoretical.

A YSZ thin film was deposited on the $La_{0.85}Sr_{0.15}MnO_3$ substrate by the CVD-EVD method, using $ZrCl_4$ (>99% purity) and YCl_3 (>99.9% purity) vapor mixture as metal sources, and water vapor as an oxygen source. The apparatus used to carry out the CVD-EVD process was described elsewhere.[8,9] After the CVD-EVD reaction at 1273 K for 3 h, a transparent film was deposited on the porous substrate. X-ray diffraction spectrum of the deposited film showed the single-phase cubic fluorite structure. EPMA spectrum showed the film containing yttrium and zirconium. From SEM observations, the deposited YSZ film was about 7 μm thick, and neither pore nor crack was observed in the film.

On this YSZ film, a thin $LaMnO_3$ film was deposited by a vapor-phase process. As shown in Figure 1, $LaCl_3$ (>99.9% purity) and $MnCl_2$ (>99% purity) vapor mixture was supplied to the YSZ surface as metal sources, and oxygen gas humidified at room temperature was supplied to the $YSZ/La_{0.85}Sr_{0.15}MnO_3$ interface as an oxygen source. The $LaCl_3$ was heated at 1083 K and the $MnCl_2$ was at 873 K. Each vaporized chloride was supplied to the substrate using Ar gas at a rate of 50 cm^3(STP)min^{-1} as a carrier. The pressure in the reactor was maintained at $1.3X10^2$ Pa during the reaction. The vapor-phase deposition of $LaMnO_3$ was conducted at 1273 K for 3 h.

After the vapor-phase reaction, the YSZ film was covered with a thin black film. We confirmed by XRD, SEM and EPMA observations that perovskite-type $LaMnO_3$ film with the thickness of 2.9 μm was prepared on the YSZ by the vapor-phase deposition. At the surface of the $LaMnO_3$ contacting with metal chloride vapor, a thin LaOCl layer was observed although the deposition mechanism of LaOCl was not clear yet.

To increase crystallinity of the deposited $LaMnO_3$ and remove the LaOCl layer, the substrate was annealed at 1373 K in air for 5 h and then treated with diluted HClaq (7% HCl). After these treatments, XRD peaks of the $LaMnO_3$ and YSZ were observed, and no other impurity phase existed. Figure 2 shows a scanning

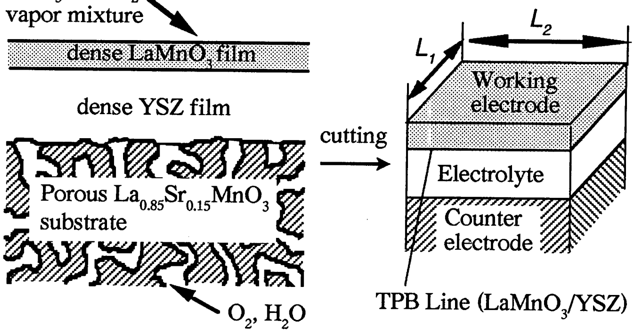

Figure 1. Schematic diagram of a vapor-phase deposition of $LaMnO_3$ on YSZ film/porous $La_{0.85}Sr_{0.15}MnO_3$ substrate.

electron micrograph of a cross-section of the deposited $LaMnO_3$ film on the YSZ film after such treatments. From this SEM image, a thin and dense $LaMnO_3$ film was uniformly deposited on the YSZ film, and no pore or crack was observed in the film at least within the scale of SEM observation. For examining chemical uniformity of the $LaMnO_3$ film, La and Mn distributions along the film thickness were observed by EPMA line analysis (Figure 2). This result indicated that La and Mn were uniformly distributed in the $LaMnO_3$ film, and the La/Mn ratio of the deposited $LaMnO_3$ film was in the range of 0.97-0.99. From these results, we concluded that dense and thin $LaMnO_3$ film is successfully prepared on thin YSZ film by the vapor-phase processes.

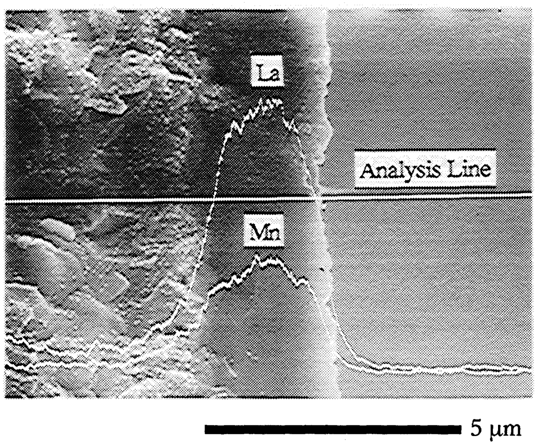

Figure 2. Scanning electron micrograph and EPMA line analysis of a cross-section of the deposited $LaMnO_3$ film /YSZ film interface.

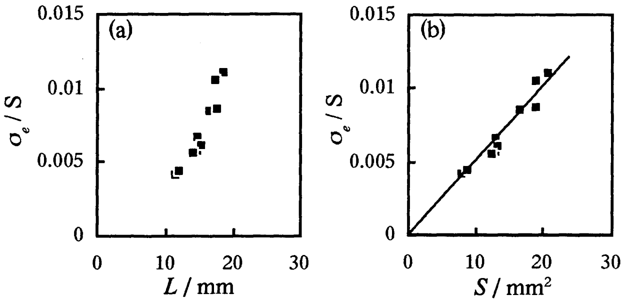

Figure 3. Dependence of electrode interface conductivity (a) on the three-phase-boundary length (*L*), and (b) on the electrode surface area (*S*).

The prepared $LaMnO_3$ film/YSZ film/porous $La_{0.85}Sr_{0.15}MnO_3$ cell was cut into rectangular pieces which were served for AC impedance measurements. The deposited dense $LaMnO_3$ film was used as a working electrode and the porous $La_{0.85}Sr_{0.15}MnO_3$ substrate was used as counter and reference electrodes because of low polarization of the counter electrode. The AC impedance analyses were performed in air at 1273K, over frequency range of 100 kHz - 1 mHz, and applied AC voltage between the $LaMnO_3$ film and porous $La_{0.85}Sr_{0.15}MnO_3$ was set to less than 10 mV.

As shown in Figure 1, the length of the three-phase-boundary ($LaMnO_3$ film/YSZ film/gas), *L*, and the apparent surface area of $LaMnO_3$ electrode, *S*, is given by

$$L = 2 \times (L_1 + L_2) \quad [1], \qquad S = (L_1 \times L_2). \quad [2]$$

AC impedance measurements were conducted for cells that had various *L* and *S*, and then electrode interface resistance R_e was obtained from the impedance plots. Inverse of R_e is defined as electrode interface conductivity, σ_e which is considered to be proportional to the electrode reaction rate.[10] Figure 3 shows the dependence of σ_e on *L* and *S* at 1273 K. The relationship between σ_e and *L* was not linear, but the σ_e increased linearly with *S*. Hence, the oxygen reduction mainly occurred at the $LaMnO_3$ electrode surface and the oxide ions can be transported through the $LaMnO_3$ film to YSZ electrolyte when the $LaMnO_3$ layer was sufficiently thin.

References and Notes

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