IMAGING AND ANALYSIS OF ACTIVE SITES FOR OXYGEN REDUCTION AT CATHODE/ELECTROLYTE INTERFACES

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ABSTRACT

Oxygen reduction active sites were visualized and analyzed around the O₂/cathode/ytrria-stabilized zirconia (YSZ) electrolyte interfaces by isotope oxygen exchange (¹⁶O/¹⁸O exchange) and secondary ion mass spectrometry (SIMS) analysis. The mesh shaped LaMnO₃ and Au cathodes were fabricated to determine the contact at the O₂/cathode/YSZ interface (TPB) precisely. The ¹⁸O SIMS images of the mesh cathode surface showed a higher concentration than those of the YSZ substrate, which indicated the promotion of oxygen surface exchange on the cathodes. Although ¹⁸O could diffuse into the LaMnO₃ bulk to some extent, it could not diffuse into Au cathode. A mesh shaped ¹⁸O image was observed on the YSZ surface, which indicated the promotion of oxygen incorporation at the LaMnO₃/YSZ interface. On the other hand, the Au/YSZ interface was inactive for oxygen incorporation. The microstructure change at the LaMnO₃/YSZ interface was significant, whereas no change was observed at the Au/YSZ interface.

INTRODUCTION

Around the O₂/cathode/electrolyte interfaces (three phase boundaries, TPB) in solid oxide fuel cells (SOFCs), oxygen reduction can occur with an incorporation of oxygen molecules into the solid materials. In order to improve the cathode performances, the reaction mechanism must be clarified with respect to transports of oxygen around the O₂/cathode/electrolyte interfaces. So far, a number of analyses have been reported about the oxygen reduction mechanism by the electrochemical measurements with using porous LaMnO₃ cathodes (1-8), dense LaMnO₃ layers (9-12), and LaMnO₃ mesh cathode (13) on the Yttria-Stabilized Zirconia (YSZ) electrolyte. These conventional electrochemical measurements are based on the observation of electronic movements, and they are sometimes very complicated to analyze the movements of oxygen. On the
other hand, it is important to analyze the movements of oxygen around the 
O2/cathode/electrolyte interface for designing the optimum cathode/electrolyte interface 
structure (such as oxygen surface exchange and diffusion of oxygen in solid materials).

In order to visualize and analyze the movements of oxygen directly, we have 
adopted the isotope oxygen exchange (16O/18O exchange) technique and the SIMS 
analysis for the quenched samples (14-19). This analytical technique succeeded in 
determining the active sites for oxygen reduction and visualizing those active sites at the 
LaMnOx mesh/YSZ interfaces. However, the effects of cathode materials remain to be 
clarified on the transports of oxygen (the adsorption, the diffusion, and the incorporation 
of oxygen) around the O2/cathode/YSZ, TPB interfaces. In this report, the transports of 
oxygen are compared between the mesh shaped LaMnOx cathode and Au (gold) cathode 
on YSZ electrolyte. The difference of the movements of oxygen at the surface, in the 
cathode bulk, and around the cathode/YSZ interface will be discussed on the basis of 
SIMS images. In addition, the morphological change around the mesh 
cathodes/electrolyte interface will be discussed.

**EXPERIMENTAL**

**Samples**

Powders of La0.8Sr0.2MnO3 (LSM) were prepared by mixing appropriate 
amounts of La2O3, SrCO3, and MnCO3. The mixed powders were fired at 1273 K for 5 h 
in air. Obtained powders were in a single phase confirmed by X-ray powder diffraction 
(13). A La0.8Sr0.2MnO3 (LSM) dense film was fabricated by RF-sputtering technique on a 
sintered 8 mol% Y2O3 stabilized ZrO2 (YSZ) pellet (polycrystal or single crystal). During 
the RF-sputtering, the total pressure was about 10⁻³ Pa in a chamber, and the substrate 
was heated at 973 K. A mesh-shaped LSM cathode was fabricated by photolithography 
with Ga⁺ ion etching technique (13). Figure 1a shows a SEM image of the LSM mesh on 
the YSZ electrolyte. The width and the thickness of the LSM mesh parts are about 2 µm 
and 0.5 µm, respectively.

An Au-mesh electrode on YSZ was prepared by putting a grid mesh (JEOL 
Datum, 400 mesh) on a single crystal YSZ. The Au-mesh/YSZ samples were heated at 
1283 K for 2 h to be attached. Figure 1b shows an optical microscope image of the 
Au-mesh/YSZ sample observed from the YSZ substrate side. As shown in Fig.1b, the 
contact interface is well defined between the Au mesh and the YSZ substrate.

**Isotope Oxygen Exchange (16O/18O Exchange Experiments)**

Figure 2 shows a schematic diagram of cathodic polarization process with 
isotope oxygen exchange (16O/18O exchange in Fig.2a) and a schematic diagram of the 
16O/18O exchange-circulation system (Fig.2b). A platinum (Pt) wire was attached to the 
mesh electrode as a current collector. The reference electrode (R, Pt wire) was attached to 
the side of the YSZ electrolyte. The counter electrode (C, Pt paste) was made on the 
opposite side of the mesh electrode. Under a cathodic polarized condition, the mesh 
cathode/YSZ samples were initially annealed at 973 K in 16O2 atmosphere for more than 
1 h at a pressure of about 0.1 bar, and then the atmosphere was quickly switched to 18O2 
at the same oxygen partial pressure. The 16O/18O exchange was performed for 600 s 
under a cathodic polarized condition at the same total oxygen partial pressure. The
samples were quenched from 973 K to 298 K within 30 s by flowing the N$_2$ gas to the quartz-glass sample chamber.

**SIMS Analysis**

After the $^{16}$O/$^{18}$O exchange, the samples were analyzed by secondary ion mass spectrometry (SIMS, ims-5f, CAMECA) in its imaging mode or depth profile mode. The SIMS imaging measurement was made over the mesh cathode/YSZ surface or over the YSZ surface after removing the mesh cathode. A finely focused primary Cs$^+$ beam (ca. 0.2-0.3 μm in diameter) was scanned on the surface of the mesh cathode/YSZ or the YSZ. The measured secondary ions were $^{16}$O', $^{18}$O', La$^{16}$O', Mn$^{16}$O', Y$^{16}$O', Au', and Zr$^{16}$O'.

**RESULTS AND DISCUSSION**

**SIMS Images of the Mesh Cathode/YSZ Surface Under Cathodic Polarization**

Figure 3 shows examples of SIMS images over the mesh cathode/YSZ samples after the $^{16}$O/$^{18}$O exchange under the cathodic polarization. The whiter color in these images indicates the higher secondary ion signal counts (the higher concentration of respective secondary ion). The applied cathodic voltage was set at about -0.4 V against the reference electrode (cathodic polarization is about -0.35 V). Fig.3a and Fig.3b show the secondary ion images at the top surface layer for the mesh LSM/YSZ and the mesh Au/YSZ ($^{16}$O' & $^{18}$O'), respectively. It is clear that the higher $^{18}$O' concentration is observed both on the mesh cathode surfaces. This suggests the promotion of oxygen surface exchange on the mesh cathodes, regardless of the cathode materials. After SIMS sputtering over the mesh cathode/YSZ surface for 1 min. (sputtering depth is about 10-50 nm), the images of $^{16}$O' and $^{18}$O' were observed again over the mesh cathode/YSZ (Fig.4). The SIMS images show different concentration between LSM (Fig.4a) and Au (Fig.4b). Although the higher $^{18}$O' concentration is observed again just below the top surface layer of the LSM mesh, the lower $^{18}$O' concentration is observed below the Au mesh surface. This may have originated from the difference in the adsorption and diffusivity of oxygen around the cathode surface. Although oxygen can diffuse into LSM via the oxygen vacancies, it can not diffuse into Au under cathodic polarization.

**SIMS Images of $^{18}$O' on the YSZ Surface Under Cathodic Polarization**

After removing the mesh cathodes on the YSZ electrolyte with HCl and aqua regia, SIMS imaging analysis was made again on the YSZ surface to determine the active sites for oxygen incorporation. Figure 5 shows examples of SIMS images of $^{16}$O' and $^{18}$O' on YSZ surface after removing the LSM mesh and Au mesh cathodes. In Fig.5a, high concentration of $^{18}$O' is observed at the contact parts of LSM/YSZ with a shape of the mesh. This indicates that the LSM mesh/YSZ contact interface is more active for oxygen incorporation than the other parts on the YSZ surface. Many spots of high $^{18}$O' concentration are observed on the YSZ surface, which correspond to the pathways of oxygen diffusion from the LSM mesh to YSZ under the cathodic polarization. In addition, the O$_2$/LSM/YSZ (TPB) interface is one of the highest $^{18}$O' concentration (14, 17) on YSZ. Thus, the TPB area is one of the most active sites for oxygen incorporation. Furthermore, this SIMS image suggests that the oxygen diffusion inside LSM cathode...
can affect the distribution of active sites for oxygen incorporation on YSZ surface.

The YSZ surface after removing the Au mesh electrode (Fig.5b) shows distinct high \(^{18}O^+\) concentration lines at the edge of the mesh, with a low intensity of \(^{18}O^+\) at the Au mesh/YSZ interface. This indicates the oxygen blocking at the Au mesh/YSZ contact interfaces and oxygen can only incorporate into YSZ at the \(O_2/Au/YSZ\) three phase boundaries (TPB). The higher \(^{18}O^+\) concentration parts are limited to the edge parts of Au-mesh/YSZ within a few \(\mu m\). Therefore, the active sites do not expand so much from the TPB to the outside or the inside of Au mesh cathode on YSZ surface, contrary to the LSM mesh/YSZ samples. These figures clearly indicate the effects of electrode materials on the distribution of oxygen reduction active sites at the cathode/YSZ interfaces.

### Morphological Change at the Cathode/Electrolyte Interface

In the previous section, we have shown the distribution of active sites for oxygen incorporation on the YSZ surface. Especially at the LSM/YSZ interface, the active sites for oxygen incorporation are distributed in many spots. This can be related to the change of the interface morphology of cathode/YSZ, which was affected by the cation diffusion between LSM and YSZ (19). Figure 6 shows scanning electron microscopy (SEM) and optical microscope images of the YSZ surface after removing the LSM mesh and Au mesh cathodes. The interface between LSM and YSZ changed in its morphology (Fig.6b). This is due to the cation diffusion associated with grain growth of LSM (19). The Mn dissolution occurred only at the LSM/YSZ/LSM triple phase junction, not at the LSM/YSZ two-phase boundary. As a result, as the triple phase junction, YSZ volume expanded towards the LSM/LSM boundaries. These parts correspond to the convex parts of YSZ in Fig6b and also correspond to hot spots in Fig.5a. After the cathode polarization experiment, the convex parts of YSZ disappeared to form the flat surface of YSZ under the LSM cathode area. In addition, small pores were created over the YSZ surface with and without cathodes.

In contrast to the LaMnO\(_3\) cathode, the YSZ surface after removing the Au-mesh is very smooth (Fig.6d). Almost no cation interdiffusion is observed between Au-mesh and YSZ substrate, without any morphological change on the YSZ surface.

### CONCLUSIONS

Oxygen transports were imaged and analyzed by the \(^{16}O/^{18}O\) exchange technique with secondary ion mass spectrometry (SIMS) analysis. Mesh shaped cathodes (LaMnO\(_3\) and Au) were fabricated on the YSZ electrolyte to determine the cathode/YSZ electrolyte interfaces precisely. The oxygen transports were compared between the LaMnO\(_3\) mesh and the Au mesh cathodes under the cathodic polarization. The \(^{18}O^+\) concentration of the mesh cathode surface was higher than that of YSZ, which indicated the promotion of oxygen exchange on the cathode surface. Although \(^{18}O\) could diffuse into the LaMnO\(_3\) bulk to some extent, it could not diffuse into Au cathode. This suggested a difference in the diffusivity of oxygen in the cathode bulk. The active sites for oxygen incorporation at the cathodes/YSZ interface were analyzed on the YSZ surface after removing the mesh cathodes. The LaMnO\(_3\)/YSZ interface was the active site for oxygen incorporation, whereas the Au/YSZ interface was inactive for oxygen incorporation. The \(O_2/cathode/YSZ\) (TPB) interfaces of both mesh cathodes were the most active for oxygen incorporation. The microstructure change at the LaMnO\(_3\)/YSZ
interface was significant, whereas no change was observed at the Au/YSZ interface. This change had a relation with cation diffusion at the interface.

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Fig. 1 Microstructures of the mesh cathodes on yttria-stabilized zirconia. (a): Scanning electron microscope image of La$_{0.9}$Sr$_{0.1}$MnO$_3$ mesh and (b): Optical microscope image of Au mesh.

Fig. 2 Schematic drawing of the $^{16}$O/$^{18}$O exchange experiment. (a): Schematic drawing of cathodic polarization and (b): Schematic drawing of the closed $^{16}$O/$^{18}$O exchange gas circulation system.
Fig. 3 SIMS images \( (^{16}\text{O}^- \text{ and } ^{18}\text{O}^-) \) of mesh cathodes on YSZ electrolyte at the top surface. (a): La\(_{0.9}\)Sr\(_{0.1}\)MnO\(_3\) mesh/YSZ, (b): Au mesh/YSZ.

Fig. 4 SIMS images \( (^{16}\text{O}^- \text{ and } ^{18}\text{O}^-) \) of mesh cathodes on YSZ electrolyte near surface after sputtering 1 min (Sputtered depth, about 10-50 nm). (a): La\(_{0.9}\)Sr\(_{0.1}\)MnO\(_3\) mesh/YSZ, (b): Au mesh/YSZ.
Fig. 5 SIMS images of $^{16}\text{O}^-$ and $^{18}\text{O}^-$ for YSZ surface after removing the mesh cathodes. (a): LSM mesh/YSZ, (b): Au mesh/YSZ.

Fig. 6 SEM images of LSM mesh/YSZ and optical images of Au mesh/YSZ before and after removing the mesh cathodes. (a): LSM mesh/YSZ, (b): YSZ surface after removing the LSM mesh. (c): Au mesh image, (d): YSZ surface after removing the Au mesh.