SIMS Measurement of the Deuterium Ion Diffusion in $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ Proton Conductor

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The diffusion of deuterium ions in the polycrystalline $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ proton conductor was investigated using a high resolution SIMS. A rectangular block ($12 \times 12 \times 2\text{mm}$) of the oxide was thermally treated in a D_2O atmosphere and quenched. Then a SIMS sample ($12 \times 1 \times 2\text{mm}$) was cut out from the block. The mass spectrum of the D_2O treated sample was compared with that of H_2O treated sample. The secondary ions of $M/e=2$ and 20 were observed, however, the ions of $M/e=21$ and 22 which were expected as OHD_2^+ and OD_3^+ were not detected with the D_2O treated sample. The gradient of the ion intensities of $M/e=2$ and 20 could be observed when the oxide block was exposed to a D_2O vapor for a short time of 150 s at 575°C . A theoretical curve of one dimensional diffusion was fitted to the measured depth profile of the ion intensities. The obtained diffusion coefficient of the deuterium ion was $8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 575°C .

1 INTRODUCTION

The perovskite-type oxide of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ exhibits proton conduction at high temperature in a hydrogen or water containing atmosphere¹⁾. This material can be applied to various solid state electrochemical devices such as fuel cells, steam electrolyzers and gas sensors^{2,3)}.

The diffusion coefficient of protons in this oxide has been estimated by electrochemical method^{4,5)}. It is expected that we get more precise data on the proton diffusion by using a high resolution SIMS. However, there was no report on the measurement of the proton diffusion by SIMS, because the sample preparations were disturbed by atmospheric water. Therefore, we use deuterium ions as diffusing species to avoid the interference.

In this study, we treat the samples of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ in an elevated temperature with D_2O vapor for a short period, and measure the concentration profile of the deuterium ions using a high resolution SIMS. Then the profile data are analyzed to determine the diffusion coefficient of the ions.

cient of the ions.

2 EXPERIMENTAL

The sample preparation was carried out by the same method as described in a previous paper⁶⁾. The density of the sintered disk was 5.53 g cm^{-3} (95% of the theoretical value⁷⁾). A rectangular parallelepiped block ($12 \times 12 \times 2\text{mm}$) was first cut out from the sintered disk. The oxide block was placed in a silica boat ($50 \times 15 \times 8\text{mm}$) and was inserted in a 28mm diameter vitreous silica tube in a furnace. The surfaces of the block were exposed, at an elevated temperature, to the stream of synthetic air which had been saturated with D_2O ($>99.75\%$, Wako Chemical) at room temperature. The flow rate of the air was 30 ml min^{-1} .

Fig. 1 The heat treated oxide block and the SIMS sample. The surface A was exposed to D_2O vapor, and the surface B was used for the measurement of depth profile.

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Table 1 Heat treating conditions of SIMS samples. Samples 1 and 2 were used for the mass survey measurement. Samples 3 and 4 were used for the measurement of secondary ion intensity distribution.

Sample No.	Heat treating condition
1	H ₂ O, 800°C, 4h
2	D ₂ O, 800°C, 4h
3	H ₂ O, 800°C, 4h → D ₂ O, 575°C, 150 s
4	H ₂ O, 800°C, 4h → D ₂ O, 575°C, 4h

Table 2 Typical conditions of the SIMS measurement.

Residual pressure	4×10^{-7} Torr
Primary ion species	Cs ⁺
Primary acceleration voltage	10kV
Primary current	1×10^{-8} A
Polarity of secondary ion	Negative
Raster size	$250 \times 250 \mu\text{m}$

Figure 1 shows the cutting out of a SIMS sample from the heat treated oxide block. The top plane of the sample indicated as A in the figure is the D₂O exposed surface and the side plane indicated as B was used for the measurement of depth profile. The surfaces of the sample were polished with an emery paper in a dry condition. The heat treating conditions in this study are in Table 1.

Samples 3 and 4 were treated at 800°C for 4h in the air which had been saturated with H₂O at room temperature. Then Sample 3 was heated to 575°C and exposed for a period of 150 s to the air containing D₂O, and it was rapidly cooled to room temperature by taking the silica tube out of the furnace. Sample 4 was heated in the same D₂O atmosphere for 4h. The D₂O atmosphere was maintained until the sample was cooled to room temperature.

Gold layers of 75nm thickness were deposited on the surfaces of the samples by sputtering to prevent the charging up during the SIMS measurement. The measurement was made using an ion micro analyzer (CAM-ECA IMS-4F). Typical conditions for the SIMS measurement are in Table 2. The secondary ion intensities

of $M/e=2$, 18, 20 and 32 were initially monitored as the sample were sputtered by the primary ions. Then, after the values became stable, the intensities of these ion species were recorded. In order to compare the ion intensity data among the different samples, each value of measured intensity was normalized by that of O₂⁻ ($M/e=32$). Each plot in the depth profiles represents the averaged value over 50 scans.

3 RESULTS AND DISCUSSION

The results of mass survey measurement of Samples 1 and 2 are shown in Fig. 2. The secondary ions of $M/e=2$ and 20 appeared only when samples were heat treated in D₂O atmosphere. It is noted that the intensity of $M/e=21$ and 22 which were expected as the ion species

Fig. 2 Result of the mass survey measurement for H₂O treated (Sample 1), and D₂O treated (Sample 2).

Fig. 3 Intensity distributions of the secondary ions of $M/e=2$, 18 and 20 in Sample 3.

Fig. 4 Intensity distributions of the secondary ions of $M/e=2$, 18 and 20 in Sample 4.

of OD_2H^+ and OD_3^+ , were not observed. The secondary ion species of $M/e=20$ was not mentioned in the report of Ishigaki⁸⁾ measuring the same series of oxide samples which were heat treated in D_2O atmosphere. From these results, the diffusing deuterium ions in polycrystalline $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\sigma}$ can be detected by SIMS measurement as secondary species of $M/e=2$ and 20.

Figure 3 shows the depth profiles of the ion intensities of $M/e=2$, 18 and 20 measured with Sample 3. The values of intensity for $M/e=2$ and 20 reduce with the distance from the surface, however, the intensity of $M/e=18$ is constant. The depth profiles of these ion species for Sample 4 are shown in Fig. 4. The uniform

Fig. 5 The theoretical curve of Eq. 1 with $D=8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, fitting to the depth profile data of $M/e=2$ and 20 in Figs. 3 and 4.

distribution of the ion intensities indicates that the sample was saturated with deuterium ions when it was heated at 575°C for 4h in the D_2O atmosphere.

The calculation of the diffusion coefficient of the deuterium ion was carried out using the Fick's second law. The diffusion can be treated as one-dimensional system. The diffusion coefficient D was obtained using the following equation⁹⁾:

$$\frac{C-C_0}{C_1-C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \times \exp\{-D(2n+1)^2 \pi^2 t / 4l^2\} \cos \frac{(2n+1)\pi x}{2l} \quad (1)$$

where C is the concentration at x , C_0 is initial concentration, C_1 is the concentration at the surface, x is the distance from the center of sample, t is diffusion time and l is a half of the thickness of sample. In Fig. 5, the theoretical curve of Eq. 1 was fitted to the experimental data of $M/e=2$ and 20. The data in Figs. 3 and 4 were used in the fitting in the regions of the inside and the surface of the sample, respectively. The obtained diffusion coefficient of deuterium ion was $8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. This value is slightly larger than the reported value from Uchida *et al.*⁴⁾ and is slightly smaller than that from Fukatsu *et al.*¹⁰⁾. It should be noted that the diffusion coefficient of deuterium ion in this oxide is extremely larger than that of oxide ion in YSZ ¹¹⁾ at the same temperature.

4 CONCLUSIONS

The diffusion properties of deuterium ion in polycrystalline $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ proton conductor have been investigated using a high resolution SIMS.

(1) When the mass spectrum of D_2O treated samples was compared with that of H_2O treated samples, the secondary ions of $M/e=2$ and 20 were observed and the ions of $M/e=21$ and 22 which were expected as OHD_2^+ and OD_3^+ were not observed.

(2) The concentration gradient of the deuterium ion could be observed when the sample was exposed to a D_2O atmosphere for a short time of 150 s at 575°C .

(3) Using the concentration profile data, the diffusion coefficient of the deuterium ions at that temperature was calculated as $8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

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