

HYDROGEN ABSORPTION OF ION-IRRADIATED PROTON CONDUCTING OXIDE CERAMICS

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Introduction

Development of a hydrogen-air fuel cell which consists of proton conducting oxides as a solid electrolyte and hydrogen storage metals as a hydrogen source have been proposed recently¹. This closed-type fuel cell, making unnecessary the supply of hydrogen gas from outside, is promising as compact electric-power generating system satisfying the increasing ecological demands.

The hydrogen transport from the hydrogen storage metal to the proton conducting oxide is one of the most significant points for the closed-type fuel cell. Moreover, it is necessary to be readily achievable for the application of the fuel cell at lower temperature below 573 K.

In the present study, to enhance the hydrogen absorption and transport at lower temperature, the surface modification of the proton conducting oxide ceramics were carried out with 10 keV ion irradiation. The relation between ion-irradiated oxide ceramics and hydrogen absorption from vapor was experimentally investigated at room temperature using ion beam analysis system.

Results and discussion

Specimen used in the present study were typical proton conducting oxide ceramics of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ which were perovskite-type and exhibits high protonic conductivity under hydrogen-containing atmosphere at temperature above 573 K. The dimension was $\phi 8 \times 1 \text{ mm}^3$ in size. After removing residual hydrogen atoms by heating at 873 K for 10 min in a high vacuum of $8 \times 10^{-6} \text{ Pa}$, 10 keV D_2^+ (5 keV D^+) or 10 keV He^+ ions were irradiated at normal to the specimen surface at room temperature. The flux was about $2.5 \times 10^{14} \text{ ions/cm}^2\text{s}$. The concentrations of D or He retained in the ceramics reached to the saturation at a fluence of about 1.0×10^{18} and $3.0 \times 10^{17} \text{ ions/cm}^2$, respectively. Then a little amount of D or He was spontaneously released. It has been reported in the reference² that the saturation concentration by D^+ ion implantation is $\text{D}/\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta} = 1.1$. The projected ranges of D and He were about 139 nm and 169 nm and the range stragglings of D and He were 65 and 84 nm, which were calculated using

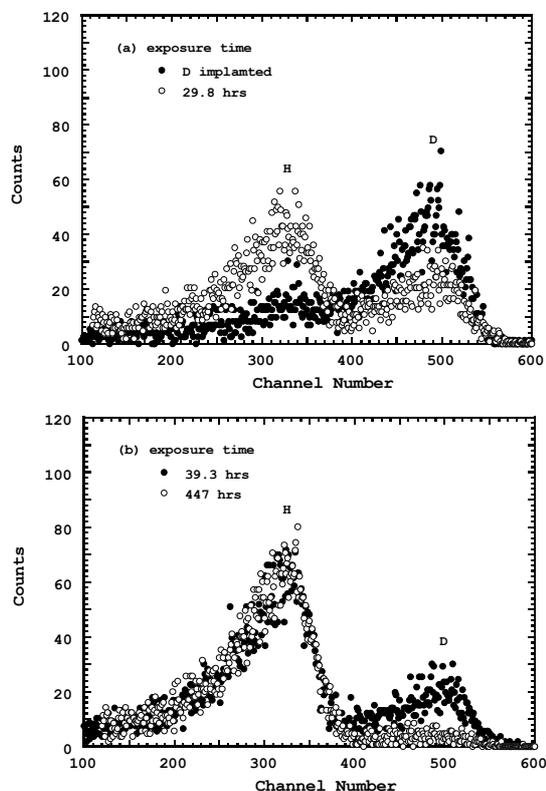


Fig. 1 ERD spectra of H and D recoiled from the ceramics after (a) D^+ ion saturation implantation and Ar gas exposure times for 29.8, (b) 39.3 and 447 hrs.

TRIM code³. Then the irradiated ceramics were exposed in 99.998 wt% Ar gas atmosphere of 1 atom, where water of about 10.98 mg/cm^2 was included. **Figs. 1(a)** and **(b)** show typical elastic recoil detection (ERD) spectra of hydrogen retained in ceramics after 10 keV D_2^+ ion irradiation and Ar gas exposure times such as 19.8, 39.2 and 447 hrs, measured using 2.8 MeV He^{2+} ion probe beam from a tandem accelerator. The vertical and horizontal axes correspond to concentrations of H or D retained and energies of H or D recoiled, respectively. The abnormal exchange of D for H was observed as D was released and H was absorbed with the increase of the exposure time. The concentrations of H and D

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(H or D/SrCe_{0.95}Yb_{0.05}O_{3-δ}) were plotted against the exposure time in Fig. 2, where the average counts over 30 channels of peak area in ERD spectra, the elastic recoil cross-sections of H and D to 2.8

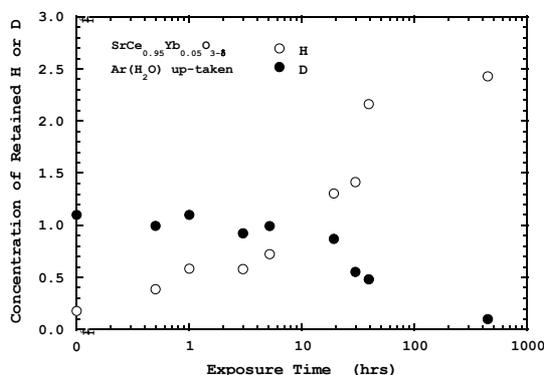
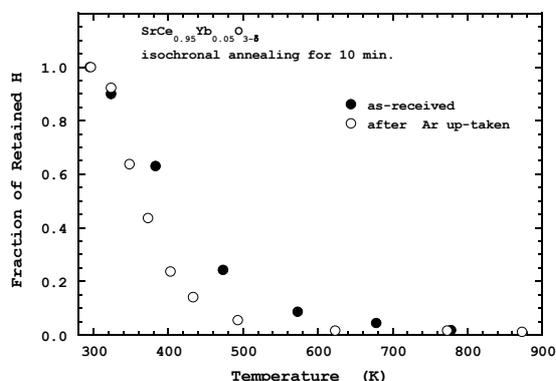


Fig. 2 Exchange of D for H against Ar gas exposure time

MeV He⁺ ion at recoil angle of 30° (300 and 450 mb/Sr)⁴ and so on were taken into account. The abnormal exchange rate became faster at the exposure time of about 30 hrs and hereafter later for further time. The concentration of H absorbed at the exposure time of 447 hours was about twice as much as that after the saturation implantation of D. The interesting results show the increase of activated trapping sites by the ion bombardment. It is assumed that the absorption of H is induced due



to dissociative adsorption of H₂O at the ceramics

Fig. 3 Isochronal annealing at several temperatures for 10 min for as-received and Ar up-taken specimens

surface and diffusion. D is released with the molecular formation of HD by combining with H diffused.

Fig. 3 shows results of isochronal annealing measurements at temperatures of 296–873 K for 10 min after Ar up-taken, as compared with that of as-received specimen. The re-emission rate after Ar up-taken is faster than that for as-received. The result indicates that H₂O or H trapped at new activated trapping sites produced by the ion bombardments are detrapped and released easily.

Conclusions

The hydrogen absorption of the proton conducting oxide ceramics by ion bombardment has been investigated using ion beam analysis systems. The oxide ceramics irradiated with 10 keV D₂⁺ or He⁺ ions at room temperature were exposed in the Ar gas atmosphere with vapor. The concentration of hydrogen absorbed in the ceramics increased with increasing the exposure time, because the hydrogen atoms dissociated from water adsorbed on the ceramics surface and were trapped into activated vacancy through the diffusion. Moreover, the concentration became higher than the saturation concentration by hydrogen ions implantation.

References

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