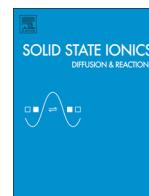




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## Hydrogen solubility and diffusivity in a barium cerate protonic conductor using tritium imaging plate technique

K. Yamashita, T. Otsuka, K. Hashizume\*

Interdisciplinary Graduate School of Engineering Science, Kyushu Univ., Kasuga, Japan

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### ABSTRACT

A tritium imaging plate technique has been applied to visualize hydrogen distribution and examine hydrogen solubility and diffusivity in a proton-conducting oxide, Y-doped BaCeO<sub>3</sub> (BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-α</sub>). Tritium charging of the BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-α</sub> specimens was carried out by a gas absorption method using partially tritiated water vapor (HTO, 3 kPa, T/H ~ 10<sup>-6</sup>) at temperatures ranging from 673 K to 873 K for a given time. After charging, tritium distributions of the surface and cross section of the halved specimens were visualized using an imaging plate technique. From the tritium concentration and distributions of the surface and cross section, hydrogen solubility and hydrogen (tritium) diffusivity of the BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-α</sub> specimens were determined.

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### 1. Introduction

Perovskite-type oxides have received much attention as good protonic conductors under a hydrogen-containing atmosphere at elevated temperatures. These proton-conducting ceramics have been expected to be used as solid electrolytes for various electrochemical devices such as a fuel cells, hydrogen sensors, and hydrogen pumps [1–7].

To date, hydrogen solubility and diffusivity in oxide ceramics have been reported by many investigators using several experimental techniques such as conductivity measurement and thermal analysis (TG-DTA); i.e. hydrogen solubility was first measured by thermal analysis, followed by calculation of diffusivity from the solubility and conductivity data. Although this is a commonly used method, it is not a direct measurement of proton migration; therefore, the proton diffusivity measurement can be affected by other electric carriers in the conductivity measurement and experimental errors of hydrogen solubility in thermal analysis. Alternatively, ion beam microanalysis (SIMS, ERDA and NRA) [8,9] can allow for the measurement of hydrogen solubility and diffusivity directly. Although these methods have superior space resolution of hydrogen in the depth direction at a localized position, the information is generally limited near the surface of the protonic conductors. Therefore, two-dimensional distribution of hydrogen cannot be obtained directly.

The tritium imaging plate (TIP) technique uses tritium as a radioactive tracer to directly assess hydrogen solubility and diffusivity from

visualized tritium distribution in tritium-dissolved materials. The imaging plate (IP) technique was originally used in biological and medical fields to measure two-dimensional radioisotope distribution and recently its applications have extended to materials and energy sciences [9–12]. However, this technique has seldom been applied to proton-conducting materials such as the perovskite type oxides.

In this paper, we report the experimental results of the visualization of hydrogen distribution in BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-α</sub>, which is a well-known perovskite-type protonic conductor, by using the TIP technique. Based on these results, hydrogen solubility and diffusivity were determined for the oxide.

### 2. Experimental

#### 2.1. Sample preparation and exposure to HTO vapor

The BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-α</sub> powder (TYK Co.) was die-pressed into a cylindrical shape under 200 MPa of isostatic-pressure and sintered at 1873 K for 5 h. The densities of the sintered pellets were greater than 98% of the theoretical density. The black surface layers were removed with an abrasive paper. The pellets were 7 mm in diameter and 2 mm in thickness.

Fig. 1 shows the experimental apparatus. Using this apparatus, the BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-α</sub> specimens were vacuum annealed at 973 K for 1 h, followed by exposure to ca. 3 kPa of partially tritiated water vapor (HTO, T/H ~ 10<sup>-6</sup>) at 673–873 K for 5–60 min. After the exposure experiment, the specimens were cooled down to room temperature. To measure the inside of the specimen, its surface was slightly ground with an abrasive paper to remove adsorbed tritium, and the disk was cut in half.

\* Corresponding author at: 6-1 Kasuga-koen, Kasuga-shi, 816-8580, Japan. Tel./fax: +81 92 583 7544.

E-mail address: [hashi@nucl.kyushu-u.ac.jp](mailto:hashi@nucl.kyushu-u.ac.jp) (K. Hashizume).

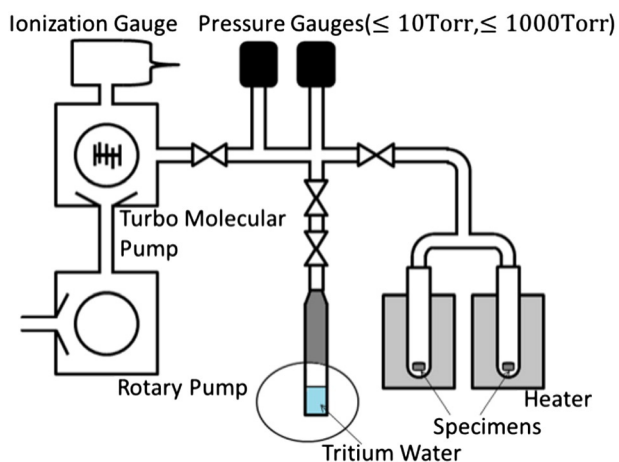


Fig. 1. Schematic of apparatus for HTO vapor exposure of specimens at elevated temperatures.

A low-speed diamond saw (Isomet™, Buehler Ltd.) was used to cut the specimens at a cutting speed of approximately 50 rpm, and IsoCut™ Fluid (Buehler Ltd.) was used as the cooling media. Once cut, the specimens were washed with acetone to remove the coolant.

## 2.2. Imaging plate technique

The tritium-charged specimens were placed on an IP in a dark box in order to expose the IP to  $\beta^-$  rays emitted from the tritium adsorbed on and dissolved in the specimen. The IP used was TR-2025 (FUJIFILM Co.), which was suitable for measuring the low energy  $\beta^-$  rays and had a wide dynamic range for the radiation energy. Considering the tritium content in the specimen, the duration of IP exposure was 3 h for the surface and 24 h for the cross section. After exposure, the IP was set in an IP Reader (BAS-2500, FUJIFILM Co.) to measure the photostimulated luminescence (PSL) intensity. The space resolution of the obtained intensity was 50  $\mu\text{m}$ . Although PSL intensity is an arbitrary unit, it is proportional to the product of the radiation energy emitted from tritium and the IP exposure time allowing for conversion of PSL intensity to hydrogen concentration in the specimen.

Tritium ( $T_{1/2} = 12.3$  y,  $\beta^-$  decay) emits low energy electrons, the maximum and mean energies of which are 18.6 and 5.7 keV, respectively and its maximum range is ca. 1  $\mu\text{m}$  in  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\alpha}$ . Therefore, the

tritium distribution obtained with the IP technique provides information about tritium existing on and up to 1  $\mu\text{m}$  from the surface.

## 3. Results and discussion

### 3.1. Visualization of hydrogen (tritium) distribution

The hydrogen (tritium) distribution in  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\alpha}$ , which was exposed to HTO vapor, was visualized using the IP technique. Fig. 2 shows the IP images of the specimen surface and its cross section at 773 K. From Fig. 2(a), it was found that hydrogen was distributed uniformly on the specimen surface. Fig. 2(b) shows the time evolution of tritium penetration into the specimen. The tritium distribution in Fig. 2(b) seemed to be rather ambiguous due to the relatively low tritium concentration in the cross section. As seen in Fig. 2(a) and (b), the PSL intensities between the surface and near-surface bulk in the cross section largely differed. The reason for this discrepancy can be derived from the tritium density on the surface and in the bulk. The TIP method is a radiation detection technique for measuring the surface and near-surface tritium. After tritium loading, the amount of tritium adsorbed on the specimen surface was much higher than that dissolved in terms of the atomic ratio of tritium (hydrogen) and ions of the specimen oxide (H/Oxide). Even in an equilibrium state, the tritium and ion ratios between the surface and near-surface bulk were very different (ca. 1/1 and 0.01/1, respectively). Moreover, the  $\beta^-$  rays emitted outside from the surface were absorbed in the IP directly, while the  $\beta^-$  rays from the bulk were absorbed by the specimen itself, even within the range of the  $\beta^-$  ray (ca. 1  $\mu\text{m}$ ). Consequently, the PSL intensity of the specimen cross section became weak, compared with that of the surface. Although the PSL intensity of the cross section was weak, it was sufficient for evaluation of diffusivity and solubility.

Fig. 2(c) shows the IP image of standard sample autoradiographic [ $^3\text{H}$ ] microscales (RPA506 and RPA507, Amersham Biosciences Co.). The  $^3\text{H}$  (tritium) activity is arranged in eight layers of polymer, the radioactivities of which range from 3.7 Bq/mg to 4070 Bq/mg. The PSL intensity was originally given as numerical data by the IP reader. The PSL intensity is proportional to the tritium activity or tritium number density over a wide range. The PSL intensities obtained from the specimen were calibrated and converted to tritium activities of the surface or bulk based on that of the standard sample. In determining the tritium activity of the specimen, the absorption and range of the  $\beta^-$  rays in the standard sample and oxide specimens were taken into consideration. Finally, we converted the tritium activity to hydrogen number density using the hydrogen isotope abundance ratio ( $T/H \sim 10^{-6}$ ).

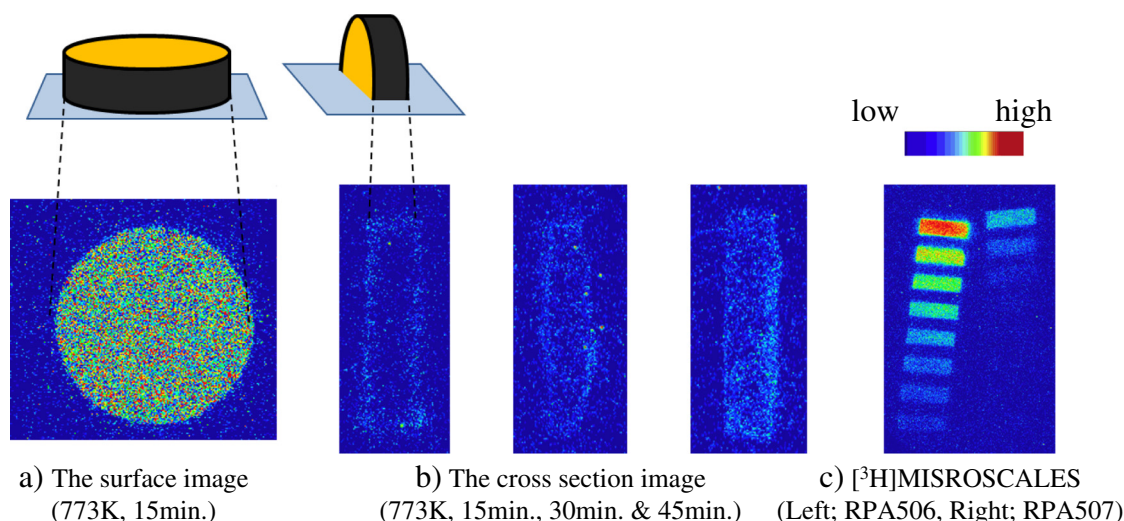


Fig. 2. IP images of (a) specimen surface, (b) cross section, and (c) autoradiographic [ $^3\text{H}$ ] microscales.

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