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Exchange Reaction of Hydrogen Isotopes on Proton Conductor Ceramic of Hydrogen Pump for Blanket Tritium Recovery System

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Electrochemical hydrogen pump using ceramic proton conductor has been investigated to discuss its application for the blanket tritium recovery system of the nuclear fusion reactor. As the series of those work, the transportation experiments of H_2-D_2 mixture via ceramic proton conductor membrane have been carried out. Then, the phenomenon that was caused by the exchange reaction between the deuterium in the ceramic and the hydrogen in the gas phase has been observed. So, the ceramic proton conductor which doped deuterium was exposed to hydrogen under the control of zero current, and the effluent gas was analyzed. It is considered that the hydrogen in the gas phase is taken as proton to the ceramic by isotope exchange reaction, and penetrates to the ceramic by diffusion with replacement of deuteron.

Keywords: fusion reactor, blanket, tritium, hydrogen pump, hydrogen sensor, isotope exchange

1. Introduction

Proton conductor ceramic is one of the functional materials applicable to a nuclear fusion reactor system. One of the use is a hydrogen sensor. When one side of the proton conductor membrane comes in contact with the reference gas and the other side comes in contact with target material (for example, sweep gas or liquid breeder), the electromotive force (EMF) is observed between membrane. From this EMF, hydrogen concentration in the target material can be known[1-5]. Kondo et al. have discussed about application of ceramic hydrogen sensor to measure hydrogen concentration in the liquid breeder material[6]. The other use is a hydrogen pump. In case of a solid breeder blanket of a nuclear fusion reactor, bred tritium is purged out by passing helium (He) based sweep gas through breeder zone of the blanket. To enhance release rate of tritium from the blanket and to decrease tritium inventory in the blanket, the dominant chemical form at the released of tritium is controlled to be HT by use of hydrogen (H_2) addition He sweep gas. As the result of using the H_2 addition sweep gas, the chemical contents of the sweep gas are expected to be H_2, HT, H_2O and HTO. So, a blanket tritium recovery system (BTR) has to separate hydrogen isotopes (HT, H_2, HTO and H_2O) from He, and send them to main fuel cycle system. The present authors have proposed to apply electrochemical hydrogen pump to BTR[7]. It can selectively extract hydrogen isotopes from the sweep gas via the proton conductor membrane. Its driving force of hydrogen transportation is not only the pressure difference, but also the electric potential difference. Therefore, it may be possible to extract hydrogen isotopes from the low hydrogen partial pressure system and from the hydrogen compound via decomposition. These advantages are suitable for BTR, and it may be possible to establish smart BTR by using hydrogen pump. So, the authors have investigated the ionic transportation properties of hydrogen isotopes[8-13].

When the author investigated the transportation properties of H_2-D_2 mixture as one of a series of those work, the phenomenon that seems to be the contribution of exchange reaction between H_2 in gas phase and D_2 in ceramic has been observed[9]. So, in this work, the mass transfer model including the isotope exchange reaction was assumed, and the author has compared the calculation with the experimental observation to evaluate the reaction rate constant.

2. Experimental

Fig.1 shows a schematic diagram of an experimental apparatus. The electrochemical hydrogen pump is a double

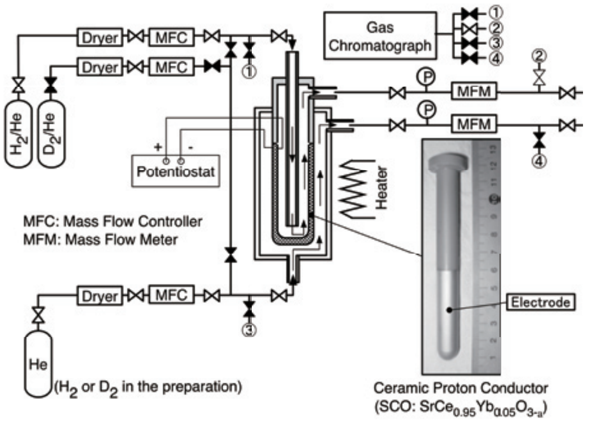

Fig.1 A schematic diagram of the experimental apparatus.

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Table 1 Experimental conditions.

Proton Conductor	$SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$	
Size (mm)	Test Tube ϕ12 x L105 x t1	
Electrode	Porous Pt inside: $17cm^2$, axial distance: 5.5cm	
	Anode (in)	Cathode (out)
Gas	HH/He or DD/He	He
Press. (kPa)	96.0–111.5	100.6–101.4
Flow Rate (l/min. STP)	0.2. 0.6	0.2
Q_2 (%)	0.0995–0.104	–
Temp. (K)	873	

pipe. The outer pipe is the quartz tube and the inner pipe is the proton conductor ceramic. When the voltage is applied between the outer and the inner surface electrode of the proton conductor ceramic tube, hydrogen transfers through the tube in spite of the chemical potential difference, and it works like a pump. The proton conductor ceramic used in this work was a strontium cerate that had added the ytterbium of 5% (SCO: $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$), and was made by TYK Co. Its shape was a test tube type (one end was closed). The size was 105mm in length, 12mm in outer diameter, and 1.0mm in thickness. The porous platinum electrodes were attached on the inside and outside surface, and its length in axial direction was 56mm from the closed end (outside).

The experiments were carried out as follows. At first, as the preparation, the deuterium (hydrogen) transportation experiment was carried out to exchange the proton (deuteron) in the ceramic to the deuteron (proton). A detailed procedure of the transportation experiment has been described in our previous report[9]. The concentrations of hydrogen isotopes used in the preparation were about 0.1% and 100%. After that, the current was controlled to be zero by using the potentiostat to prevent the ionic deuterium (hydrogen) transport. And then, the hydrogen pump was purged by He until no deuterium (hydrogen) detected in the effluent gas by gas chromatograph (GC). In this situation, hydrogen (deuterium) was introduced to the one side of the ceramic membrane of the hydrogen pump, and the effluent gas from the hydrogen pump was analyzed by the GC. Hydrogen (deuterium) concentration in the introduced gas was about 1000 ppm. Its flow rate was adjusted to become 0.2 or 0.6 l/min (S.T.P.). He gas was introduced to another side with 0.2 l/min (S.T.P.) of flow rate, however, no hydrogen isotopes were detected in the effluent gas. The experimental temperature was 873K. The experimental conditions were listed in table 1.

3. Results and Discussion

Fig.2a shows concentration changes of hydrogen isotopes in the outlet gas of the hydrogen pump. H_2/He mixture (H_2: 1002 ppm) was introduced to the hydrogen pump after the D_2 transportation experiment. The hydrogen pump was controlled to be zero in electric current when H_2 was introduced (Electromotive force measurement mode). D_2 and HD has been detected in the outlet gas at first, and their concentrations decreased with the elapsed time. In the effluent gas of the He purge side, hydrogen isotopes were not detected by the gas chromatograph. Fig.2b is same with Fig.2a, but HD has been distributed as $1/2H_2$ and $1/2D_2$ to H_2 and D_2, respectively. The amount of D_2 released from the hydrogen pump was calculated from the release curve and it was 2.6 x 10^{-4} mol-D_2, and the amount of H_2 taken to the ceramic was also calculated to 3.0 x 10^{-4} mol-H_2 in this case. The release curve of H_2 and that of D_2 seem to be symmetry. During He purge, hydrogen isotopes have not been detected in the effluent gas. So, the present author considered that the most of D_2 has been released by isotope exchange reaction with H_2.

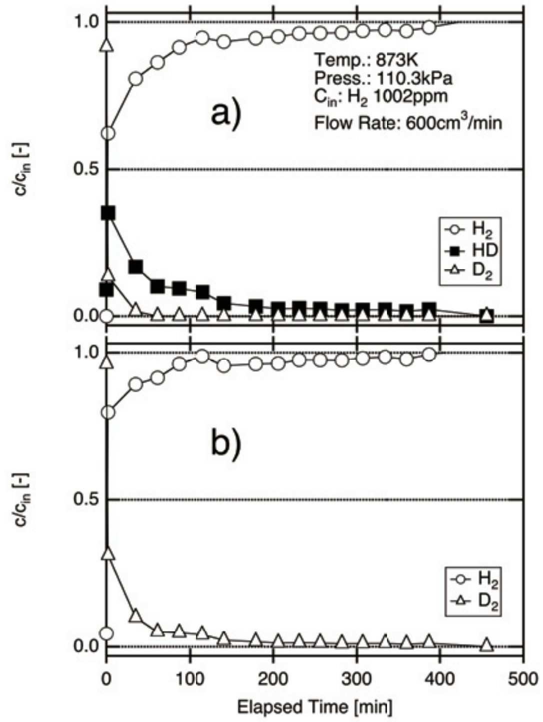

Fig.2 Change of the hydrogen isotope concentrations in the effluent gas of the hydrogen pump. a) ordinary release curve, and b) release curve of which HD is treated as $1/2H_2$ and $1/2D_2$.

Fig.3 shows the concept of the mass transfer model that takes into account the isotope exchange reaction on the surface of the electrode of the proton conductor ceramic. Deuteron in the ceramic is replaced by the hydrogen (proton) via isotope exchange reaction on the surface of the electrode. Then, proton diffuses to the ceramic with replacing to deuteron. Platinum (Pt) has been used as the electrode. Generally, Pt has a catalytic function for dissociation of hydrogen molecule. So, the reaction has been assumed to occur on the surface of electrode dominantly. At that time, the current between the electrodes is controlled to become zero. So, in ideal, hydrogen and deuterium are not released from another side

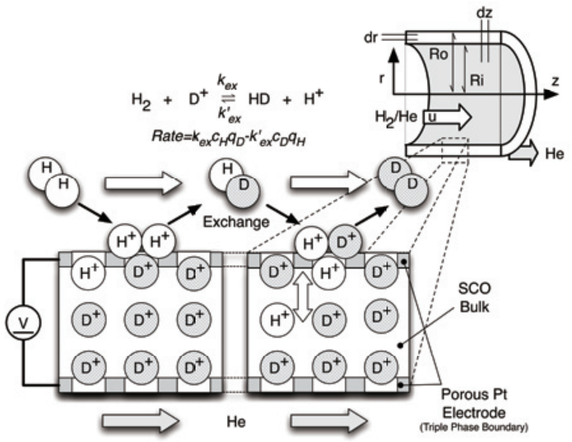

Fig.3 A schematic of the mass transfer process.

of the ceramic membrane of the hydrogen pump. Finally, the deuteron in the ceramic membrane is replaced by the proton. In this experimental system, HD appears at the outlet of hydrogen pump. However, HD was treated as $1/2H_2$ and $1/2D_2$ for simple calculation as shown in Fig.2b. So, the following relations were assumed;

$$
\begin{aligned}
&c_1 = c_{HH} + \tfrac{1}{2}c_{HD},\\
&c_2 = c_{DD} + \tfrac{1}{2}c_{HD},\\
&c_0 = c_1 + c_2,\\
&q_0 = q_1 + q_2 = \overline{q}_1 + \overline{q}_2,
\end{aligned}
\tag{1}
$$

where c is concentration of gaseous hydrogen isotope [mol/cm^3]. Subscripts "*HH*", "*HD*" and "*DD*" mean H_2, HD and D_2, respectively. q is concentration of hydrogen isotope in the proton conductor ceramic [mol/cm^3]. $\overline{q}$ is the average concentration of hydrogen isotope in the minute section of the ceramic in axial direction [mol/cm^3]. Subscripts "*1*" and "2" mean H_2 and D_2 after the distribution of HD, respectively.

The mass balance of hydrogen isotopes in the axial direction of the hydrogen pump is described as;

$$D_{L,i}\frac{\partial^2 c_i}{\partial z^2} = u\frac{\partial c_i}{\partial z} + \frac{\partial c_i}{\partial t} + a_s\frac{\partial \overline{q}_i}{\partial t} \quad (i=1,2),\tag{2}$$

where D_L is the axial dispersion coefficient of hydrogen isotope [cm^2/s], t is time [s], u is the gas velocity [m/s], z is the axial distance [cm], a_s is the ratio of the cross section of the proton conductor ceramic in radial direction to the cross section of the flow path [cm^2/cm^2]. In this work, the gas velocity is considered much larger than the axial dispersion. Therefore, the term of the axial dispersion is omitted and the following equation is derived from eq.(2);

$$\frac{\partial c_i}{\partial t} = -u\frac{\partial c_i}{\partial z} - a_s\frac{\partial \overline{q}_i}{\partial t} \qquad (i=1,2).\tag{3}$$

The hydrogen concentration change in the membrane is considered to be caused by the capture of hydrogen by the surface reaction (isotope exchange) and the diffusion of hydrogen (proton) in the ceramic. When the surface reaction is the isotope exchange reaction of the gaseous hydrogen with the deuteron on the surface of electrode, the reaction rate is expressed taking into account the reverse reaction as;

$$\frac{\partial \overline{q}_1}{\partial t} = k_{ex}c_1 q_2 - k'_{ex}c_2 q_1 = -\frac{\partial \overline{q}_2}{\partial t},\tag{4}$$

where k_{ex} is the reaction rate constant of the isotope exchange reaction [cm^3/mol•s]. q means hydrogen isotope concentration of the ceramic at the surface [mol/cm^3]. Eq.(5) is derived from Eq.(4) as;

$$\frac{\partial \overline{q}_1}{\partial t} = k_{ex}\left(c_1(q_0 - q_1) - \frac{c_2 q_1}{K}\right) = -\frac{\partial \overline{q}_2}{\partial t},\tag{5}$$

where K is the equilibrium constant [-] and is the ratio of the reaction rate constant, k_{ex}, to that of the reverse reaction, k'_{ex}.

In the ceramic membrane, proton captured via isotope exchange reaction diffuses and penetrates. However, the current is controlled to become zero. So, proton captured is assumed to diffuse by replacing with deuteron. If the hydrogen ion transportation is described with the diffusion equation of one dimension, the following equation is derived;

$$\frac{\partial q_i}{\partial t} = D_s\left(\frac{\partial^2 q_i}{\partial r^2} + \frac{1}{r}\frac{\partial q_i}{\partial r}\right) \quad (i=1,2),\tag{6}$$

where D_s is the diffusion coefficient of hydrogen isotope in the ceramic [cm^2/s], and r is the distance in radial direction of the proton conductor ceramic tube [cm]. As shown in Fig.3, the author has assumed that proton diffuses in the ceramic by replacing with deuteron under the electric field. Usually, the diffusion coefficient of H_2 and that of D_2 is different. However, in this model, they have been assumed to be same.

The initial and the boundary conditions are as follows;

[Flow Path]

$$c_1(z,0) = 0 \quad (z > 0, t = 0),$$

$$\overline{q}_1(z,0) = 0 \quad (z \geq 0, t = 0),$$

$$c_1(0,t) = c_{in} \quad (t \geq 0),$$

[ceramic]

$$q_1(z,r,0) = 0 \quad (z \geq 0, R_i \leq r \leq R_o, t = 0),$$

$$\frac{\partial q_1(z,R_o,t)}{\partial r} = 0 \quad (z \geq 0, t \geq 0),$$

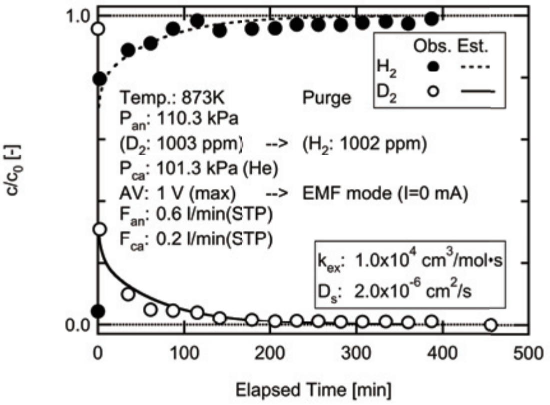

Fig.4 Comparison of the release curve between the observations and the calculations.

$$a_v D_s \frac{\partial q_1(z,R_i,t)}{\partial r}$$
$$= -k_{ex} c_1(z,t)(q_0 - q_1(z,R_i,t)) + \frac{c_2 q_1(z,R_i,t)}{K}$$
$$(z \geq 0, t \geq 0), \qquad (7)$$

where R_i *and* R_o mean the location that is the surface of ceramic tube inside and outside, respectively. a_v means the ratio of the surface area of the inside electrode on the ceramic tube to the volume of ceramic tube between the electrodes [cm^2/cm^3]. Eqs.(1,3,5-7) were solved numerically to obtain the change of hydrogen concentration in the effluent gas of the hydrogen pump. The solutions were compared with the experimental observations. And then, the reaction rate constant, k_{ex}, the equilibrium constant, K, and the diffusion coefficient, D_s, were obtained.

Fig.4 shows a comparison of the observed release curves with the calculated release curves. Change on the shape of the release curve was hardly observed even though the equilibrium constant, K, was changed. Therefore, the reverse reaction might be able to be ignored in this estimation. Estimation of rate constants and the diffusion coefficients were listed in table 2. The observed amounts of hydrogen isotope released from the ceramic were also listed in this table. The left side of the table means that D_2 has been used in transportation experiment and H_2 has been used in the exchange experiment. The right side means reverse cases. There is no difference in sample1 and 2 excluding the lot of raw material. The present author has reported about the hydrogen concentration in the SCO under various partial pressure of H_2[13]. The comparison of the results with our previous work is shown in Fig.5. The results in this work were plotted against the partial pressures of hydrogen isotope in the transportation experiments. As mentioned in the section2, the concentration of hydrogen isotope in the transportation experiments in the preparation were about 0.1% and 100%. So, the data were plotted against the partial pressures at about 10^2 Pa and 10^5 Pa. The amounts of the released hydrogen isotope from the SCO are larger than the data in our previous work. However, their differences are within one order of magnitude. In the previous work, the hydrogen concentration in the SCO has been estimated from the proton conductivity observed experimentally and the diffusion coefficient reported by Schober et al[14]. Taking into account the error range on the diffusion coefficient, the difference between this work and the previous work may be not so large.

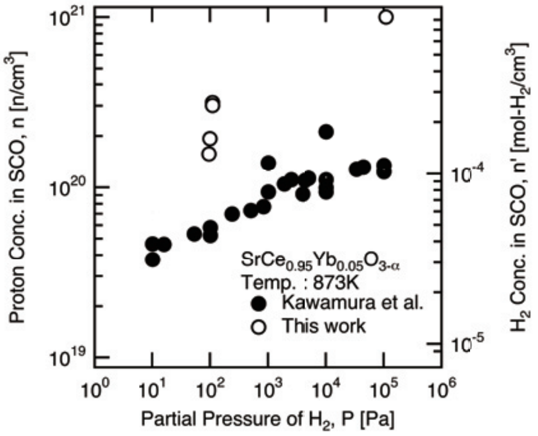

Fig.5 Comparison of hydrogen isotope concentration in the SCO between this work and the previous work.

As listed in table 2, it does not seem that there is some rule in the estimated diffusion coefficient. As mentioned before, Schober et al. have reported that the diffusion coefficient of hydrogen in SCO, D_0, is 2.185x10^{-3} cm^2/s and its activation energy, ΔH, is 0.46±0.16 eV[14]. Fig.6 shows the comparison between the diffusion coefficient estimated in this work and the reported one. The grey area in Fig.6 is caused by the error range of the activation energy. The estimated diffusion coefficients are in this area, and so may thought to be comparatively reasonable.

Table 2 The amount of hydrogen isotope released from the ceramic, the estimation of diffusion coefficient and reaction rate constant.

	D → H			H → D		
	q_0 [mol/cm^3]	D_s [cm^2/s]	k_{ex} [cm$_3$/mol•s]	q_0 [mol/cm^3]	D_s [cm^2/s]	k'_{ex} [cm^3/mol•s]
Sample 1	2.6x10^{-4}	2.0x10^{-6}	1.0x10^4	8.3x10^{-4}	5.8x10^{-7}	7.5x10^3
	2.5x10^{-4}	2.0x10^{-6}	1.0x10^4	-	-	-
Sample 2	1.6x10^{-4}	4.8x10^{-6}	1.0x10^4	1.3x10^{-4}	4.8x10^{-6}	1.0x10^4

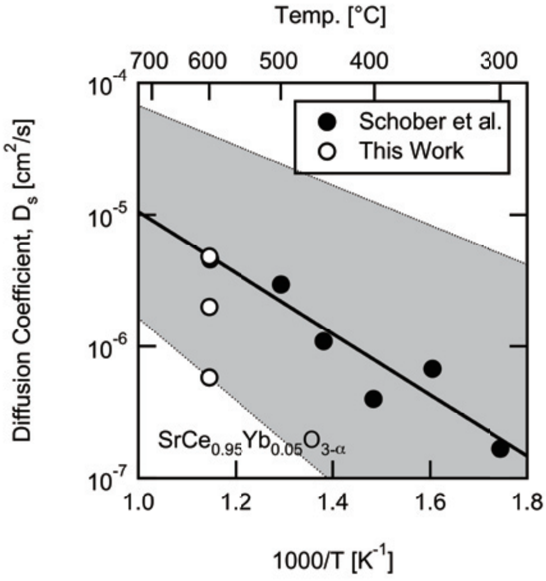

Fig.6 Comparison of the diffusion coefficient of hydrogen isotope in SCO.

There is not so large difference among the estimated reaction rate constants. Therefore, the equilibrium constant of this exchange reaction is thought to be nearly 1.0

In this work, water vapor has not been taken into account in the mass transfer model. However, water vapor is expected to be in the sweep gas of solid breeder blanket actually. Also, in this experiment, the existing of water vapor in the gas is probable. Therefore, it should be considered that the estimated parameters in this work have been affected by water vapor. Experiment and estimation of the exchange reaction between gaseous hydrogen and water vapor is necessary in future work.

From the result of this work, the author thinks that the attention may be necessary when hydrogen sensor with the proton conductor ceramic is applied to the tritium plant of fusion reactor. In case of hydrogen sensor, the reference gas, of which hydrogen isotope concentration is known, flows through one side of proton conductor membrane, and the sample gas, for example DT fuel, flows through another side of membrane. And, the electric current is controlled to become zero, and the electromotive force (EMF) is measured to know the fuel concentration. This is similar to this experimental system. So, it is probable that the fuel gas permeates through the membrane and is mixed with the reference gas. Matsumoto et al. have carried out the experiments of hydrogen isotope sensor[5], but they have not reported such phenomena. However, they have not measured the contents of hydrogen isotope mixture gas during their experiments. It is necessary to confirm experimentally whether the permeation to the reference side occur or not.

4. Conclusion

The isotope exchange reaction between the hydrogen isotope in the gas and that in the proton conductor ceramic of hydrogen pump was investigated, and the amount of hydrogen captured in the proton conductor ceramic, the diffusion coefficient of hydrogen isotope in the ceramic and the rate constant of the isotope exchange reaction were estimated using the mass transfer model.

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[1] H. Iwahara, Solid State Ionics, **77** 289 (1995).
[2] T. Yajima et al., Solid State Ionics, **79** 333 (1995).
[3] N. Miura et al., Solid State Ionics, **136-137** 533 (2000).
[4] H. Iwahara et al., Solid State Ionics, **168** 299 (2004).
[5] H. Matsumoto et al., Solid State Ionics, **175** 491 (2004).
[6] M. Kondo et al., Fusion Eng. Des., **83** 1277 (2008).
[7] T. Kakuta et al., Fusion Technol., **39** 1083 (2001) .
[8] M. Kato et al., Fusion Sci. Technol., **41** 859 (2002).
[9] Y. Kawamura et al., Fusion Sci. Technol., **41** 1035 (2002) .
[10] Y. Kawamura et al., Fusion Sci. Technol., **45** 33 (2004).
[11] Y. Kawamura et al., Fusion Eng. Des., **82** 113 (2007).
[12] Y. Kawamura et al., Fusion Eng. Des., **83** 625 (2008).
[13] Y. Kawamura et al., Nucl. Fusion., **49** 055019 (2009).
[14] T. Schober et al., Solid State Ionics, **77** 175 (1995).