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HTO electrolysis method by using proton exchange membrane fuel cell

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Abstract

The application of a proton exchange membrane fuel cell (PEMFC) system to electrolysis for HTO recovered from a solid breeder blanket is discussed in this report. The amount of gas permeation through the membrane in this system and the tritium inventory in the membrane were calculated, and it was found that the effect of these phenomena on the performance of electrolysis system can be disregarded. However, the trapped tritium in the membrane will damage the structure of the membrane, and we need to replace it about once every 10 days. This duration is so short that we should prepare other backup plans to convert HTO to HT in the blanket purge gas.

1. Introduction

The system of a proton exchange membrane fuel cell (PEMFC) can also be applied as the electrolyzer of HTO bred in the solid breeder blanket of a D–T fusion reactor, although the PEMFC may also be the effective power source for a future motor vehicle. The bred tritium in the solid breeder blanket will be recovered by a purging operation using the helium gas mixed with H_2 or H_2O, and it has been recognized in recent studies that not a little amount of bred tritium is released to the purge gas in the chemical form of HTO even when helium gas with H_2 is used as the blanket purge gas [1]. We consider that application of the PEMFC system for conversion of HTO to HT is reasonable because it is preferable to transfer bred tritium to the main fuel system in the chemical form of HT.

Fig. 1 shows the schematic diagram of a tritium recovery system. Helium with H_2 or H_2O will recover the bred tritium, and the outlet gas from the blanket will pass through the tritium separation system, e.g. palladium tubes, to permeate only H_2 and HT. Then, HTO will be introduced into the electrolysis system using PEMFC to be converted to HT. The converted HT and H_2 will go to the isotope separation system through cryogenic distillation, and T_2 will be produced and introduced to the tritium storage and supply system. Accordingly, it is important to understand the performance of the electrolysis system using the PEMFC in the tritium atmosphere and to quantify the tritium inventory in the system.

The mass transfer performance of H_2, HT, H_2O, HTO and He in the proton exchange membrane (PEM) placed in the blanket purge gas atmosphere

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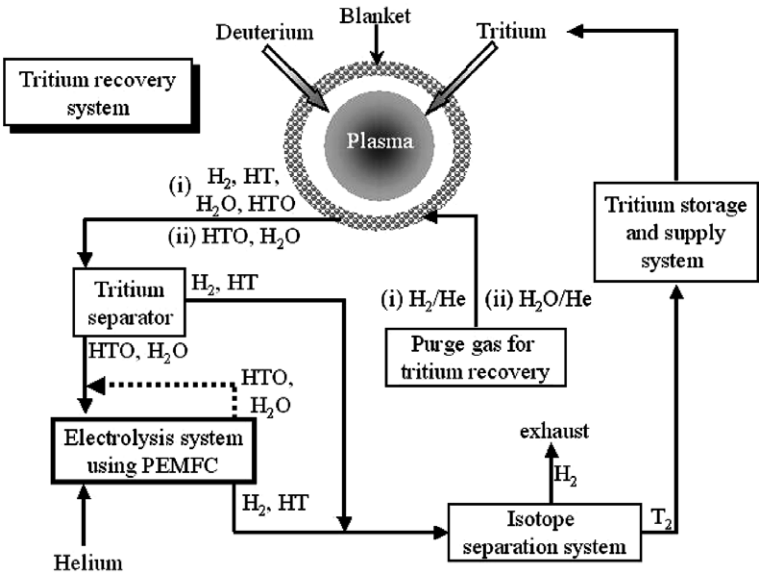

Fig. 1. Schematic diagram of tritium recovery system.

is discussed in this report using the mass transfer coefficients and adsorption isotherm of water reported by the present authors elsewhere [2]. The tritium inventory in the PEM is also discussed, where the amount of tritium both in adsorbed water and structural water in the PEM taken up through adsorption and isotope exchange reaction is estimated. Additionally, there is some concern about the effect of β-rays from tritium on the performance of PEM, and the durability time of PEM is estimated using the reported data by Iwai et al. [3].

2. Electrolysis system using PEMFC

Fig. 2 depicts the structure of the electrolysis cell and the mass transport phenomena in the PEM. The electrolysis cell consists of the gas flow channel, electrode, electrolyte membrane and Pt catalyst between electrode and membrane. This system can be used at 80 °C, the same temperature as the general PEMFC. There are some kinds of mass transport phenomena in this system, and they are listed as follows:

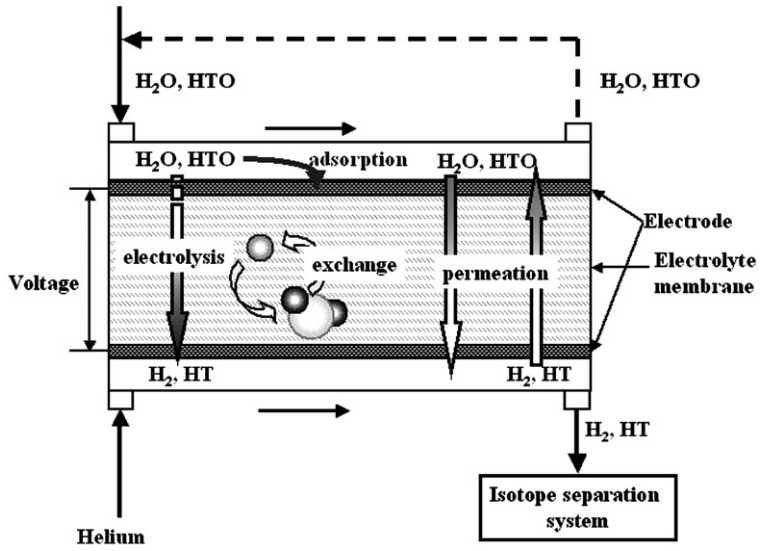

Fig. 2. Structure of the electrolysis cell and mass transport phenomena in the PEM.

(i) Electrolysis of H_2O and HTO

$$2H_2O \rightarrow 2H_2 + O_2 \quad (1)$$

$$2HTO \rightarrow 2HT + O_2 \quad (2)$$

(ii) Adsorption of H_2O and HTO onto the PEM.
(iii) Permeation of H_2, HT, H_2O, HTO, and Helium through the PEM.
(iv) Isotope exchange reaction between T^+ or adsorbed HTO and structural water in the PEM

$$T^+ + H_2O(\text{structural}) \rightarrow H^+ + HTO(\text{structural}) \quad (3)$$

$$HTO(\text{adsorbed}) + H_2O(\text{structural}) \rightarrow H_2O(\text{adsorbed}) + HTO(\text{structural}) \quad (4)$$

where T^+ is tritium ion produced by electrolysis and diffuses in the PEM, and structural water represents any kinds of crystal water or –OH group which strongly connect with the membrane structure, and we have already quantified the amount of structural water in the PEM [2].

3. Electrolysis cell for the commercial reactor

3.1. Condition and membrane size for the commercial reactor

Table 1 shows the tritium conditions for a commercial reactor of 1 GW. It is assumed here that the purge gas is helium with 100 Pa of H_2O (total pressure is 100 kPa) and the chemical form of released tritium from the blanket is only HTO. The amount of burned tritium for a 1 GW reactor will be 400 g/day, and the amount of bred tritium in the blanket should be 440 g/day if the tritium breeding ratio is 1.1. Four hundred and forty grams of T_2 is equal to about 75 mol, and water vapor (H_2O + HTO) of about 7500 mol/day needs to be electrolyzed to get HT. The relationship between the amount of electrolyzed water, Q_e (mol/s), and the necessary area of the PEM for electrolysis, A_e (cm^2), is expressed by

$$A_e = \frac{2Q_eF}{I}, \quad (5)$$

where I (A/cm^2) is the current density of the PEMFC and F (C/mol) is Faraday's constant. The necessary power for electrolysis of the water, P_e (W), is derived using

$$P_e = \frac{IA_eV_i}{\eta}, \quad (6)$$

where V_i (V) is the ideal voltage of the fuel cell and η (–) is the electrolysis efficiency of the PEMFC system. Then, A_e and P_e were calculated and is shown in Table 2. The required power for electrolysis is only 68 kW, and this value is very small compared with the total power of 1 GW. Therefore, the power for this electrolysis system can be supplied from the generated power of the reactor.

Table 1
Tritium condition for the commercial reactor of 1 GW

Burned tritium in plasma (g/day)	400
Bred tritium in blanket (g/day)	440
Recovered tritium from blanket as HTO[a] (mol/day)	150
Partial pressure of water (H_2O + HTO)[b] (Pa)	100
Total amount of electrolyzed water (mol/day)	7500

[a] It is assumed that the chemical from of released tritium from the blanket is only HTO by helium purging with H_2O.
[b] Total pressure of the purge gas is 100 kPa, and the partial pressure of HTO is 2 Pa.

Table 2
Necessary area of membrane and required power for electrolysis

Membrane	Flemion®
Thickness of the membrane (μm)	157
Density of the dried membrane (g/cm^3)	1.76
Necessary area of the membrane (cm^2)	2.37×10^4
Volume of the membrane (cm^3)	372
Current density (A/cm^2)	0.70
Electrolysis efficiency (–)	0.30
Required power for electrolysis (kW)	68.0

3.2. Gas permeation

It is important to understand gas permeation through the PEM to optimize the electrolysis system. It is known that H_2 and He can permeate through the PEM, and the diffusion coefficients in the PEM were reported [2]. It is also well known that water vapor can permeate through the PEM, and the diffusion coefficient strongly depends on the water concentration in the membrane [4–6]. The H_2 or He permeation flux, J ($mol/m^2\,s$), is derived from Fick's law as

$$J = D\frac{(C_1 - C_2)}{\delta}, \quad (7)$$

where D (m^2/s) is the diffusion coefficient in the PEM, C_1 and C_2 (mol/m^3) are the concentrations

of gas at the high concentration side and low concentration side, respectively, and δ (m) is the membrane thickness. If there is 100 Pa of H_2 at the one side of the membrane and no H_2 at the other side, the permeation flux of H_2 through the membrane at 80 °C was calculated as 1.32×10^{-8} mol/m^2 s ($D = 6.08 \times 10^{-11}$ m^2/s [2]). The amount of permeated H_2 through the membrane for 1 day in this system is 2.70×10^{-3} mol. This value is much smaller than the total amount of electrolyzed water, 7500 mol/day, and the permeation of H_2 and HT can be disregarded. The diffusion coefficient of He in the PEM at 80 °C is 1.85×10^{-10} m^2/s [2] and this is only three times larger than that of H_2. Hence, the permeation of He can be also disregarded. Meanwhile, the diffusion coefficient of water in the PEM has a tendency to decrease with dehydration, and other researchers have reported the diffusion coefficient as a function of water content [4]. In this case, 80 °C and 100 Pa of H_2O, the water content in the membrane is very small and we calculated it to be 1.42×10^{-3} g/cm^3, and the diffusion coefficient at this low water content range has been never reported. However, it is assumed to become smaller than 1.27×10^{-11} m^2/s, which was calculated and reported by Rivin et al. [5] at the water content of about 6.50×10^{-2} g/cm^3, because of the tendency of the diffusion coefficient of water in PEM. Therefore, the permeation of H_2O and HTO can be disregarded as well.

3.3. Tritium inventory and durability time of the membrane

The tritium inventory in the PEM needs to be known because some amount of tritium will be trapped in the membrane by adsorption and isotope exchange reaction. We have already determined the adsorption isotherm of water vapor on the PEM and it will be reported elsewhere. The amount of adsorbed water on the PEM at 80 °C and 100 Pa is 1.42×10^{-3} g/cm^3. Furthermore, there is some amount of structural water, 0.20 g/cm^3 [2], and it can trap tritium by the isotope exchange reaction. These values indicate that we need to consider the structural water when estimation of tritium inventory in the PEM is performed. The tritium inventory in the PEM, I_m, is expressed as

$$I_m = (Q_{ad} + Q_{st}) V_m R_{HT}, \quad (8)$$

$$R_{HT} = P_{HTO}/P_{H_2O}, \quad (9)$$

where Q_{ad} and Q_{st} (mol/cm^3) are the amount of adsorbed water and structural water, respectively, V_m (cm^3) is the volume of PEM, R_{HT} (–) is the isotope ratio in the gas phase, and P_{HTO} and P_{H_2O} are the partial pressure of HTO and H_2O in the gas phase, respectively. In the condition shown in Tables 1 and 2, the tritium inventory in the PEM was estimated as 6.24×10^{-2} mol (HTO), and 99% of this inventory was the result of the structural water. This inventory is very small compared with the whole amount of tritium in the reactor, and it will not affect the fuel recycle system. However, we have some concerns about the effect of irradiation from β-particles from the trapped tritium to the membrane structure. It has been reported that β-rays from tritium damage the structure of the membrane, and the tensile strength and ion exchange capacity of the membrane will be decreased [3]. Consequently, the performance of electrolysis system will deteriorate. According to Ref. [2], the exposure to 9 TBq/kg of tritiated water for two years corresponds to an irradiation dose of 530 kGy, and the strength and ion exchange capacity of the membrane decrease to 43% and 80%, respectively, when the membrane absorbs 850 kGy dose. We calculated the durability time of the membrane, and it is shown in Table 3. In this case, the concentration of tritiated water in the PEM is 1.09×10^3 TBq/kg. Then, the irradiation dose to the PEM from the trapped tritium is 85.6 kGy/day. It is assumed here that we need to replace the PEM when it adsorbs 850 kGy dose, and the durability time is only 9.9 days. This is very short duration, but we can extend the durability time by adding more H_2O to the blanket purge gas. Fig. 3 shows the relationship of the H_2O concentration in the blanket purge gas and the durability time of the PEM. This figure shows the necessary area of the membrane for electrolysis as well. We

Table 3
Durability time of the membrane

Membrane	Flemion®
Thickness of the membrane (μm)	157
Volume of the membrane (cm^3)	372
Adsorbed HTO (g/cm^3-membrane)	2.85×10^{-5}
Trapped HTO to the structural water (g/cm^3-membrane)	4.00×10^{-3}
Total amount of trapped HTO (TBq/kg-membrane)	138
Irradiation dose (kGy/day)	85.6
Durability time[a] (day)	9.9

[a] Durability time means the time when the PEM absorbs 850 kGy dose.

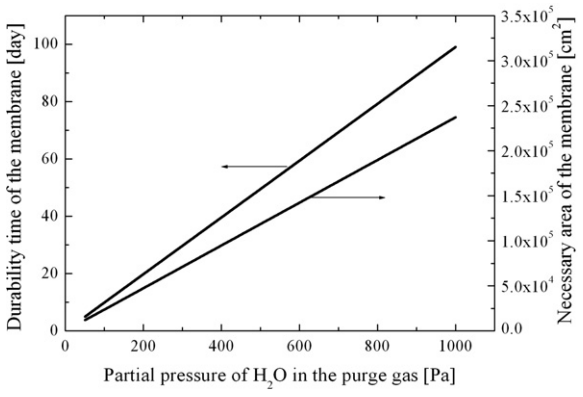

Fig. 3. The relationship between the H_2O concentration in the blanket purge gas and the durability time of the membrane.

can use the membrane for about 3 months if we add 1000 Pa of H_2O to the blanket purge gas. However, the electrolysis of water is equal to the production of H_2, and it could burden the isotope separation system. Accordingly, we need to prepare other backup plans to convert HTO to HT, and some plans are mentioned below:

(i) PEMFC using other polymer membranes have high tolerance for radiation.
(ii) Catalyst bed at the inlet of bred tritium recovery system in order to apply the isotope exchange reaction to convert HTO to HT.
(iii) Other fuel cells, e.g. solid oxide fuel cell.

Whatever we select, the tritium inventory, durability time, and burden the isotope separation system need to be estimated.

4. Conclusion

The system of a PEMFC can be applied in the electrolysis system for HTO from blanket purge gas. The effects of gas permeation through the membrane and tritium inventory in the membrane can be disregarded because these amounts are very small compared with whole amount of tritium in the fuel recycle system. However, the electrolyte membrane will be irradiated by β-rays from tritium because there are some amounts of structural water which can easily trap tritium. The durability time of the membrane was estimated as only 9.9 days when it is used under the condition shown in Tables 1–3. Accordingly, we need to prepare other backup plans for conversion of HTO to HT, and the tritium inventory, durability time, and burden on the isotope separation system need to be understood whatever we select.

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