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Study on Hydrogen Isotope Separation and Enrichment Using Various Electrochemical Processes

種々の電気化学的プロセスを用いた水素同位体分離・濃縮の研究

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Chapter 1: General Introduction

1.1 Overview of the Global Energy Situation

1.1.1 Global Energy Demand and Challenges for a Carbon-Neutral Society

Global energy demand has been increasing. According to the International Energy Agency, it increased at an average annual rate of 1.3% between 2013 and 2023. In 2024, the global energy demand rose by 2.2%, exceeding the average annual growth rate of 1.3%. Among all sectors, the demand for electricity increased markedly by 4.3%. This trend is driven by the increasing use of electrical appliances, structural shifts toward electricity-intensive manufacturing such as smart factories, increasing power demand in data centers, artificial intelligence, and digitalization, and the electrification of end-use sectors, including transportation. Furthermore, the demand for electricity is expected to increase rapidly in the coming years.

Many countries are working toward realizing a decarbonized society. The Intergovernmental Panel on Climate Change has set a global goal to achieve net-zero CO₂ emissions by 2050. Despite these initiatives, approximately 60% of global electricity generation still relies on fossil fuels, and the corresponding CO₂ emissions from the energy sector accounted for approximately 76% of total global CO₂ emissions in 2021.

Therefore, achieving both a massive energy supply and a reduction in CO₂ emissions has become a major challenge. Hydrogen energy is considered a promising solution to this challenge. It does not emit CO₂ during combustion and can be produced using electricity derived from renewables. Hydrogen can also serve as a means of long-term and large-scale energy storage, helping to maintain the balance between electricity supply and demand. Owing to these properties, hydrogen is considered an important component in realizing a sustainable, clean-energy society.

1.1.2 Significance of Hydrogen Energy in Japan's Energy Strategy

Considering the rising energy demand and need for clean energy, it is important to develop hydrogen energy technologies in Japan. Japan is a resource-poor country that relies on imported fossil fuels to meet its energy demands. Approximately 70% of Japan's electricity is generated by thermal power plants, and over 97% of the fossil fuels employed are imported. However, Japan is surrounded by oceans and has abundant water resources. The establishment of hydrogen-based energy systems can significantly contribute to achieving energy independence.

Renewables, such as solar and wind power, are infinite in terms of resources and can be produced domestically. Japan has promoted the use of renewables. However, the power generation per unit area of renewable energy remains low, at less than 10% of that of thermal power generation^[1]. In addition, the cost of electricity generated from renewables in Japan is higher than that from thermal power generation^[2]. Considering these factors and the limited land area in Japan, the widespread adoption of renewable energy is limited, and the development of highly efficient, low-cost power generation methods is essential.

Nuclear fusion has attracted significant attention as a potential energy source capable of achieving carbon neutrality and providing a large energy supply. Fusion reactors are characterized by high power generation per unit area and use hydrogen isotopes, one of which is contained in seawater, as fuel. Therefore, the advancement of hydrogen energy in Japan is not only essential for achieving energy independence but is also closely linked to the realization of fusion reactors.

1.2 Fundamentals of Hydrogen Isotopes

Hydrogen isotopes are employed as fuel in nuclear fusion reactors. There are three types of hydrogen isotopes. Their characteristics are summarized as follows:

Table 1-1. Summary of hydrogen isotopes.

Isotope	Symbol	Protons	Neutrons	Mass number	Natural abundance
Protium	H	1	0	1	99.9 %
Deuterium	D	1	1	2	0.014 %
Tritium	T	1	2	3	-

Protium, denoted as H, has a mass number of one and consists of one proton and one electron. Its natural abundance is approximately 99.99%, indicating that nearly all hydrogen on Earth exists as H.

Deuterium, denoted as D, has a mass number of two and consists of one proton, one neutron, and one electron. The natural abundance of D is approximately 0.014%. It is widely used in various fields, including materials science, medicine, and nuclear engineering. In materials science, D is used to extend the lifetime of organic light-emitting diode displays and semiconductor devices^[3–5]. In the medical field, D is used to prolong the effectiveness of pharmaceuticals and as a tracer in chemical and biological reactions^[6–8]. In the nuclear field, D serves as a moderator in nuclear fission reactors and as a fuel in nuclear fusion reactors^[9,10].

Tritium, denoted as T, has a mass number of three and consists of one proton, two neutrons, and one electron. T is a radioactive isotope that emits low-energy β -rays

with a maximum energy of 18.6 keV. Although external exposure to tritium is minimal, internal exposure can pose health risks if it is inhaled or ingested. The half-life of T is approximately 12 y; therefore, T is nearly absent in nature. T is primarily produced when heavy water is used as a moderator in nuclear fission reactors and absorbs neutron radiation^[11]. T is expected to serve as a fuel in nuclear fusion reactors^[9,10].

1.3 Overview of Nuclear Fusion Reactors

The commercialization of fusion reactors represents a global collaborative effort aimed at achieving practical operation by approximately 2050^[12]. The International Thermonuclear Experimental Reactor (ITER) is currently under construction in France and is scheduled to begin operation by 2035. Two principal approaches to plasma confinement have been explored: magnetic and inertial. ITER employs the magnetic confinement approach because the energy consumption associated with inertial confinement currently exceeds the achievable power output.

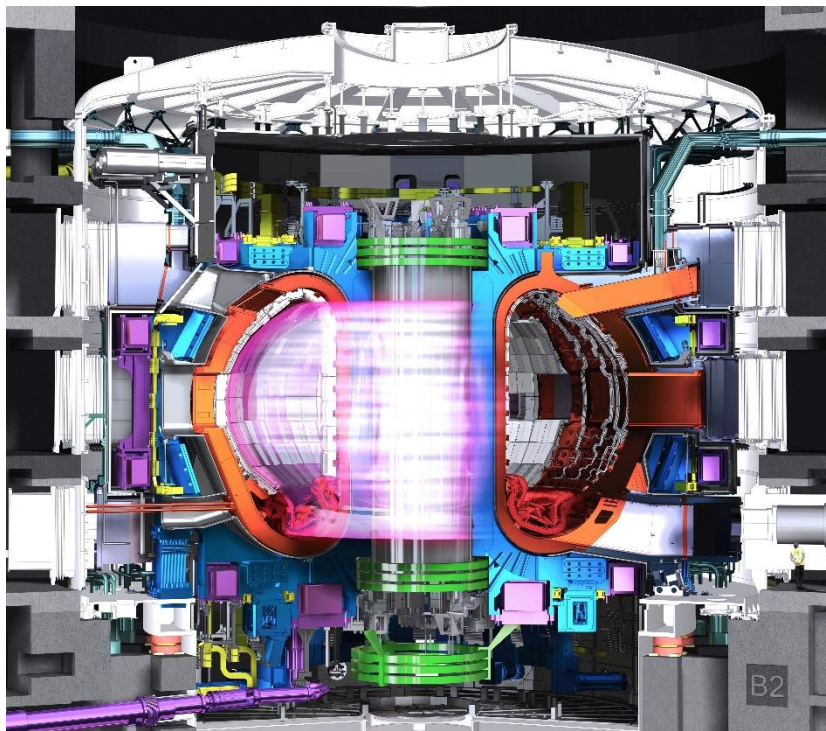


Figure 1-1. Schematic of the cross-sectional structure of the fusion reactor at ITER
(Credit: © ITER Organization).

Figure 1-1 shows a cross-sectional view of the fusion reactor planned for construction at ITER. The fusion reaction occurs within the device positioned at the center of the facility. The interior of the device consists of a toroidal space. Within this space, the fuel is converted into plasma and undergoes a fusion reaction. To prevent contact with the reactor components, the plasma is confined and controlled using multi-directional magnetic fields.

The fusion reaction involving D and T proceeds as follows:



Electricity is generated by recovering energy from neutrons emitted during the reaction. The extraction of neutron energy is facilitated by a wall-like structure known as the "blanket." This blanket is composed of numerous interconnected modules, systematically arranged to cover the interior of the reactor. Each module contains distinct types of internal components.

One such component is the T breeding material, which is used to produce T. The T demand in future demonstration or commercial reactors ($\approx 100 \text{ kg yr}^{-1}$) substantially exceeds the current annual supply from existing facilities (e.g., heavy-water reactors, only a few kilograms per year)^[13,14]. To overcome this shortage, T breeding blankets have been proposed^[15]. During the fusion reaction, the lithium (Li) and beryllium (Be) within the blanket react with neutrons released during the fusion reaction. The Li isotope ${}^6\text{Li}$ reacts with the neutrons to produce T, as follows:



The beryllium isotope, ^9Be , is expected to play a crucial role in efficiently multiplying neutrons:



Equations (1-2) and (1-3) show that efficient T breeding in the blanket can be achieved using Li and Be.

The second component is a coolant, which is essential for removing heat from the blanket. Because the blanket directly encounters high-temperature plasma, effective thermal management is critical. During reactor operation, the coolant circulates continuously through the blanket to maintain stable temperatures. During this process, the coolant becomes contaminated with tritium, primarily because of permeation from the breeding material. Consequently, the coolant discharged from the blanket must undergo a tritium recovery process before being recirculated^[16]. Although water and He gas are widely considered primary coolant candidates, molten salts have also been investigated at the research stage. Molten salts are particularly promising because they can simultaneously serve as a breeding medium and a coolant^[17].

1.4 Hydrogen Isotope Recovery Processes from Fusion Reactor Coolants

The process for recovering hydrogen isotopes from coolants in fusion reactors is selected based on the type of coolant employed. For water or helium gas, the Combined Electrolysis Catalytic Exchange (CECE) method is used^[9,18]. For molten salts, various extraction processes are currently under investigation, with one such approach being the gas–liquid contact method^[19,20].

1.4.1 Combined Electrolysis Catalytic Exchange

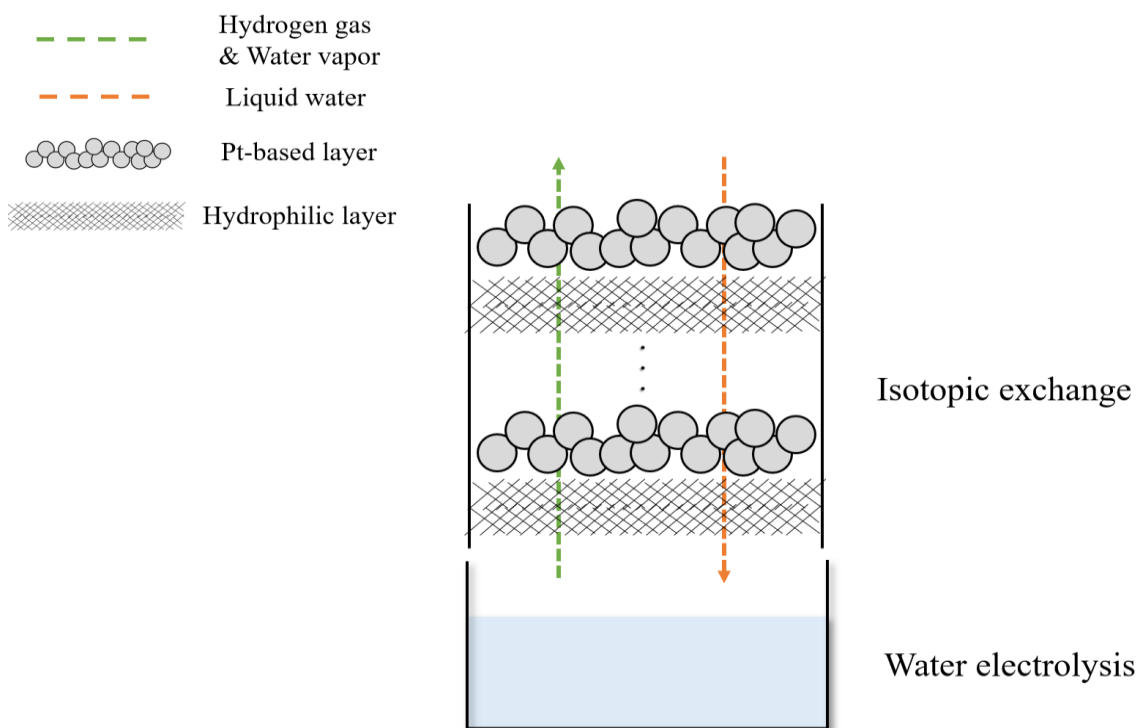
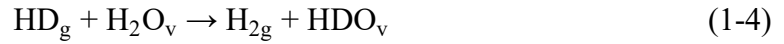


Figure 1-2. Schematic of the CECE method.

The CECE process is a separation technique that integrates isotope exchange and

water electrolysis. A schematic of the system is shown in Figure 1-2. The CECE system comprises an electrolyzer and an isotope-exchange column. The hydrogen gas generated in the electrolyzer is introduced at the bottom of the isotope-exchange column and exits at the top. Conversely, water is fed downward from the top of the column. Two types of packed layers are installed in the column. The first is a Pt-based catalyst layer, in which an equilibrium reaction occurs between hydrogen gas and water vapor, as expressed by the following equation:



where g and v denote the gas and vapor phases, respectively. This reaction is referred to as vapor-phase catalytic exchange (VPCE) and occurs on the surface of the Pt catalyst.

The other layer is packed with a hydrophilic material, within which an equilibrium reaction readily occurs between water vapor and liquid water, as expressed by the following equation:



where l denotes the liquid phase. This reaction is referred to as a liquid-phase catalytic exchange (LPCE). The LPCE process occurs at the interface between the water vapor and liquid phases. Thermodynamically, heavy isotopes are enriched in the liquid phase through the water vapor phase. The equilibrium constants of the VPCE and LPCE reactions, denoted as K_1 and K_2 , respectively, are calculated using the following equations^[21–23]:

$$K_1 = \text{Exp.} \left(\frac{2380}{T^2} - \frac{449.2}{T} + 0.2735 \right) \quad (1-6)$$

$$K_2 = \text{Exp.} \left(\frac{26398.8}{T^2} - \frac{89.607}{T} + 0.0758 \right) \quad (1-7)$$

where T denotes the absolute temperature. At 298 K, K_1 is approximately 3.5, and K_2 is approximately 1.1. Because the column consists of multiple stages, both VPCE and LPCE reactions occur continuously throughout the system. Consequently, heavy isotopes become increasingly concentrated in the lower part of the column, which also leads to larger equipment sizes and higher costs. However, water management presents another challenge. When the platinum catalyst is covered with liquid water, it is deactivated, preventing the VPCE reaction from proceeding and significantly decreasing the overall separation performance.

1.4.2 Water Electrolysis

Water electrolysis is employed as a component of the CECE process. Unlike physical processes, such as cryogenic distillation or isotope exchange, water electrolysis is a chemical process. In this separation technique, the difference in the electrochemical reaction rates between isotopes is exploited. Hydrogen and oxygen gases are produced, as expressed by the following equation:



In this process, lighter isotopes exhibit higher reaction rates; thus, they are

preferentially enriched in the gas phase, whereas heavier isotopes are concentrated in the liquid phase. Since the discovery of D in the 1930s, numerous studies have examined the effects of electrolytes, electrode materials, and catalysts on isotope separation^[24–28]. The separation factor of this method is 3–8, which is higher than that achieved using other techniques, and enables high isotopic purity. However, electrolysis requires considerable energy, and the associated cost increases with processing scale.

1.4.3 Gas–Liquid Contacting

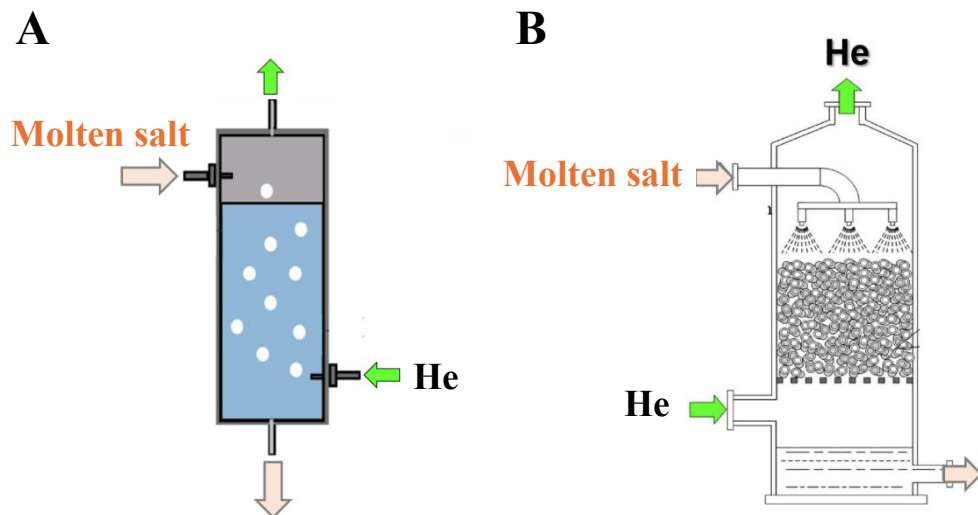


Figure 1-3. Schematic of the gas–liquid contacting methods: (A) gas sparging and (B) packed and spray tower.

The gas–liquid contacting method involves bringing a liquid (molten salt) into

contact with a gas to transfer hydrogen isotopes from the liquid phase to the gas phase. Various approaches are currently under investigation, examples of which are illustrated in Figure 1-3.

Gas sparging (Fig. 1-3A) uses a gas bubbling technique in a vertical column^[19,28]. In this configuration, molten salt is introduced from the top, whereas gas is injected from the bottom, establishing a counter-current flow. This arrangement facilitates the mass transfer of hydrogen isotopes from the liquid phase to the gas phase through the gas–liquid interface of the rising bubbles.

A packed and spray tower (Fig. 1-3B) is a process designed to achieve more efficient gas–liquid contact^[29]. In this configuration, the molten salt is sprayed from the top of the column, establishing a counter-current flow against the gas rising from the bottom. Additionally, the column is filled with packing material to significantly increase the gas–liquid interfacial area, thereby enhancing mass transfer.

However, these gas–liquid contacting methods generally suffer from low mass-transfer efficiency. Consequently, large-scale equipment is required to achieve sufficient removal of hydrogen isotopes from the liquids^[30].

1.5 Electrochemical Methods for Hydrogen Isotope Separation

Fusion reactors require hydrogen isotope separation technologies with low energy consumption, high throughput, and high separation performance in compact systems. Conventional processes separate hydrogen isotopes based on their physical properties, whereas electrochemical approaches do so based on their chemical properties. Although physical methods require adjustment of the apparatus size to control processing capacity, electrochemical methods can be controlled by regulating the electric current, which allows for a compact and scalable system design.

Electrochemistry involves reactions that entail the transfer of electrons between species. In electrochemical systems, oxidation (in which electrons are released) and reduction (in which electrons are accepted) occur as conjugate pairs. A general charge-transfer reaction can be expressed in terms of oxidized species (O) and reduced species (R) as follows:



When the reaction proceeds in the forward direction, it corresponds to reduction, whereas when it proceeds in the reverse direction, it represents oxidation. Each reaction is characterized by its electrode potential (E), which is determined using the Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{\alpha_{\text{ox}}}{\alpha_{\text{red}}} \quad (1-10)$$

where E° is the standard electrode potential, R is the gas constant, F is the Faraday

constant, and n is the number of electrons involved in the reaction. a_{ox} and a_{red} represent the activities of the oxidized and reduced species, respectively. The electrode potential E varies with temperature and concentration relative to E° .

Electron transfer is observed as an electric current. The net current density i is expressed using the cathodic current density i_c and anodic current density i_a as follows:

$$i = i_c - i_a \quad (1-11)$$

From the Butler–Volmer equation, current i can be expressed as follows:

$$i = i_0 \{ \exp(-\alpha z F \eta / RT) - \exp(1 - \alpha) z F \eta / RT \} \quad (1-12)$$

where i_0 denotes the exchange current density, α is the charge-transfer coefficient, and η represents the overpotential. This equation indicates that current can be controlled by adjusting the electrode potential. That is, the type and direction of the electrochemical reactions can be selectively controlled by varying the potential.

Electrochemical reactions can be broadly classified into electrolytic and battery reactions. Electrolysis requires external energy input; however, owing to the wide variety of possible reactions, it has been extensively investigated. A representative example is water electrolysis, which plays a crucial role in the development of hydrogen-based energy systems. During electrolysis, water is decomposed into hydrogen and oxygen gases using external electrical energy. In contrast, battery reactions generate electrical energy spontaneously. The types of reactions are constrained by factors such as electromotive force and material properties.

Electrochemical systems require both electrodes and electrolytes. The electrode

serves as a site for electrochemical reactions where electron transfer occurs at the interface with the electrolyte. The electrode at which oxidation occurs is referred to as the anode, and that at which reduction occurs is referred to as the cathode. The electrolyte is responsible for ion transport. It must fulfill several requirements, including high ionic conductivity, chemical and thermal stability, mechanical robustness, and good interfacial compatibility with the electrodes. Various types of electrodes and electrolytes have been developed and selected based on the intended reactions and applications.

1.5.1 Fuel Cell

Fuel cells directly convert the chemical energy of hydrogen into electrical energy, thereby achieving high energy conversion efficiency. Because the primary reaction product is water, fuel cells have minimal environmental impact and are considered a key technology for the advancement of hydrogen-based energy systems^[31].

William Grove, a British scientist, first demonstrated a fuel cell in 1839 and reported a gas cell that could generate electricity through the reverse reaction of water electrolysis^[32]. Research on fuel cells has since advanced considerably; six representative types of fuel cells are summarized in Table 1-2^[33]. Each type differs in terms of electrolyte, fuel, and operating temperature.

Table 1-2. Fuel cell types and their characteristics.

Type	Electrolyte	Operation temperature	Fuel
Alkaline Fuel Cell (AFC)	aqueous KOH	100 °C	H ₂
Phosphoric Acid Fuel Cell (PAFC)	H ₃ PO ₄	200 °C	H ₂
Molten Carbonate Fuel Cell (MCFC)	Li ₂ CO ₃ –K ₂ CO ₃	650 °C	H ₂ , CO, CH ₄
Solid Oxide Fuel Cell (SOFC)	ZrO ₂ + Y ₂ O ₃	650–1000 °C	H ₂ , CO, CH ₄
Direct Methanol Fuel Cell (DMFC)	PEM	80 °C	CH ₃ OH, H ₂ O
Polymer Electrolyte Fuel Cell (PEFC)	PEM	80 °C	H ₂

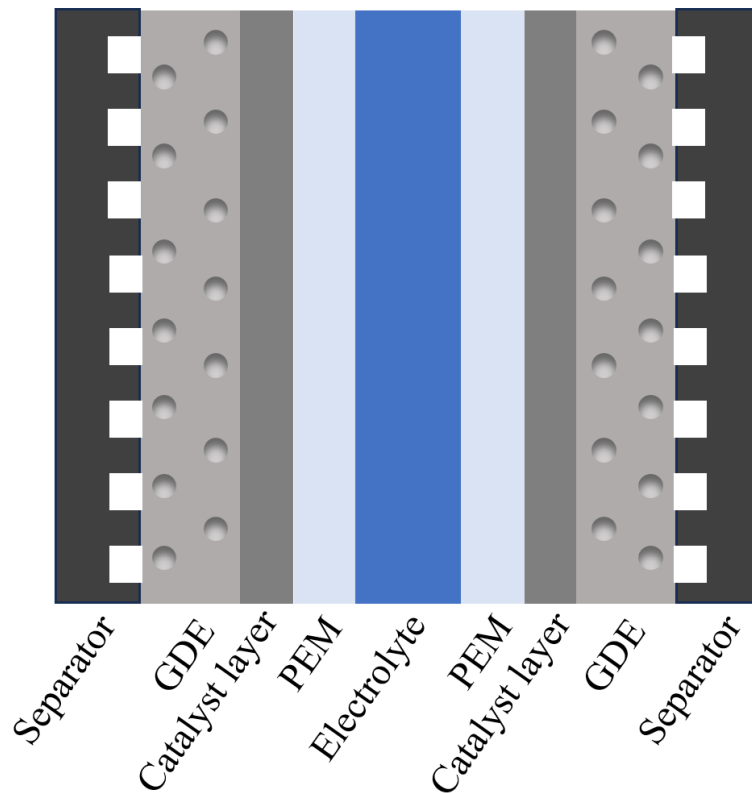
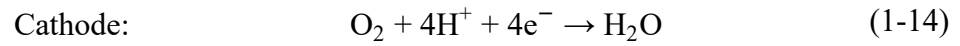
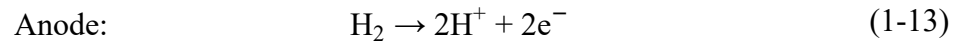


Figure 1-4. Schematic of a PEFC.

PEFCs are widely used in applications such as automobiles and residential distributed power systems owing to their easy start-up and shutdown, compactness, and lightweight design. The cell structure of a PEFC is shown in Figure 1-4. From the center outward, the cell consists of a PEM, catalyst layers, gas diffusion electrodes (GDEs), and separators. Nafion is the most commonly used PEM^[34]. It is a fluorinated polymer containing numerous sulfonic acid groups. Protons are transported along these sulfonic acid sites, enabling selective proton conduction in Nafion. Nano-sized platinum (Pt) particles supported on carbon carriers are widely used as catalysts. The catalyst surface is coated with an ionomer, through which the protons are transported. GDEs are porous

structures that supply reactant gases to the catalyst layer, facilitating the removal of the produced water. The separator functions as a flow channel for the reactant gases.

The electrochemical reactions at the anode and cathode can be expressed as follows:



The hydrogen fuel is oxidized at the anode, releasing protons and electrons. The generated protons pass through the membrane and migrate to the cathode, whereas the electrons flow through an external circuit to reach the cathode. At the cathode, oxygen receives electrons and protons to form water. Because the standard electrode potentials of the anode and cathode reactions are 0 and 1.23 V, respectively, the theoretical electromotive force of the cell is 1.23 V. However, in practice, owing to electrical resistance and overpotential losses, the actual cell voltage typically ranges from 0.6 to 0.9 V.

PEFCs can also be used for hydrogen isotope separation^[35–37]. Heavier hydrogen isotopes tend to react preferentially during the electrode reactions at the anode and cathode^[38]. Consequently, the unreacted gas is enriched with lighter isotopes, whereas the water produced is enriched with heavier isotopes. Owing to their power generation capability and compact cell structure, PEFCs enable energy-efficient and effective isotope separation. Furthermore, a combined electrolysis and fuel cell process that integrates the PEFC operation with water electrolysis has been proposed^[39,40]. In this process, the

hydrogen and oxygen gases generated by water electrolysis are supplied to the PEFC. Through fuel cell reactions, the heavy isotopes in the supplied gas are enriched in the produced water, and electrical energy is simultaneously generated. The isotope-enriched water and the generated electrical energy are then reused for water electrolysis. Thus, the energy consumed during electrolysis is partially compensated by the power produced by the PEFC, enabling efficient hydrogen isotope enrichment.

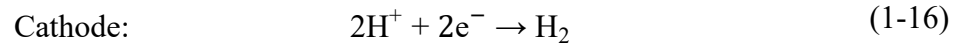
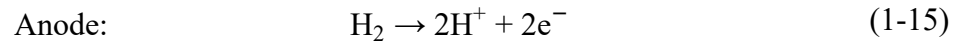
1.5.2 Molten Salts

Molten salts are liquid electrolytes that are composed solely of ions. Because maintaining a liquid state consisting only of ions requires considerable energy, they are generally processed at high temperatures. Those that can be used at relatively low temperatures, typically below 150 °C, are termed low-temperature molten salts or ionic liquids. The molten salts exhibit high electrical conductivity, chemical stability, and thermal stability. As they are completely water-free, molten salts are widely employed in metal electrorefining, electroplating, and recycling processes, such as Al electrorefining and Ti electrodeposition^[41,42].

Molten salts have the potential to enable energy-efficient hydrogen isotope separation, because the high temperatures required can be sustained using waste heat from industrial processes. In molten salts, hydrogen isotopes exist as anions, which may result in separation behaviors distinct from those observed in aqueous systems. Owing to their relatively high radiation resistance, molten salts have been investigated for applications in the separation and purification of spent nuclear fuels^[43]. Therefore, it is feasible to apply molten salts within the blankets of fusion reactors. This approach simplifies system configuration and reduces costs by enabling direct tritium recovery from the blanket.

1.5.3 Electrochemical Hydrogen Pumping

Electrochemical hydrogen pumping selectively transports hydrogen gas through a membrane via electrochemical reactions. In this process, the reversible hydrogen electrode reaction is as follows:



Therefore, the theoretical electrolysis voltage is 0 V, indicating that the process operates with minimal power consumption. Similar to fuel cells, solid polymer electrolyte membranes are widely used, and the use of solid oxide electrolytes has also been reported^[44]. The cell structure is identical to that of a PEFC and consists of a PEM, catalyst layers, GDEs, and separators. As this cell is compact and cost-effective, it has been employed for hydrogen purification and compression^[45,46]. Applications in hydrogen isotope separation have also been investigated, with efficient separation achieved using graphene-based layers^[47,48].

1.6 Concept and Purpose of the Study

In fusion reactor blankets, tritium accumulated in the coolant must be effectively removed and recycled as fuel to ensure operational safety. For the ITER project, the CECE method has been selected to recover hydrogen isotopes from water and gas coolants. Meanwhile, gas–liquid contacting is currently being investigated as a primary technique for extracting hydrogen isotopes from molten salts. However, these conventional methods often have low recovery efficiencies, necessitating large-scale facilities. Consequently, there is a pressing need for a novel separation method that achieves high separation efficiency to enable a more compact design.

In this study, electrochemical methods for separating hydrogen isotopes from fusion reactor coolants were investigated. Electrochemical techniques allow control of processing capacity through an electric current, enabling a compact system design. PEFC offers potential energy savings through power generation and compact cell configurations. Molten salt electrolysis might be adopted for tritium extraction from breeder blankets. This method offers potential advantages, such as system simplification and energy savings through high-temperature operation. Electrochemical hydrogen pumping may be employed as an improved method for CECE catalytic exchange columns. A compact design and high energy efficiency are expected owing to its superior separation performance.

Chapter 2 describes D isotope separation using a PEFC. Hydrogen gas with various D concentrations, stored in gas tanks, was circulated through a closed-loop system equipped with a hydrogen gas recirculation line. A quadrupole mass spectrometer was installed in the circulation line to enable real-time monitoring of hydrogen isotope separation in the gas phase. The results demonstrated that hydrogen isotope separation

and enrichment are feasible at various concentrations.

Chapter 3 describes D separation using a PEFC. Hydrogen gas was supplied to the cell not only from the circulation line but also directly from the gas cylinder using a gas circulation system. The effects of hydrogen utilization and gas flow rate in the circulation line on separation performance were investigated. The results demonstrated that throughput and separation performance can be controlled at the individual cell level. Consequently, design guidelines were formulated for a system capable of flexibly adapting to fluctuating operating conditions.

Chapter 4 describes the separation of D using a LiCl–KCl–LiH–LiD molten salt system. Electrochemical measurements were conducted to determine the diffusion coefficients of H^- and D^- ions in the molten salt. A platinum black electrode was employed, and the separation performance associated with electrolysis and isotope exchange reactions was investigated. The results demonstrated the feasibility of isotope separation via molten salt electrolysis, even under high-temperature conditions.

Chapter 5 describes D separation using electrochemical hydrogen pumping with a PEM. The effect of isotope exchange reactions induced by the liquid electrolyte supplied to the cell on D separation was investigated. Mass balance analysis was performed to validate the measurement results, ensure data accuracy, and clarify the distribution of D. Furthermore, the effects of current density and D concentration in the liquid electrolyte on separation performance were examined. The results presented a novel alternative with high separation efficiency, serving as a potential replacement for the catalytic exchange process in CECE systems.

Chapter 6 summarizes the outcomes of this study. The study's findings are expected to contribute to advances in hydrogen isotope separation technologies.

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***Chapter 2: Protium enrichment by polymer electrolyte
fuel cell with hydrogen gas circulation***

2.1 Introduction

Hydrogen has three isotopes: protium (H), deuterium (D) and tritium (T). D and T are widely utilized in medicine^[1,2], materials science^[3,4], and nuclear technology^[5]. Now, nuclear fusion has attracted much attention for achieving both decarbonization and large-scale energy production. However, the natural abundances of D and T are extremely low, approximately 0.015 % and 1×10^{-16} %, respectively^[6]. At one hand, it is essential to extract and purify D from seawater. On the other hand, T is produced either in nuclear fission reactors (via neutron moderation) or in the blanket region of fusion reactors^[7,8], where the recovery of unreacted materials and purification of cooling water is required [9,10].

Hydrogen isotope separations have been investigated^[11], *ex.* cryogenic distillation^[12,13], water electrolysis^[14,15], membrane separation^[16,17], sorption-based techniques such as quantum sieving^[18,19] and gas chromatography^[20,21], as well as laser isotope separation^[22]. Chemical exchange methods exemplified by Combined Electrolysis Catalytic Exchange (CECE)^[23,24] and Girdler Sulfide (GS) process^[25,26] are widely employed in commercial applications. However, they need large-scale facilities due to the low separation efficiency. CECE process requires huge electric energy for water electrolysis, while the GS process demands frequent maintenance due to equipment corrosion.

We have focused on polymer electrolyte fuel cell (PEFC) for hydrogen isotope separation and reported that D is preferentially reacted^[27-29]. PEFC can be operated at small scales and reduce operational costs through power generation. Kaninski et al. proposed an H/D separation system using a PEFC^[30]. They operated PEFC under low current densities ($< 80 \text{ mA cm}^{-2}$) and supplied a mixed hydrogen gas containing D.

Although high separation factors ranging from 4.2 to 9.1 were observed, detailed operating conditions such as cell temperature and flow parameters were not discussed. Yanase et al. investigated a PEFC stack consisting of 13 cells^[31]. The D separation factor ranged from 3.5 to 4.0. The performance was improved as the hydrogen flow rate decreased, or the power current increased. Pozio et al. studied the H/D isotope effect in PEFC using a Pt-Ru/C catalyst^[32]. The separation factor increased from 2.8 to 4.3 with increasing current density from 20 to 100 mA cm⁻², while it remained about 2.8 at $i > 140$ mA cm⁻². The saturation was explained by mass transport limitations of H^+ and D^+ within the ion exchange membrane.

In industrial isotope separation processes, the concentration difference of the target isotope between the inlet and outlet is typically large. In many studies on D separation, the primary objective has been heavy water production, with a focus on the circulation of liquid phases. Previously, we performed D separation via water electrolysis, using a PEM electrolyzer with the same electrode configuration as a PEFC^[33]. In that study, by circulating the electrolyte, D was successfully enriched in electrolyte from 64.7 at. % to 94.7 at. %. In contrast, in PEFC that use hydrogen gas as fuel, a gas circulation system is commonly employed in practical applications such as fuel cell vehicles to enhance fuel utilization^[34,35]. Many previous studies on D separation using PEFC have been conducted in single-pass systems without gas circulation. From the perspective of energy efficiency, D separation with gas circulation systems are essential. In our previous work, we conducted D separation using a PEFC equipped with a gas circulation system. We demonstrated that this system led to improve hydrogen utilization and separation factor^[29]. However, the study did not employ a hydrogen gas tank into the system, and

the separation was performed using a small gas volume, resulting in limited H enrichment and low separation performance.

In this study, we integrated a hydrogen gas tank into the circulation line, enabling separation over a larger gas volume and achieving substantial H enrichment. In addition, a mass spectrometer was introduced into the gas circulation line, allowing real-time monitoring of H concentration changes during the separation process.

2.2 Experimental

2.2.1 Experimental setup

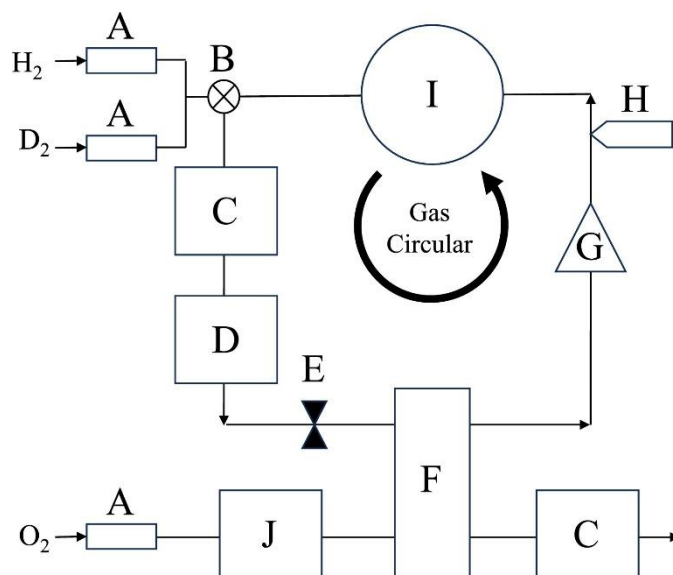


Figure 2-1. Schematic of the experimental setup of hydrogen gas circulation system (A:Mass flow controller, B:3-way valve, C:cord trap, D:QMS, E:pressure gauge, F: PEFC, G: miniature pump, H:Flowmeter with a needle valve, I: Gas tank, J:bubbler).

A schematic diagram of the hydrogen gas circulation line is shown in Fig. 2-1. A JARI standard cell (FC Development Corp., Japan) was used as the PEFC. Both the anode and cathode consisted of carbon paper (TGP-H-120, Toray Industries, Japan) loaded with platinum catalyst (0.3 mg cm^{-2}). The electrode area was 1.0 cm^2 . The electrodes were hot-pressed to a proton exchange membrane (NRE 212, DuPont, USA). Hydrogen gas was circulated in closed system by three-way valve. Pure H₂ and D₂ gases were mixed in various ratios ($\text{H/D} = 10, 1.0, 0.1$) and stored in a 1000 mL tank. Air in the circulation line was replaced with a mixed hydrogen gas of H₂ and D₂. The gas replacement was performed for 3 h in a single-pass mode by disconnecting the circulation

line from 3-way valve (point B in Fig. 2-1). After the gas replacement, the circulation line was reconnected. The total volume was measured using the accumulated flow meter until the gas was supplied up to 1000 mL. During the measurements, the gas volume in the experimental system was measured using a scaling tank equipped with a vertically movable lid. The volume was read directly from the scale corresponding to the position of the lid. A miniature pump (APN-085EX-1-W, Iwaki, Japan) and a flowmeter with a needle valve (RK1200, KOFLOC, Japan) were used in the line. The mixed hydrogen gas was supplied to the anode at a flow rate of 4 mL min⁻¹. A pressure gauge (AP-C30, Keyence, Japan) was also installed to continuously monitor the gas pressure. The pressure gauge measures gauge pressure, and in the present measurements, the pressure was monitored within a range of ± 5 kPa relative to atmospheric pressure. Power generation was galvanostatically controlled at 0.24 A cm⁻² using a variable resistor (PLZ164WA, Kikusui Electronics Corp., Japan). The cell temperature was maintained at 343 K. Pure O₂ gas from a cylinder was supplied to the cathode at a flow rate of 20 mL min⁻¹ through a flow controller (MC 200 SCCM, Alicat Scientific, USA). The O₂ gas was humidified using a bubbler maintained at 323 K before introduction into the cell.

A quadrupole mass spectrometer (QMS, Qulee-HGM 202, Ulvac Inc., Japan) was connected to the circulation line to measure mass numbers 2 (H₂), 3 (HD), and 4 (D₂). Water vapor in the circulating gas was cooled and collected using a cold trap at 228 K before the introduction to the QMS. The separation performance was evaluated using separation factor, α_t . It was calculated based on the atomic ratio of [H] to [D] in the gas phase using the following equation:

$$\alpha_t = \frac{\frac{[H]_t}{[D]_t}}{\frac{[H]_{ini}}{[D]_{ini}}} \quad (2-1)$$

where [L] represents the atomic concentration of hydrogen isotopes. The subscripts ini and t denote the initial time of and a given time of the experiment, respectively.

Water vapor supplied to the cathode was collected at the cell outlet using a cold trap. The recovered vapor was analyzed by attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy (FTIR-4200, JASCO International, Japan). FTIR measurements were performed in the range of 400–4000 cm^{-1} with a resolution of 2.0 cm^{-1} and 100 scans. The reference spectrum was recorded in ambient air.

2.2.2 Simulation of separation factor during power generation

In this study, the separation factor α_{ini} within the fuel cell during power generation was assumed to be constant. Based on a theoretical mass balance calculation, the theoretical separation factor α was derived. The separation factor at time $t + dt$, denoted as α_{t+dt} , is expressed as follows:

$$\alpha_{t+dt} = \frac{\frac{[H]_{t+dt}}{[D]_{t+dt}}}{\frac{[H]_{ini}}{[D]_{ini}}} \quad (2-2)$$

where [L] represents the atomic concentration of hydrogen isotopes. The subscripts ini and t denote the initial time of and a given time of the experiment, respectively. At time t, let $V_{H,t}$ and $V_{D,t}$ denote the amounts of H and D gases present in the system, respectively.

The atomic concentrations $[H]_t$ and $[D]_t$ can then be expressed as follows:

$$[H]_t = \frac{V_{H,t}}{V_{H,t} + V_{D,t}} \quad (2-3)$$

$$[D]_t = \frac{V_{D,t}}{V_{H,t} + V_{D,t}} \quad (2-4)$$

From Eqs. (2-3), and (2-4), the amounts of H and D gases supplied to the fuel cell ($V_{H,in,t}$, $V_{D,in,t}$) are expressed as follows:

$$V_{H,in,t} = [H]_t \times Q = \frac{V_{H,t}}{V_{H,t} + V_{D,t}} \times Q \quad (2-5)$$

$$V_{D,in,t} = [D]_t \times Q = \frac{V_{D,t}}{V_{H,t} + V_{D,t}} \times Q \quad (2-6)$$

where Q denotes the volume rate of supplied gas. On the other hand, the composition of the gas at the cell outlet can be expressed using α_{ini} as follows:

$$\alpha_{ini} = \frac{\frac{[H]_{out,t}}{[D]_{out,t}}}{\frac{[H]_t}{[D]_t}} \quad (2-7)$$

where, the subscript *out* denotes the cell outlet. From Eqs. (2-3), (2-4) and (2-7), the amounts of H and D gases at the outlet ($V_{H,out,t}$, $V_{D,out,t}$) can be calculated as follows:

$$V_{H, out, t} = \frac{[H]_{out, t}}{[H]_{out, t} + [D]_{out, t}} \times \left(Q - \frac{IV}{2F}\right) = \frac{\alpha_{ini} V_{H, t}}{\alpha_{ini} V_{H, t} + V_{D, t}} \times \left(Q - \frac{IV}{2F}\right) \quad (2-8)$$

$$V_{D, out, t} = \frac{[D]_{out, t}}{[H]_{out, t} + [D]_{out, t}} \times \left(Q - \frac{IV}{2F}\right) = \frac{V_{D, t}}{\alpha_{ini} V_{H, t} + V_{D, t}} \times \left(Q - \frac{IV}{2F}\right) \quad (2-9)$$

where, F is the Faraday constant, V is the molar volume of an ideal gas, and I is the applied current. In addition, a portion of the hydrogen gas in the system is released. From Eqs. (2-3), and (2-4), the amounts of H and D gases released ($V_{H, leak, t}$, $V_{D, leak, t}$) can be expressed using the released gas volume L as follows:

$$V_{H, leak, t} = [H]_t \times L = \frac{V_{H, t}}{V_{H, t} + V_{D, t}} \times L \quad (2-10)$$

$$V_{D, leak, t} = [D]_t \times L = \frac{V_{D, t}}{V_{H, t} + V_{D, t}} \times L \quad (2-11)$$

From Eqs. (2-5) - (2-10), and (2-11), the amounts of H and D gases at time $t + dt$ can be calculated as follows:

$$\begin{aligned} V_{H, t+dt} &= V_{H, t} - (V_{H, in, t} - V_{H, out, t}) - V_{H, leak, t} \\ &= V_{H, t} \left(1 - \frac{L + Q}{V_{H, t} + V_{D, t}} + \frac{\alpha_{ini}}{\alpha_{ini} V_{H, t} + V_{D, t}} \times \left(Q - \frac{IV}{2F}\right) \right) \end{aligned} \quad (2-12)$$

$$\begin{aligned} V_{D, t+dt} &= V_{D, t} - (V_{D, in, t} - V_{D, out, t}) - V_{D, leak, t} \\ &= V_{D, t} \left(1 - \frac{L + Q}{V_{H, t} + V_{D, t}} + \frac{1}{\alpha_{ini} V_{H, t} + V_{D, t}} \times \left(Q - \frac{IV}{2F}\right) \right) \end{aligned} \quad (2-13)$$

From Eqs. (2-1) - (2-4), (2-12), and (2-13), the separation factor α_{t+dt} can be calculated as follows:

$$\alpha_{t+dt} = \frac{\frac{V_{H,t+dt}}{V_{D,t+dt}}}{\frac{[H]_{ini}}{[D]_{ini}}} = \alpha_t \times \frac{1 - \frac{L+Q}{V_{H,t} + V_{D,t}} + \frac{\alpha_{ini}}{\alpha_{ini}} \frac{V_{H,t} + V_{D,t}}{V_{H,t} + V_{D,t}} \times \left(Q - \frac{IV}{2F}\right)}{1 - \frac{L+Q}{V_{H,t} + V_{D,t}} + \frac{1}{\alpha_{ini}} \frac{V_{H,t} + V_{D,t}}{V_{H,t} + V_{D,t}} \times \left(Q - \frac{IV}{2F}\right)} \quad (2-14)$$

2.3 Results and Discussion

The experiment started after filling a gas tank with a mixture of H₂ and D₂ gases from gas cylinders. As shown in Fig. 2-1, the mixed gases passed through PEFC during the filling process. When the gas volume in the tank reached 1000 mL, the gas supply was stopped. During power generation, the partial gas pressure gradually decreased due to consumption by PEFC. Therefore, the measurement was terminated when the gas volume was reduced to 100 mL.

Since power generation was conducted under a constant current, the gas volume decreased at a constant rate. The concentration of H (C_H) in the gas depended on the remaining gas volume in the tank, or equivalently, the gas consumption (R). The value of R was calculated using the following equation:

$$R = \frac{V_{\text{con}}}{V_{\text{ini}}} \times 100 \quad (2-15)$$

where V_{con} is the volume of hydrogen gas consumed by power generation, and V_{ini} is the initial volume one. The QMS installed in the gas circulation line continuously monitored C_H . It was calculated using ion currents obtained from QMS as follows:

$$C_H = \frac{2i_{\text{H}_2} + i_{\text{HD}}}{2i_{\text{H}_2} + 2i_{\text{HD}} + 2i_{\text{D}_2}} \times 100 \quad (2-16)$$

where i_x represents the ion current of component x .

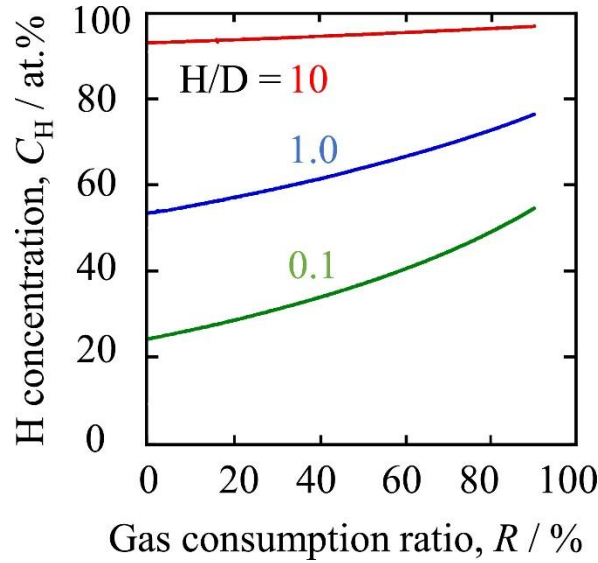


Figure 2-2. Dependency of H concentration on gas consumption ratio during power generation using mixed hydrogen gas with initial H/D ratios of 10 (red), 1.0 (blue), and 0.1 (green).

Regardless of the initial H concentration, C_H increased with increasing R (Fig. 2-2). It increased to 54.6 at. % (H/D = 0.1), 76.4 at. % (H/D = 1.0) and 96.9 at. % (H/D = 10). H was enriched in the gas through the PEFC reaction. As R increased, the volume of hydrogen gas decreased, thereby weakening the dilution effect within the tank. Furthermore, under initial H/D ratios of 1.0 and 0.1, C_H exhibited an exponential increase at high R (> 60 %). This behavior is probably due to the less remaining time of the gas in the tank. Thus, the reaction time interval is shorter. A similar trend was observed in previous study on D enrichment via electrolysis, where a rapid increase in D concentration in the electrolyte was recorded at high electrolyte consumption^[33]. This pronounced the *apparent* separation performance. The present result suggests the hydrogen gas in PEFC can be considered functionally as the electrolyte in water

electrolysis.

In Fig. 2-2, the initial C_H before starting power generation was higher than the H/D ratio supplied from the gas cylinder. This indicates that C_H naturally increased during the filling process. To confirm this phenomenon, C_H in the circulation line was monitored during the introduction of a mixed gas with $H/D = 0.1$ (Fig. 2-3). For the first 4 h after the start of measurement, dry O_2 gas was supplied to the cathode. Interestingly, C_H remained identical to the concentration from the gas cylinder. When humidified O_2 gas was supplied to the cathode, C_H increased and stabilized at approximately 24.6 at. %. To check the D mass transportation, the water vapor in the cathode exhaust was collected using a cold trap. It was analyzed by ATR-FTIR. Surprisingly, D was enriched by 78 at. %. This indicates that the D transported from the gas to water vapor through the membrane.

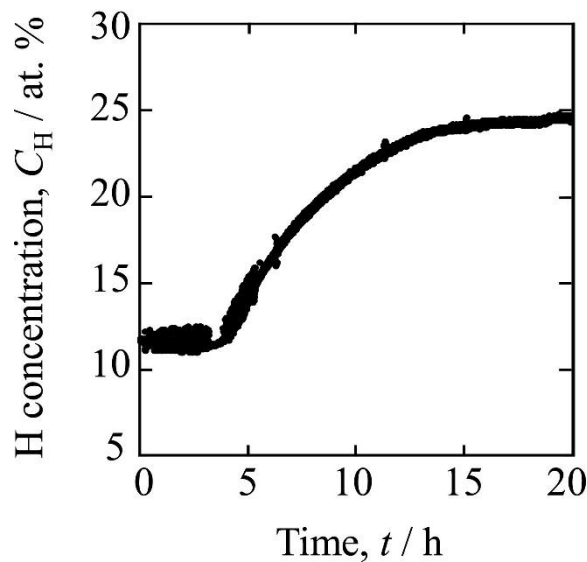


Figure 2-3. Time variation of H concentration in the mix hydrogen gas ($H/D = 0.1$) due to water vapor without power generation.

This might be explained by the vapor phase chemical exchange reaction (VPCE), which can be represented by the following equation:



where, the subscripts (g) and (v) denote the gas phase and vapor phase, respectively. We have confirmed that the occurrence of VPCE in PEFC^[36]. Based on our current understanding, the mechanism of D transport is considered as follows: The PEM separating the anode and cathode always contains some absorbed water. At the anode side, isotopic exchange between gas and the water content within the PEM occurs. The exchanged D species then migrate through the hydrated membrane toward the cathode side. Once reaching the cathode, the D atoms can exchange into the water vapor and be removed from the system via the outlet gas stream.

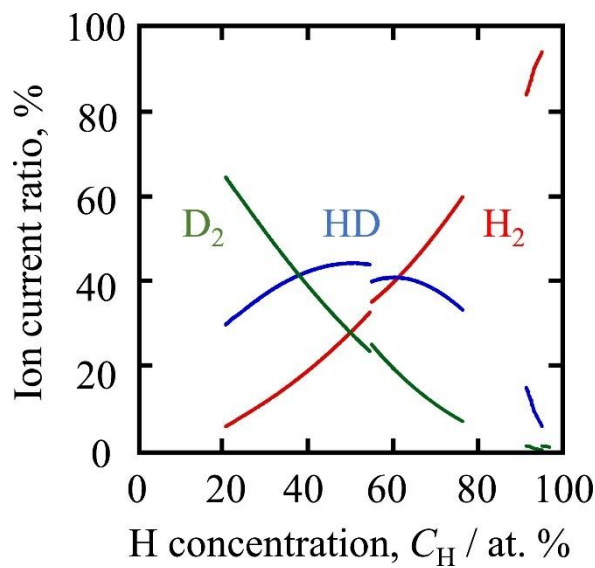


Figure 2-4. Ion current ratio of H_2 , HD, and D_2 in hydrogen gas vs. H concentration.

At an initial concentration of $H/D = 0.1$, the volume of D_2 gas introduced during the filling process was ten times larger than that of H_2 gas. However, in practice, D_2 accounted for approximately 64 % of the gas composition in the tank, while about 30 % of the gas was converted to HD. This is attributed to the disproportionation reaction occurring on the platinum catalyst, where H_2 and D_2 are converted to HD, as represented by the following equation:



As hydrogen gas was consumed during power generation, C_H increased due to the preferential reaction of D. In this initial concentration region, the D_2 fraction in the gas phase significantly decreased from approximately 64 % to 23 %, while the H_2 fraction increased from about 5.8 % to 33 %. The HD fraction gradually increased from approximately 30 % to 44 %.

At an initial H/D ratio of 1.0, the initial C_H was nearly the same as that observed in the later stage of the $H/D = 0.1$. However, the composition of the gas species differed. Compared to the results for $H/D = 0.1$, the fractions of H_2 and D_2 were higher, while the HD fraction was lower. This suggests that the equilibrium of Eq. (2-18) differed between the two conditions. Under these experimental conditions, the maximum HD fraction observed was approximately 44 %. This value is lower than the thermodynamically predicted maximum of 65 % at $H/D = 1.0$, as calculated by García-García et al.^[37]. This discrepancy may be attributed to differences in gas volume or the influence of product water generated during power generation. The product water may have covered the platinum catalyst surface, blocking the reaction sites for Eq. (2-18) and thereby inhibiting

the disproportionation reaction. As power generation progressed, C_H increased. Correspondingly, following the same behavior as observed in the $H/D = 0.1$ case, the H_2 fraction increased, while the D_2 fraction decreased. The HD fraction, in contrast, began to decline.

At an initial H/D ratio of 10, the results were plotted in the region where C_H exceeded 91 at. %. As shown in Fig. 2-2, C_H remained relatively constant despite the change in gas volume due to power generation. However, with increasing C_H , the H_2 fraction increased from approximately 84 % to 94 %, while the HD fraction significantly decreased from around 15 % to 5.8 %. D_2 was almost undetectable in the hydrogen gas.

In this circulation system, the H concentration in the tank increased as hydrogen gas was consumed. To evaluate the relationship between gas consumption and the H enrichment, the separation factor, α_t in Eq. (2-1) was considered. A value of $\alpha_t > 1$ indicates H enrichment in the gas phase. Since the reaction was conducted under constant current, the relationship between t and R can be expressed by Eq. (2-19).

$$t = \frac{2FV_{\text{ini}}}{100VI} \times R \quad (2-19)$$

where, F is the Faraday constant, V is the molar volume of an ideal gas, and I is the applied current. When the gas is circulated, the separation reaction occurs repeatedly. This implies that the *apparent* separation factor increases with reaction time. From the mass balance calculation, α_t can be estimated as a function of t .

$$\alpha_{t+dt} = \alpha_t \times \frac{1 - \frac{L+Q}{V_{H,t} + V_{D,t}} + \frac{\alpha_{ini}}{\alpha_{ini} V_{H,t} + V_{D,t}} \times \left(Q - \frac{IV}{2F}\right)}{1 - \frac{L+Q}{V_{H,t} + V_{D,t}} + \frac{1}{\alpha_{ini} V_{H,t} + V_{D,t}} \times \left(Q - \frac{IV}{2F}\right)} \quad (2-20)$$

where L represents the volume rate of hydrogen gas out from the system, and Q denotes the volume rate of supplied gas. $V_{H,t}$ and $V_{D,t}$ represent the remaining gas volume of H and D, respectively, at t . The initial separation factor α_{ini} is original value non-gas circulation system^[28]. The detailed derivation of Eq. (2-20) is provided in the supplementary material.

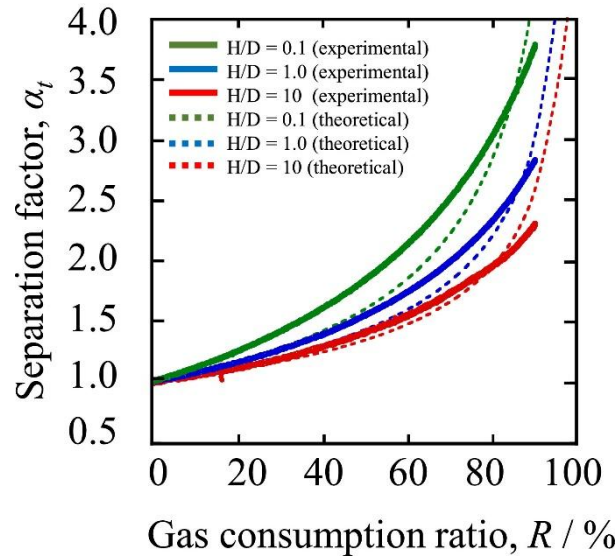


Figure 2-5. Separation factor α_t vs. H concentration on hydrogen gas consumption ratio during power generation using mixed hydrogen gas with initial H/D ratios of 10 (red), 1.0 (blue), and 0.1 (green). Solid lines represent the experimental data, and dashed lines indicate the theoretical data.

Fig. 2-5 shows the variation in the separation factor α_t as a function of R . The solid lines represent experimental values. H was enriched in the tank. The experimental α_t increased by 2.3, 2.8, and 3.8 for initial H/D ratios of 10 (red line), 1.0 (blue one), and 0.1 (green one), respectively. The variation of α_t was exponential to R . In other words, a high R corresponds to a long reaction time. Moreover, since the gas volume in the tank is small, the H enrichment in the cell is more easily reflected in the gas concentration in the tank.

The dashed lines in Fig. 2-5 represent the estimation by Eq. (2-20). This value increased significantly when the initial H/D ratio was low. When R was below 80 %, the calculated values were lower than the experimental data. This indicates that, when a large amount of gas remained in the tank, H enrichment was promoted not only by the fuel cell reaction but also by VPCE. However, as gas consumption increased, water was generated within the cell, likely leading to flooding in the catalyst layer and deactivation of the platinum surface for VPCE. The discrepancy between the calculated and experimental values depended on the initial H/D ratio. At higher H concentrations, the water generated in the cell accumulates on the platinum catalyst surface, leading to partial catalyst deactivation. As a result, the vapor-phase chemical exchange reaction (VPCE) becomes less active, and the equilibrium of Eq. (2-17) shifted to the left.

2.4 Conclusions

In this study, D separation was conducted using a PEFC for mixed hydrogen gases with initial H/D ratios of 0.1, 1.0, and 10. The PEFC was equipped with hydrogen gas circulation system. As the gas volume decreased from 1000 mL to 100 mL, C_H exponentially increased to 54.6 at. %, 76.4 at. %, and 96.9 at. %, respectively. ATR-FTIR analysis revealed that the D concentration in the water vapor at the cathode was approximately 78 at. %. These results indicate that VPCE occurred, and D transferred from the anode gas to the water vapor at the cathode.

In this experiment, α_t during power generation was calculated from the QMS results. H was enriched in the hydrogen gas in the tank. As the volume of hydrogen gas in the tank decreased, changes in H concentration were more easily reflected, resulting in an exponential increase in α_t with respect to R . α_t exhibited values different from the calculated values. During the initial part of power generation, VPCE was actively occurring and α_t was higher than the calculated values. However, as VPCE was suppressed by the product water covering the platinum catalyst, the increase of α_t became lower than the calculated values.

The results of this study may contribute to understanding the separation process within a single-pass PEFC. R in this study can be regarded as the hydrogen gas utilization rate in a single-pass PEFC.

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***Chapter 3: Effect of anode gas circulation on deuterium
isotope separation by polymer electrolyte fuel cell***

3.1 Introduction

Deuterium(D) and tritium (T), which are hydrogen isotopes, are widely used in nuclear applications^[1], materials science, and medical fields^[2]. New methods of effectively separating and recovering individual isotopes would be desirable to satisfy these increasing demands.

Various methods of separation have been studied on the basis of physicochemical approaches. Chemical exchange methods between water-hydrogen^[3] and hydrogen-hydrogen sulfide are also used commercially^[4]. Cryogenic distillation based on the difference in boiling points of hydrogen isotopes is used in the head separation process^[5]. New strategies have also been reported, such as hydrogen pumping with graphene^[6,7] and sieving with zeolites^[8].

Water electrolysis is well known for having a high separation efficiency^[9-16], where alkaline electrolysis is most commonly used. Recently, water electrolysis with solid polymer membranes has also been shown to provide effective isotopic separation^[11-13]. Alternatively, D may be separated through hydrogen fuel cell reactions, which are the reverse of the electrolysis process^[17-22]. When a mixture of H₂ and D₂ gases is supplied to a PEFC, D becomes enriched in the water phase and H is enriched in the gas vented from the cell. Pozio et al. reported effective isotopic separation at a Pt-Ru catalyst anode^[18], where the isotopic separation and its dependence on current density were studied by electrochemical impedance measurements and infrared analysis.

Isotope separation is evaluated by the separation factor α , which denotes the change in the ratio of H and D isotope content of gas entering and leaving the cell. Typically, when the feed gas flow rate is much larger than the rate of oxidation, α approaches 1.0, because the majority of the feed gas passes through the

cell. Yanase et al. reported that α typically ranges from 3.46 to 3.99 and increases at lower feed gas flow rates or at higher rates of oxidation^[21]. We have previously reported that α increases together with the gas consumption ratio^[23,24]. Tanii et al. conducted experiments with a modified fuel cell stack^[23] that allowed gas to flow through individual cells in sequence. This unique configuration markedly improved α by prolonging the reaction distance and residence time. Thus, H enrichment in the output gas depends not only on the nature of the electrochemical catalysts, but also on engineering factors, such as the gas flow in the PEFC system.

The PEFC system has been extensively developed for automobiles to allow hydrogen gas to circulate, improving gas utilization^[25] and water management^[26]. Although isotope separation mechanisms within a single cell have been extensively studied, the influence of gas circulation has received little attention. We consider that the application of anode gas circulation may improve isotope separation efficiency in PEFCs.

Here, we studied a gas circulation system for isotope separation. Respective enrichment of H and D in the gas and water phases were investigated as various circulating gas rates and power currents.

3.2 Experimental

3.2.1 Experimental setup

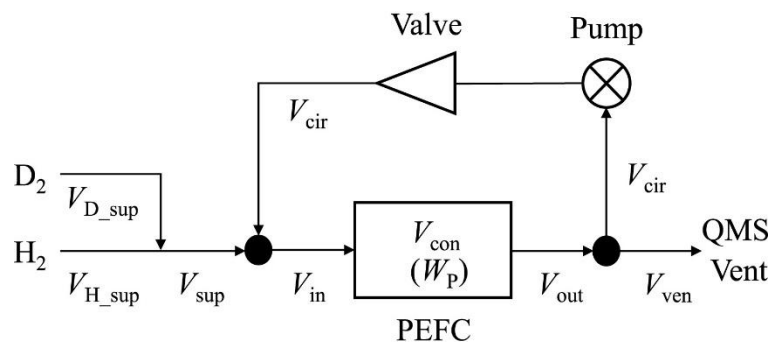


Figure 3-1. Schematic illustration of hydrogen gas circulation setup with some gas rate symbols.

The PEFC was a Japan Automobile Research Institute (JARI) standard single cell (FC Development Corp., Japan). The anode and cathode were carbon paper (TGP-H-120, Toray Industries, Japan) loaded with Pt catalyst (0.3 mg cm^{-2}). The electrode area was 25 cm^2 . Both electrodes were hot-pressed with a proton exchange membrane (NRE 212, DuPont, USA). Power generation was galvanostatically controlled by a variable resistor (PLZ164WA, Kikusui Electronics Corp., Japan). The cell was operated at room temperature. Pure O_2 gas from a cylinder was supplied to the cathode at a flow rate of $20 \times 10^{-3} \text{ L min}^{-1}$ through a flow controller (MC 200 SCCM, Alicat Scientific, USA).

Hydrogen gas was circulated in the form of pure H_2 and D_2 (99.9%D) gas (Fig. 3-1). A flow controller was installed in each gas line. The hydrogen gas discharged from the PEFC was divided into either a vent or circulation line. A small pump (APN-085EX-1-W, Iwaki, Japan) and a flow meter with a needle valve (RK1200, KOFLOC,

Japan) were fitted to the circulation line. The flow rate of the circulating gas V_{cir} was adjusted with the use of a flow meter. A pressure gauge (AP-C30, Keyence, Japan) was installed in the circulation line and constantly monitored the gas pressure.

A quadrupole mass spectrometer (QMS, Qutee-HGM 202, Ulvac Inc., Japan) was connected to the vent line. Isotopes in the gas with mass number $m = 2$ (H_2), 3 (HD), and 4 (D_2), were monitored. The atomic ratio of [H] to [D] in the gas was evaluated by the separation factor (heads separation factor on H) α as:

$$\alpha = ([\text{H}]_{\text{out}}/[\text{D}]_{\text{out}}) / ([\text{H}]_{\text{sup}}/[\text{D}]_{\text{sup}}) \quad (3-1)$$

Where [L] reflects the atomic concentration of the hydrogen isotopes, and the subscripts out and sup indicate the gas output from the PEFC and that supplied from the cylinder, respectively.

3.2.2 Mass flow chart

Fig. 3-1 shows the mass flow chart of hydrogen gas. The gas circulation flow rate V_{cir} was varied, while the overall flow rate of the gas supply, $V_{\text{sup}} (= V_{\text{H_sup}} + V_{\text{D_sup}})$, was fixed. The gas circulation ratio λ is defined as:

$$\lambda = V_{\text{cir}} / V_{\text{sup}} \quad (3-2)$$

And the gas utilization ratio U is expressed by the gas consumption rate V_{con} divided by the total flow rate of the hydrogen gas inlet to the cell V_{in} as:

$$U = V_{\text{con}} / V_{\text{in}} = V_{\text{con}} / (V_{\text{sup}} + V_{\text{cir}}) \quad (3-3)$$

V_{con} was calculated from the power current I and expressed by λ and U from Eqs. (3-2), (3-3) as:

$$V_{\text{con}} = V_{\text{mol}} \times (I \times 60) / 2F = (1 + \lambda) \times V_{\text{sup}} \times U \quad (3-4)$$

Where F is the Faraday constant, and V_{mol} is the molar volume rate of hydrogen gas.

While gas is consumed at the anode, water is produced by the fuel cell reaction at the cathode. The water production rate W_p was calculated from the power current I or expressed by λ and U from Eq. (3-4) as:

$$W_p = W_{\text{mol}} \times (I \times 60) / 2F = (1 + \lambda) \times V_{\text{sup}} \times U \times W_{\text{mol}} / V_{\text{mol}} \quad (3-5)$$

Where W_{mol} is the molar volume of the liquid water.

The flow rate of the vent gas, V_{ven} , is calculated as:

$$V_{\text{ven}} = V_{\text{out}} - V_{\text{cir}} = (V_{\text{in}} - V_{\text{con}}) - V_{\text{cir}} = (V_{\text{sup}} + V_{\text{cir}}) - V_{\text{con}} - V_{\text{cir}} = V_{\text{sup}} - V_{\text{con}} \quad (3-6)$$

3.3 Results and Discussion

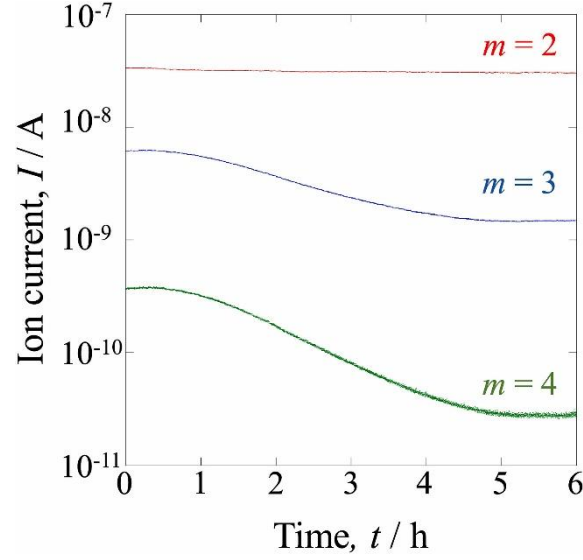


Figure 3-2. Typical QMS data of the anode gas during the separation experiment, (red: H₂, blue: HD, green: D₂).

Fig. 3-2 shows the typical QMS data of the anode gas during the separation experiment ($\lambda = 0.7$, $U = 0.55$). The vertical axis is the ion current, which corresponds to the partial pressure of each element. The horizontal axis corresponds to the time from starting the power generation. We detected three gas components, H₂ ($m = 2$), HD ($m = 3$) and D₂ ($m = 4$). Clearly the more consumption of HD and D₂ was demonstrated by the power generation. The separation factor was obtained after confirming the steady state of the data.

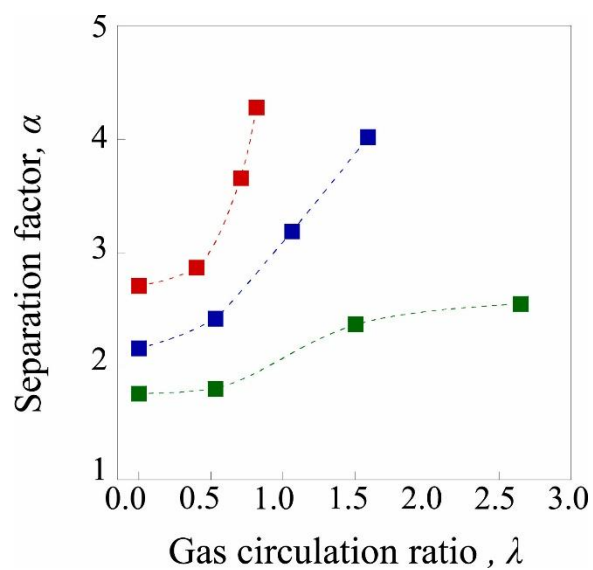


Figure 3-3. Dependence of separation factor α on circulation stoichiometry λ at various gas utilization rates, U (red: $U = 0.55$, blue: $U = 0.3$, green: $U = 0.2$).

Table 3-1. Summary of experimental parameters.

Gas utilization rate (U)	Gas supply ratio (λ)	Circulation gas volume ($V_{\text{cir}}/10^{-3} \text{ L min}^{-1}$)	Current density ($I/A \text{ cm}^{-2}$)
0.20	0.00	0.0	0.013
0.20	0.53	6.0	0.020
0.20	1.50	17	0.032
0.20	2.65	30	0.050
0.35	0.00	0.0	0.023
0.35	0.53	6.0	0.035
0.35	1.06	12	0.047
0.35	1.59	18	0.059
0.55	0.00	0.0	0.036
0.55	0.40	4.5	0.050
0.55	0.71	8.0	0.061
0.55	0.81	9.2	0.061

Fig. 3-3 shows the relationship between α and λ for each U . The experimental conditions are summarized in Table 3-1. The value of α increased as the circulation rate was increased from $\lambda = 0$. Higher gas circulation rates increased the enrichment of H in the gas phase, $C_{H(g)}$. This result is likely because the gas residence time in the circulation system was prolonged, allowing the separation reaction to occur repeatedly. Moreover, the gas volume influenced the separation. In Eq. (3-2), λ is defined as the ratio of V_{cir} to V_{sup} , such that at low λ , V_{sup} with 90 at%H is greater than V_{cir} with $C_{H(g)} > 90$ at%H [see Fig. 3-4 (b)]. Therefore, H dilution by V_{sup} increased as λ decreased.

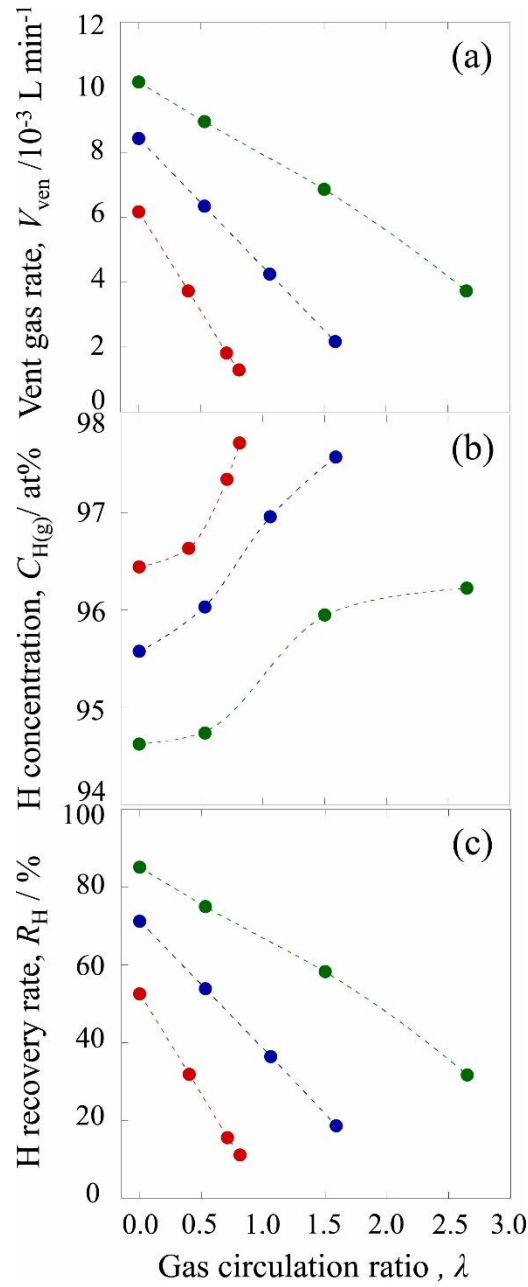


Fig. 3-4. Vent gas parameters including: (a) vent gas rate, V_{ven} ; (b) H concentration, $C_{\text{H(g)}}$; and (c) H recovery rate, $R_{\text{H(g)}}$ plotted against λ for various U values (red: $U = 0.55$, blue: $U = 0.3$, green: $U = 0.2$).

Separation also depended on U , and the relationship between α and U has been previously explained as an *apparent* effect^[23]. When a PEFC consumes a small volume of hydrogen gas, much of the outlet gas is unreacted. Therefore, $C_{H(g)}$ remains close to that of the inlet gas. The maximum value of α decreased from 4.3 to 2.6 as U decreased from 0.55 to 0.20 (Fig. 3-3).

The relationship between V_{ven} and λ is shown in Fig. 3-4(a). Notably, V_{ven} reached its maximum at $\lambda = 0$ (i.e., with no gas circulation). From Eqs. (3-4), (3-6), V_{ven} decreases proportionally with λ , with a slope that depends on U . Hence, when the PEFC is operated with low gas circulation and low gas utilization, V_{ven} becomes large. For instance, V_{ven} was approximately $9.0 \times 10^{-3} \text{ L min}^{-1}$ at $U = 0.2$ and $\lambda = 0.5$, reflecting that approximately 80% of the input V_{sup} was vented from the system. Conversely, the venting of V_{sup} decreased to approximately 10% at $U = 0.55$ and $\lambda = 0.8$.

The value of $C_{H(g)}$ was obtained directly from the QMS data. Fig. 3-4(b) shows the relationship between $C_{H(g)}$ and λ . Enrichment of $C_{H(g)}$ was greater at high U and λ . For example, the maximum value was approximately 97.8 at% at $U = 0.55$ and $\lambda = 0.8$. The value of α was calculated by fixing the ratio ($[H]_{\text{sup}}/[D]_{\text{sup}} = 10.0$) in the denominator of Eq. (3-1). However, the present calculation did not compensate the mixture of $C_{H(g)}$ in either V_{sup} and V_{cir} . When λ decreased (i.e., because of smaller V_{cir} or larger V_{sup}), $C_{H(g)}$ decreased owing to the dilution of V_{sup} .

Hydrogen gas is oxidized to hydron at the anode, whereas hydron react with oxygen that is reduced at the cathode forming water. We estimated how much H was recovered from V_{ven} [Fig. 3-4(c)], where the H recovery rate, $R_{H(g)}$, was obtained as follows:

$$R_{H(g)} = \frac{[H]_{out} \times V_{ven}}{[H]_{sup} \times V_{sup}} \times 100 \quad (3-7)$$

$$[H]_{out} = C_{H(g)} \quad (3-8)$$

The plots in Fig. 3-4(c) are similar to those in Fig. 3-4(a), although in the latter R_H was a function of $C_{H(g)} \times V_{ven}$. We attribute this result to the small $C_{H(g)}$ variation (<4%) over the range of λ values. The value of R_H decreased as λ increased. Gas circulation promoted H mass transport from the anode to cathode, because it increased the gas utilization. The H was output as water at the cathode. For the same reason, R_H decreased with increasing U : 32%–85% at $U = 0.2$, 19%–71% at $U = 0.35$, and 11%–53% at $U = 0.55$.

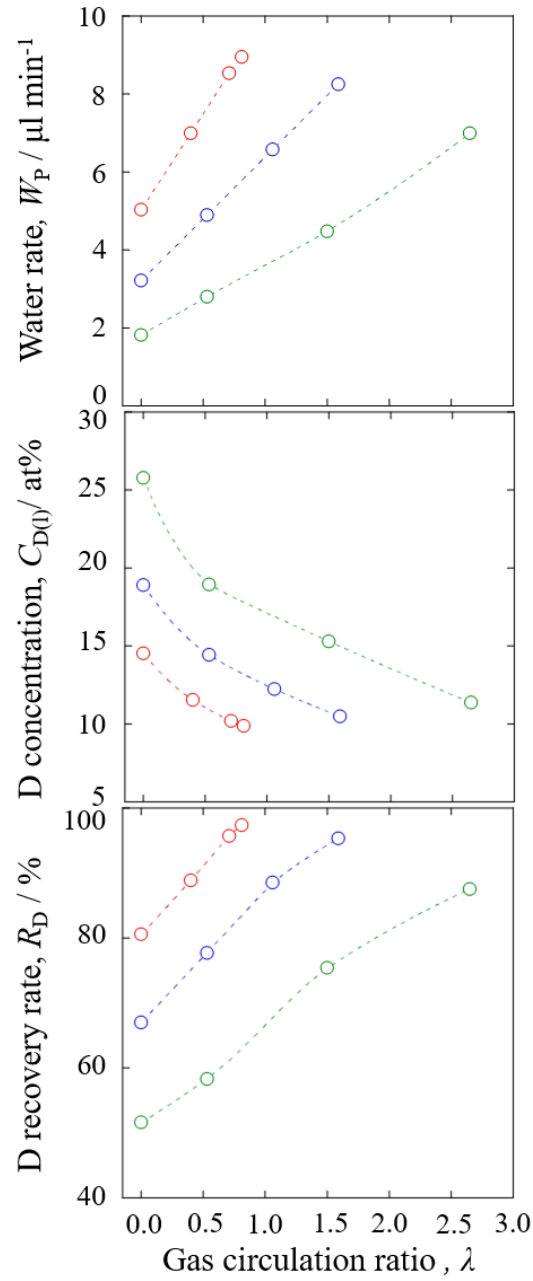


Figure 3-5. Product water parameters including: (a) water production rate; $\dot{W}_p$, (b) D concentration, $C_{D(l)}$; and (c) D recovery rate, R_D plotted against λ for various U values (red: $U = 0.55$, blue: $U = 0.3$, green: $U = 0.2$).

Whereas H enriches in the gas phase, D concentrates in the water phase. We characterized the water (Fig. 3-5) in the same manner as for the gas (Fig. 3-4). Fig. 3-5(a) shows the relationship between W_p and λ at each U . W_p increases together with λ , owing to improved gas utilization. Therefore, the profiles in Fig. 5(a) appear to be the inverse of those in Fig. 3-4(a).

The D concentration in the water phase, $C_{D(l)}$, was obtained as:

$$C_{D(l)} = \frac{[D]_{\text{sup}}V_{\text{sup}} - [D]_{\text{out}}V_{\text{ven}}}{V_{\text{con}}} \times 100. \quad (3-9)$$

Overall, $C_{D(l)}$ was higher than the D concentration in V_{sup} (9 at%D), as shown in Fig. 3-5 (b). The maximum value of $C_{D(l)}$ occurred at each value of U when no gas was circulated ($\lambda = 0$). The values were 25.8% at $U = 0.2$, 18.9% at $U = 0.35$, and 14.5% at $U = 0.55$. Hence, $C_{D(l)}$ decreased as λ increased. This result is attributed to the $C_{H(g)}$ variation. As discussed regarding Fig. 3-4(b), gas circulation increases $C_{H(g)}$ in the hydrogen gas. Thus, as λ increases, the D concentration in V_{in} decreased close to the initial concentration of 9 at%D.

The D recovery rate, $R_{D(l)}$, was calculated as:

$$R_{D(l)} = \frac{\frac{C_{D(l)}}{100} \cdot \frac{W_p}{W_{\text{mol}}}}{\frac{V_{D,\text{sup}}}{V_{\text{mol}}}} \quad (3-10)$$

The results of Fig. 3-5(c) show that gas circulation had a positive effect on $R_{D(l)}$. Notably, W_p increased with increasing λ [Fig. 3-5(a)]. A corresponding greater mass of D

was transported from the anode to the cathode, increasing the total output of D from the cathode. We note that $R_{D(l)}$ did not show the same plot profiles as discussed in Fig. 3-4(c), because the $C_{D(l)}$ variation was greater than that of $C_{H(g)}$. The value of $R_{D(l)}$ depends on U , which controls the D mass transport as: 52%–88% at $U = 0.20$, 67–95% at $U = 0.35$, and 81–97% at $U = 0.55$. The present results indicate that almost 100% of the D from V_{sup} was recovered at $\lambda = 0.81$ and $U = 0.55$.

3.4 Conclusions

In this study, a circulation system of hydrogen gas was employed for hydrogen isotope separation by PEFC in which 10 at% D was introduced. The effect of λ on H and D separation was investigated. As λ increased, H was concentrated in the gas at the anode outlet due to the prolonged residence time and repeated separation reactions. As the gas utilization increased, D was separated more efficiently. The separation factor at this time was 4.2, and the separation factor was 1.8 when $\lambda = 0$ and $U = 0.20$.

Calculations using the mass balance showed that D transported to the product water at the cathode. As λ increased, the current increased with promoting H transportation to the cathode. This diluted the D concentration in the water at the cathode. The concentration decreased with increasing the gas utilization rate. The calculation of the recovery rate $R_{D(l)}$ demonstrated that most of the supplied D could be recovered as produced water.

Our results supported that the gas circulation helped the isotope separation more efficiently. The desired volume or concentration of the isotope production could be controlled by λ .

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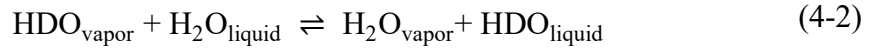
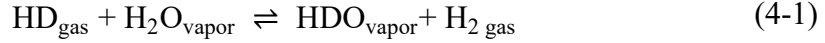
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***Chapter 4: Deuterium Isotope Separation using LiCl–
KCl–LiH–LiD Molten Salt***

4.1 Introduction

Hydrogen is a promising material for decarbonization. It comprises three isotopes: protium (H), deuterium (D), and tritium (T). The demand for D and T is continuously increasing in the materials^[1,2] and medical fields^[3,4]. Moreover, a fusion reactor based on the DT reaction⁵ could be a key to establishing a carbon-neutral society. Therefore, novel and efficient methods are required to separate hydrogen isotopes.

A few methods, such as cryogenic distillation^[6,7] and hydrogen-hydrogen sulfide exchange reactions (Girdler sulfide process)^[8], have been commercially employed to separate hydrogen isotopes. Moreover, the water-hydrogen exchange reaction has been extensively investigated because of its simple reaction system^[9]. The reaction proceeds via the following two steps given in Eqs. 4-1 and 4-2:



The reactions in Eqs. 4-1 and 4-2 are known as vapor-phase chemical exchange (VPCE) and liquid-phase chemical exchange (LPCE), respectively, depending on the state of the water. The VPCE occurs on the catalyst surface, whereas the LPCE occurs at the interface between the liquid and gas phases. The catalysts can be modified with surfactants to overcome the complex water-management problem. Ye et al. studied the effect of a foaming agent, such as polymethyl methacrylate (PMMA), on the separation efficiency at different hydrogen gas flow rates and observed that the separation efficiency decreased as hydrophobicity increased with the addition of PMMA^[9].

New methods, such as electrochemical pumping with graphene^[10,11] and sieving with zeolites^[12], have been reported for isotope separation. Additionally, water electrolysis is widely recognized for its high separation efficiency. Therefore, several studies have investigated alkaline water electrolysis and water electrolysis using proton exchange membranes (PEMs)^[13–15]. Zeng et al. performed D separation using a highly durable PEM^[16]. Isotope separation performance is evaluated using the separation factor, α , which is the $[H]/[D]$ atomic ratio of the generated gas divided by the $[H]/[D]$ atomic ratio of the electrolyte; $\alpha > 1.0$ indicates that the generated gas is enriched with H. Zeng et al. reported α values between 2.6 and 4.2, indicating that H was enriched in the evolved gas. The results varied with the D concentration, cell temperature, and current density. In our previous work, we used PEM electrolysis for D separation^[17–19]. For example, we investigated the effect of water transportation on α and reported that α (β in the literature) ranged from 2.1–2.9, decreasing with increasing current density^[17].

However, these techniques are limited by their high energy consumption and limited processing capabilities^[20,21]. In this study, we addressed these challenges by focusing on molten-salt electrolysis. Molten salts allow hydrides to dissolve as anions (H^- and D^-), which are converted into hydrogen gas through anodic reactions, and their behavior and properties may differ from those of H^+ and D^+ in aqueous solutions. Nohira et al. investigated the electrochemical behavior of H^- in LiCl–KCl eutectic melts^[22], where LiH (0.4–2.0 mol%) was used as a source of H^- ions. The diffusion coefficient of H^- was determined through cyclic voltammetry (CV) and chronopotentiometry measurements, which ranged from $1.7\text{--}2.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 673 K.

Hydrogen isotope separation via molten-salt electrolysis might also be used for tritium extraction technology from the breeding blanket of a fusion reactor. Breeding

blankets absorb neutrons released during the fusion reaction to produce tritium from lithium. Produced tritium must be extracted from the breeding blanket. Molten-salt electrolysis has been considered and studied as one of the techniques to extract tritium from the breeding blankets^[23,24]. Recently, Ito et al. proposed a process to apply liquid lithium not only to breeding blankets but also to liquid electrodes in the electrolytic extraction to simplify the multiple steps and mechanical equipment^[25]. They achieved H₂ extraction from a liquid lithium electrode containing LiH via molten salt electrolysis. Although a few reports have been on molten-salt electrolysis using hydrogen isotopes, hydrogen isotope separation and quantitative evaluation using separation factors have rarely been performed. Moreover, it is unclear whether the isotope exchange reactions occurring naturally during water electrolysis also occur in molten salts.

The current study aimed to investigate the electrochemical behavior of D⁻ in a LiCl–KCl molten-salt system with LiD as an additive. Further, we attempted D separation and compared the results with those using aqueous solutions.

4.2 Experimental

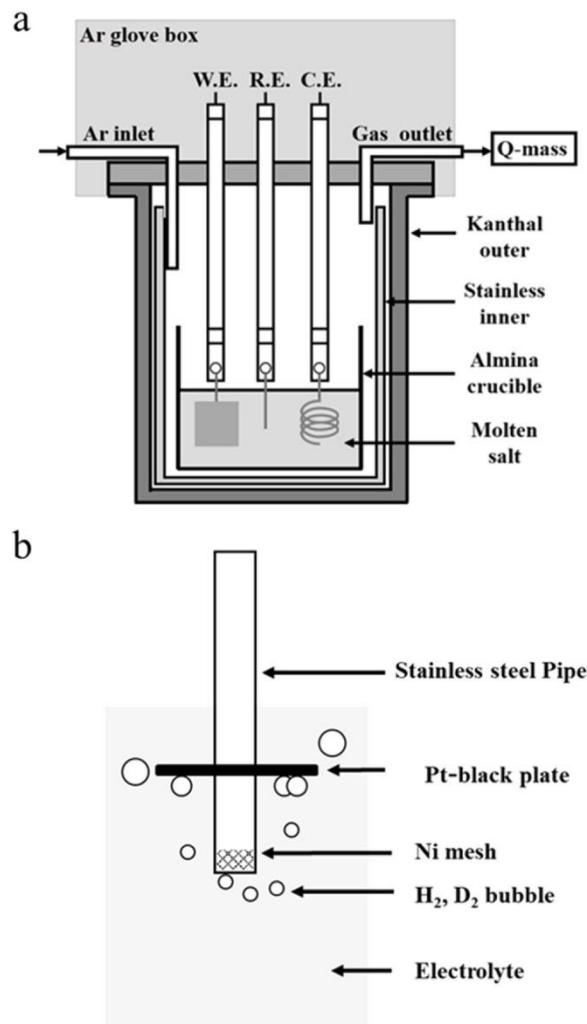


Figure 4-1. Schematic illustration of the experimental apparatus: (a) electrolysis in molten salt and (b) H–D exchange reaction in the electrolyte.

The WE for electrochemical measurement was Mo flag (ϕ 0.3 cm $\times$ 0.01 mm, Nilaco Corp., Japan), and its detailed structure has been reported previously^[26]. The WE for electrolysis was a laboratory-made square sheet (0.1 cm $\times$ 1.0 cm $\times$ 1.0 cm) of Pt-

black. The electrode was prepared by Pt electrodeposition at -76 mA cm^{-2} in an aqueous solution (100 ml) containing H_2PtCl_6 (2.0 g, Kanto Chemical Corp., Japan) and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ (0.02 g, Kanto Chemical Corp., Japan)^[27,28]. The CE was a helically bent Al wire. Al–Li alloy in the coexisting ($\alpha + \beta$) phase state, electrochemically prepared from Al wire, was used as the reference electrode (RE)^[29–31]. The potential was calibrated using Li^+/Li determined by cyclic voltammetry (CV) on a Ni electrode. Electrochemical measurements were performed using a potentiostat/galvanostat (HZ-3000; Hokuto Denko Corp., Japan).

The isotope exchange reaction in molten salt was carried out on a laboratory-made Pt-black plate ($2.0 \times 2.0 \text{ cm}^2$). This plate featured a hole in the center to insert a stainless steel pipe through it. A Ni mesh (100 mesh; Nilaco Corp., Japan) was spot welded to the pipe as a gas filter (Fig. 4-1b). The gas flow rates of H_2 and D_2 were adjusted to 1.6 ml min^{-1} .

Aqueous electrolysis was conducted at 298 K and atmospheric pressure. The electrolyte was 1 M HClO_4 with 50 at% D from D_2O (Isotec International Inc., USA). The WE was the Pt-black ($1.0 \times 1.0 \text{ cm}^2$), whereas CE and QRE were Pt wires ($\phi = 0.3 \text{ cm}$; Nilaco Corp., Japan). The isotope exchange reaction was investigated using the same setup as in the molten-salt experiment (Fig. 4-1b). The flow rate of H_2 and D_2 gases was 1.6 ml min^{-1} , and their ratio was controlled to be $\text{H:D} = 1:1$ using a mass flow controller. A quadrupole mass spectrometer (QMS) (Qulee HGM202, ULVAC Inc., Japan) was installed on the exhaust gas line of the cell.

4.3 Results and Discussions

4.3.1 Electrochemical characterization of D^-

Electrochemical data on D^- is limited; therefore, we performed CV in molten salt with 0.4 mol% LiD at 673 K (Fig. 4-2a). The Mo electrode was selected as the WE because it absorbs negligible hydrogen. When the potential is applied at various sweep rates between 0.2–5.0 $V\ s^{-1}$, anodic peak currents appear at approximately 0.75 V vs Li^+/Li , and the peak currents increase with the sweep rate. The formation of these peaks could be attributed to the rate-limiting mass transfer of the reactants. The potential was reversed in the cathodic direction at 1.0 V, and at the fastest sweep rate of 5.0 $V\ s^{-1}$, a small cathodic peak appears at approximately 0.68 V. This peak is not observed at slower sweep rates.

Some studies have investigated the electrochemical oxidation of hydride ions (H^- and D^-) in molten salts^[22,32] and reported the anodic peak current at approximately 0.7 V. Therefore, the anodic current peak is confirmed as the D^- oxidation ($2D^- \rightarrow D_2 + 2e^-$). The produced D_2 gas dissolves in the salt and forms bubbles. The small cathodic current corresponds to a reduction of the dissolved D_2 gas to D^- anions. However, the cathodic peak current is poorly defined, which contrasts with the anodic peak current. The results suggest that the concentration of the dissolved D_2 gas is extremely low, which is affected by the electrode arrangement and gas motion^[33].

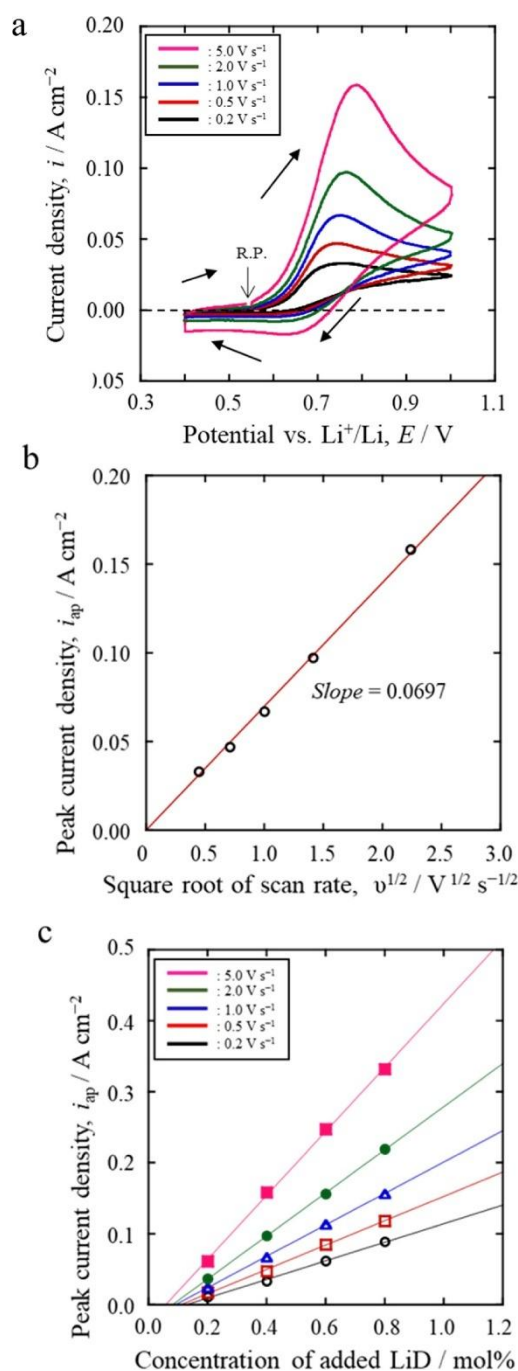


Figure 4-2. Investigation of electrochemical behavior of D^- with Mo electrode in $LiCl-KCl-LiD$ (0.4 mol%) molten salt at 673 K: (a) cyclic voltammogram at various sweep rates (0.2–5.0 $V\ s^{-1}$) in 0.4–1.0 V potential range vs Li^+/Li , (b) current density of anode peak, i_{ap} , depending on the square root of scan rate, and (c) i_{ap} at various LiD concentrations (0.2–0.8 mol%).

The diffusion coefficient of D^- , D_D , is calculated using Eq. 4-3:^[34]

$$i_{ap} = 0.446nFC_D \left(\frac{nF}{RT} \right)^{1/2} v^{1/2} D_D^{1/2} \quad (4-3)$$

where i_{ap} is the current density of the anodic peak current, C_D is the concentration of D^- , and v is the sweep rate of potential. Figure 4-2b shows that i_{ap} is proportional to $v^{1/2}$. Figure 4-2c shows the relationship between i_{ap} and the LiD concentration to determine the C_D value. The current density of i_{ap} increases linearly with increasing concentration, indicating that i_{ap} is determined by the oxidation of D^- , as discussed above. None of the straight lines fitted at any sweep rate converge to the origin, which is attributed to the consumption of LiD by side reactions with impurities, such as water and heavy metal ions. However, the concentration of consumed D^- was estimated to be 0.10 ± 0.03 mol%.

The value of C_D was obtained by subtracting the amount of LiD consumed from the amount of LiD added. The salt density was obtained from the previous data.^[35] Assuming the oxidation reaction to be a one-electron reaction ($n = 1$), D_D was estimated to be $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 673 K. This value closely corresponds with the diffusion coefficient of H^- ($D_H = 1.7\text{--}2.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), which was previously investigated via CV.^[22] Takenaka et al. reported a relatively high diffusion coefficient of D^- ($D_D = 4.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) at the same temperature^[32], which was attributed to the use of an iron electrode that was possibly influenced by hydrogen absorption and hydrogen generation.

4.3.2 D separation

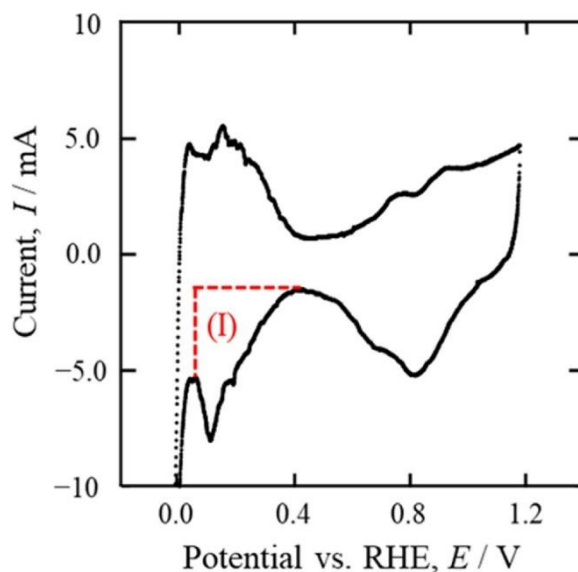


Figure 4-3. Cyclic voltammogram of Pt-black electrode in 1 M HClO₄ at 0.01 V s⁻¹ scan rate at 298 K. The hydrogen adsorption area is shown as area (I) surrounded by dotted lines.

D separation was performed using laboratory-made Pt-black electrodes. The roughness factor, R_f , of these electrodes was determined to evaluate their electrochemical surface areas (ECSA). We measured the hydrogen adsorption wave during CV in a 1 M HClO₄ solution at 298 K before the separation experiment (Area I in Fig. 4-3). Hydrogen adsorption equivalent to 210 $\mu\text{C cm}^{-2}$ has been previously reported^[27,28,36], which allowed us to estimate the roughness as $R_f \cong 106$. Current density calculations were performed using the ECSA.

In the molten-salt system, equal quantities (1.0 mol%) of LiH and LiD were introduced into the melt, followed by the initiation of potentiostatic electrolysis. The

potential is set to 0.7 V vs Li^+/Li to produce the initial anodic current density of 0.8 A cm^{-2} (Fig. 4-4a). The current density decreases considerably as the electrolysis time increases. The exact reasons for this phenomenon are unclear; however, it could be owing to a reduction in the hydride ion (H^- and D^-) concentration or bubbles adhering to the electrode. As the electrolysis continues, the current density approaches zero. The hydrogen gas generated during the electrolysis was channeled directly from the cell to the QMS. Owing to the large ECSA of the Pt-black electrode, the current flow was sufficiently high to allow hydrogen gas detection using QMS.

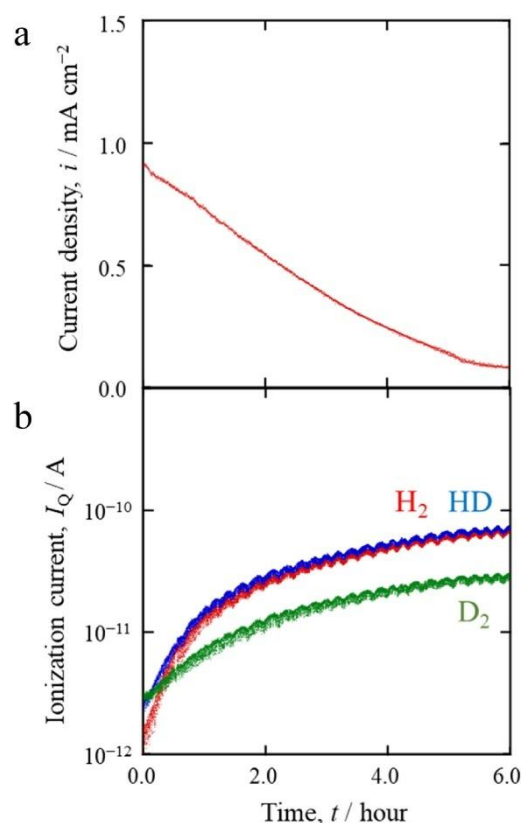


Figure 4-4. Electrolysis at 0.7 V vs Li^+/Li with Pt-black electrode in LiCl–KCl molten salt containing 1.0 mol% of LiH and LiD at 673 K: (a) time variation of current density, (b) QMS ionization current of each gas component in the hydrogen gas from the cell.

The ionization currents of the mass numbers ($m = 2, 3$, and 4) obtained using QMS are shown in Fig. 4-4b. The currents correspond to the partial pressures of the gas components (H_2 , HD, and D_2) in the hydrogen gas. The ionization currents stabilized approximately 4 h after the electrolysis initiation. This stabilization occurred because the original argon gas was replaced by the hydrogen, which filled the cells and piping, and subsequently, the currents maintained a steady state. The volumes of HD and H_2 produced were equal, and approximately twice that of D_2 . Based on the ionization currents in Fig. 4-4b, the separation factor α was calculated using Eq. 4-4 as follows:^[37]

$$\begin{aligned}\alpha &= ([H]/[D])_{\text{gas}} / ([H]/[D])_{\text{electrolyte}} \\ &= [(I_{H_2} \times 2 + I_{HD}) / (I_{D_2} \times 2 + I_{HD})]_{\text{gas}} / 1.0\end{aligned}\tag{4-4}$$

where $[L]$ represents the concentration of each atom and I_x is the ionization current of gas x . If α is greater than 1.0, substance H is enriched in the outlet gas. In this study, α was calculated to be approximately 1.6, indicating that H was concentrated in the outlet gas.

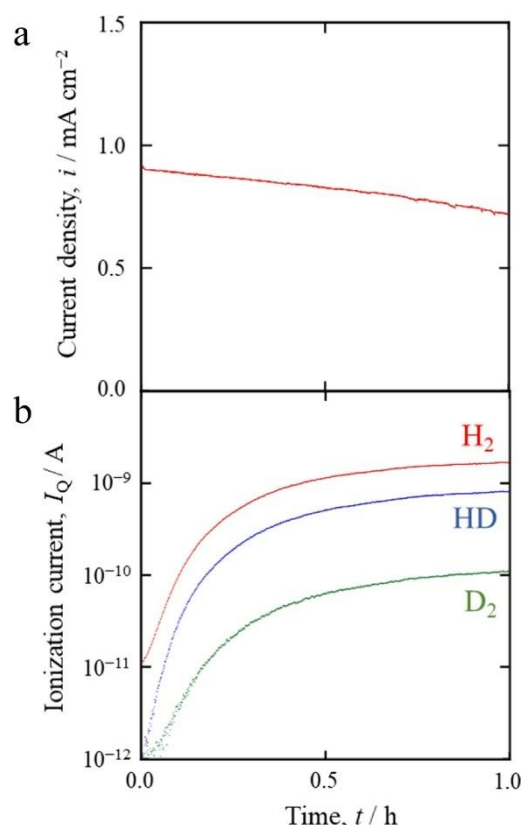


Figure 4-5. Electrolysis at -0.7 V vs RHE with Pt-black electrode in 1 M HClO₄ solution containing 50 at% D at 298 K: (a) time variation of current density, (b) QMS ionization current of each gas component in the hydrogen gas from the cell.

For comparison, the separation was conducted in an aqueous solution. The electrolyte used was 1 M HClO₄, and the D concentration was adjusted to 50 at% using D₂O. Figure 4-5a shows the transient behavior of the cathodic current density when the electrolysis was conducted at -0.7 V vs RHE at 298 K. The current density is similar to that in the molten-salt experiment, with numerous hydrogen gas bubbles evolving after the initiation of electrolysis. A marginal change in both the current value and bubble production is observed after 1 h of electrolysis. Similar to that in the molten-salt system, the hydrogen gas produced by electrolysis was analyzed using QMS (Fig. 4-5b). The gas

components are primarily H_2 , HD, and D_2 , in that order. A remarkable quantity of H is concentrated in the gas, greater than that obtained in the molten-salt system, as shown in Fig. 4-4b. The value of α is approximately 3.9. The current results agree with those of previous studies using Pt catalyst^[17,18]. The results exhibit that electrolysis in molten salt has a smaller value of α than that in aqueous solution systems.

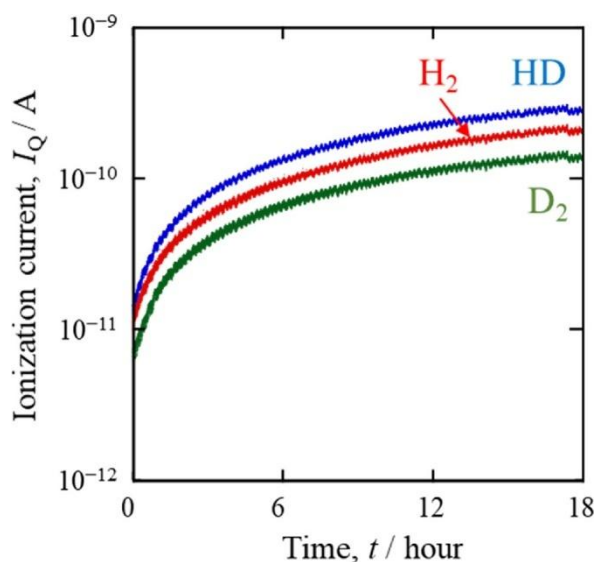


Figure 4-6. QMS ionization current of each gas component in the hydrogen gas when the gas mixture of H_2 and D_2 was introduced into LiCl–KCl molten-salt system with 1.0 mol% of LiH and LiD at 673 K.

Approximately 12 h after gas introduction, hydrogen replaces argon, and the ionization currents reach a steady state. The resulting hydrogen gas comprises HD, H_2 , and D_2 (in that order), and the value of α is approximately 1.3. The enrichment of the gas with H and the presence of a considerable quantity of HD suggest the occurrence of an

exchange reaction. However, the quantities of water vapor and water in the molten salt are insufficient to account for the water–hydrogen exchange reaction depicted by Eqs. 4-1 and 4-2. The varying ratios of H₂ and D₂ indicate that this is not a simple exchange reaction (H₂ + D₂ → HD). One possibility might involve a reaction with hydride ions, as given in Eq. 4-5.



The chemical equilibrium would shift to the right at high temperatures in Eq. 4-5. Thus, D₂ would be consumed, leading to additional HD production. The separation performance, as described by Eq. 4-5, was approximately the same as that for the separation via the molten-salt electrolysis.

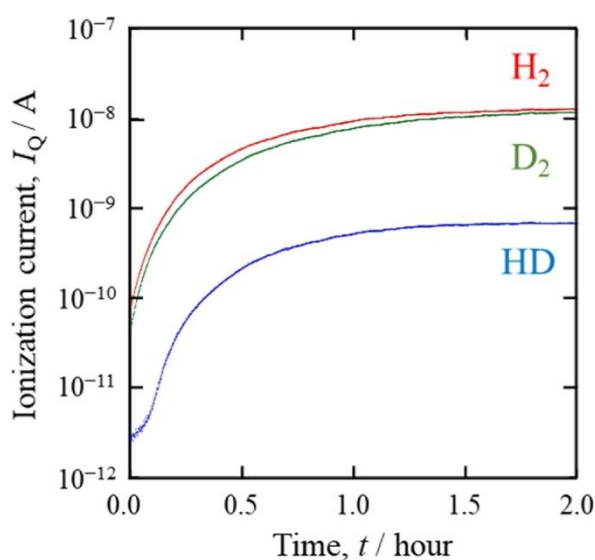


Figure 4-7. QMS ionization current of each gas component in the hydrogen gas when the gas mixture of H₂ and D₂ was introduced into 1 M HClO₄ solution at 298 K.

The ionization currents of the exchange reaction at 298 K in the aqueous solution system are given in Fig. 4-7. The ionization current remains stable for approximately one hour after the start of the measurement. In contrast to the experimental results for the molten salt (Fig. 4-6), the hydrogen gas primarily comprises H_2 and D_2 (in the same ratio) and a detectable volume of HD. The water-hydrogen exchange method is known to be less efficient than electrolysis. For example, the value of α was approximately 1.3 at room temperature^[38]. However, we obtain an $\alpha \approx 1.0$, indicating a minor exchange reaction. This could be attributed to the bubble dispersion. Furthermore, the average diameter of the bubbles is approximately 3 mm, which is larger than the filter pore size. Therefore, some bubbles could have aggregated on the filter. The poor dispersion of the bubbles probably reduces the contact efficiency between the gas and the catalyst, thereby impeding the exchange reaction. In the H–D exchange reaction, the molten-salt system exhibits higher α values than those in the aqueous solution system, contrasting with electrolysis.

4.4 Conclusions

In this study, we investigated the electrochemical behavior of D^- using a LiCl–KCl–LiH–LiD molten salt at 673 K and separated the hydrogen isotope through electrolysis and H–D exchange reaction. Further, we compared this separation performance with that of an aqueous solution system.

The electrochemical behavior of D^- in molten salts was investigated by CV in the 0.4–1.0 V range vs Li^+/Li at a sweep rate of 0.2–5.0 $V\ s^{-1}$. These tests were conducted with a Mo electrode in a LiCl–KCl electrolyte with added LiD. The diffusion coefficient of D^- was calculated to be $1.9 \times 10^{-5}\ cm^2\ s^{-1}$, which agrees with the previously reported diffusion coefficient of H^- ($1.7\text{--}2.2 \times 10^{-5}\ cm^2\ s^{-1}$).

We conducted a potentiostatic electrolysis at 0.7 V vs Li^+/Li using a Pt-black electrode in the LiCl–KCl–LiH–LiD molten salt. The value of α was 1.6, confirming H enrichment in the outlet gas. Conversely, we performed a potentiostatic electrolysis at $-0.7\ V$ vs RHE using a Pt-black electrode in 1 M $HClO_4$ with 50 at% D from D_2O , which yielded an α value of 3.9, indicating a substantial H enrichment.

The H–D exchange reaction was further investigated by spraying an H_2 – D_2 mixture gas (H:D = 1:1) onto a Pt-black plate in the same melt. The resulting α value was 1.3, confirming an enrichment of H in the emitted gas, which was different from that in the aqueous system. The molten-salt system did not contain any water vapor; therefore, the H–D exchange reaction occurred between D in the gas and H^- in the salt on the Pt-black catalyst. Additionally, an H_2 – D_2 mixture gas (H:D = 1:1) was sprayed onto a Pt-black plate in the aqueous solution to determine the occurrence of an H–D exchange reaction. The resulting α value of 1.0 indicated that a H–D exchange reaction did not occur.

In electrolysis, the molten-salt system had a lower α value than that of the aqueous solution system, while the molten-salt system had a higher α value in the H–D exchange reaction. For the further improvement of isotopes separation, it would be key point to control the three-phase interface among the electrolyte, D gas, and catalyst. The increase of the three-phase region in the molten salt would be more important for the practical facilities such as molten blankets in fusion reactors.

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***Chapter 5: Effect of Isotopic Exchange Reactions on
Deuterium Isotope Separation Using Electrochemical
Hydrogen Pumping with Liquid Electrolyte***

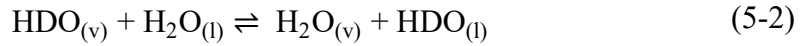
5.1 Introduction

Deuterium (D), a hydrogen isotope, is widely used not only as a process tracer but also in medical and nuclear technologies^[1-4]. Nuclear fusion reactors are considered a promising technology for achieving both decarbonization and large scale energy production^[5]. In such reactors, deuterium is used as one of the fuels. Despite the requirement for high purity and large quantities of D in fusion applications, its natural abundance is extremely low, approximately 0.015%. Therefore, D must be extracted and concentrated from sources such as seawater, wastewater from heavy water reactors, or exhaust gases from fusion reactors. Since hydrogen isotopes possess nearly identical chemical properties, their separation is difficult, and various techniques have been investigated^[6,7].

Various techniques such as absorption and quantum sieving have been studied for hydrogen isotope separation^[8,9]. In regions with high isotope concentrations, cryogenic distillation and water electrolysis are widely used^[10-14]. In contrast, for low - and medium-concentration regions, chemical exchange methods such as the Girdler Sulfide (GS) process and the Combined Electrolysis and Catalytic Exchange (CECE) process are commonly employed^[15-18]. These processes have high energy consumption and high equipment cost. The CECE process combines water electrolysis with isotopic exchange. It consists of a water electrolysis cell and some isotope exchange columns. In the CECE process, hydrogen gas generated from the water electrolysis is introduced into the bottom of the column and flows upward, while liquid water is introduced from the top and flows downward. The column is packed with two distinct layers. One is a platinum based catalyst layer, where following equilibrium reaction occurs between hydrogen gas and water vapor :



where, the subscripts g and v denote gas and vapor, respectively. This reaction is referred to as vapor phase catalytic exchange (VPCE), which proceeds on the surface of the platinum catalyst. The other layer contains a hydrophilic packing material that promotes the following equilibrium between water vapor and liquid water:



where l denotes the liquid phase. This reaction, known as liquid-phase catalytic exchange (LPCE), occurs at the vapor liquid interface. Thermodynamically, D is transferred from the gas phase to the liquid phase through the intermediate vapor phase, resulting in D enrichment in the liquid. Since the column consists of multiple stages, VPCE and LPCE occur repeatedly, producing a continuous isotopic exchange process. Consequently, the D concentration becomes higher toward the bottom of the column. This system requires a large apparatus and precise water management. The platinum catalyst surface, when covered with liquid water, loses its activity and suppresses the VPCE reaction, thereby reducing the overall separation performance. Therefore, some studies are focused on imparting hydrophobic properties to the platinum catalyst to improve hydrogen isotope separation efficiency^[19,20].

In this study, a polymer electrolyte membrane electrochemical hydrogen pump (PEM-EHCP) was employed. Since it utilizes the electrochemical oxidation and reduction of hydrogen, the energy consumption is remarkably low. Its cell configuration

is also compact. Therefore, EHCP has been widely studied for hydrogen purification and compression^[21-24]. Jackson *et al.* demonstrated hydrogen purification from CH₄ mixtures using EHCP^[25]. When a current density of 0.3 A cm⁻² was applied to gas mixtures containing 20, 50, and 80 % CH₄, the outlet hydrogen gas exhibited CH₄ concentrations of 21, 45, and 68 $\mu\text{mol mol}^{-1}$, respectively—values below the ISO standard limit. EHCP has also been applied to hydrogen isotope separation^[26,27]. Lozada-Hidalgo *et al.* employed graphene electrodes in EHCP. High separation factors of 8–10 were achieved for H₂/D₂ mixed gases^[26].

In addition, efficient D₂ generation systems using gas and liquid electrolytes have been proposed. Mondal *et al.* developed an electro dialysis-type cell using H₂ gas and NaOD/D₂SO₄ electrolytes, which generated D₂ gas with power generation^[28]. The cell consisted of an anode compartment filled with NaOD solution and a cathode compartment filled with D₂SO₄ solution, which were separated by a PEM. The pH difference between the two compartments created a potential difference, enabling D₂ evolution at the cathode instead of H₂ supplied to the anode.

Our group previously reported that VPCE occurs in a polymer electrolyte fuel cell(PEFC)^[29]. In this study, EHCP configuration was improved by introducing a liquid electrolyte to promote more efficient isotopic exchange. A schematic of the cell setup is shown in Fig. 5-1A. The liquid electrolyte was supplied to the central compartment, which was positioned between two PEMs. Each PEM is bordered on the outer side by a gas diffusion electrode (GDE) coated with platinum catalysts. In this configuration, water is transported from the electrolyte toward the catalyst layers on both the anode and cathode sides via diffusion and electro-osmotic drag. Hydrogen gas is supplied to the anode in counter flow to the electrolyte. In the flow channel, both VPCE and LPCE occur

between the transported water and the supplied hydrogen gas. D transfer proceeds through the water vapor between the gas and liquid phases. Due to the presence of numerous nanoscale platinum catalysts on the GDE, efficient hydrogen isotope separation can occur within the flow channels. Similar to that in the CECE process, the concentration of D in each phase is high near the gas inlet. This system is also expected to prevent the deactivation of platinum catalysts due to Liquid flooding, based on reports from EHCP and PEFC systems^[30,31]. Therefore, in this study, hydrogen isotope separation was investigated using a liquid electrolyte-fed EHCP system, and its separation performance was evaluated.

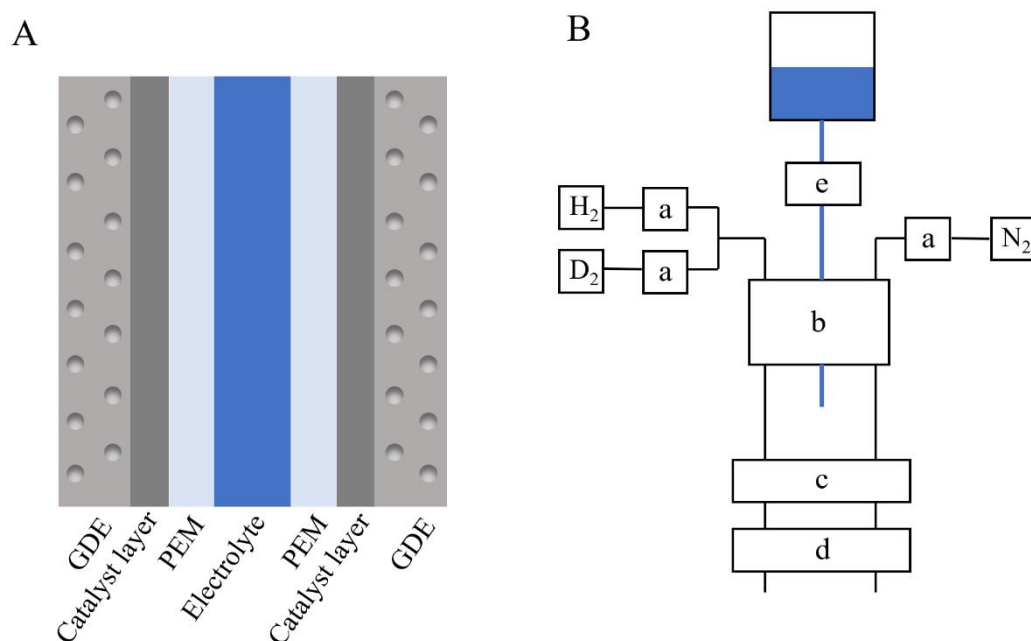


Figure 5-1. Schematic illustration of (A) the EHCP cell and (B) experimental setup (a: mass flow controller, b: EHCP cell, c: cold trap, d: QMS, e: peristaltic pump).

5.2 Experimental

5.2.1 Experimental setup

A schematic of the experimental setup is shown in Fig. 5-1B. A modified Japan Automobile Research Institute (JARI) standard single cell (FC Development Corp., Japan) was employed for the ECHP. At the center of the cell, a liquid compartment fabricated using a 3D printer was installed. The liquid compartment was positioned between two PEMs (NRE 212, DuPont, USA). On the outer side of each PEM, carbon paper electrodes (TGP-H-120, Toray Industries, Japan) as the anode and cathode were hot-pressed, respectively. The electrode area was 16 cm². Platinum catalysts (0.5 mg cm⁻²) were supported on the carbon paper. Pure H₂ and D₂ were mixed at a constant ratio (H/D = 10) and supplied to the anode at a constant flow rate. The flow rate was regulated by a mass flow controller (MC 200 SCCM, Alicat Scientific, USA). The liquid compartment was supplied with an electrolyte solution at a constant flow rate of 0.25 mL min⁻¹ using a peristaltic pump (MasterFlex 07528-30, Cole-Parmer Instrument, USA). An 0.01 M H₂SO₄ aqueous solution was used as the electrolyte. Electrolyte solutions with various H/D ratios (10, 100, and 6665) were prepared by mixing H₂O and D₂O. At an H/D ratio of 6665, the solution was prepared using only H₂O and H₂SO₄. All experiments were conducted at room temperature. The ECHP was operated under galvanostatic control using a DC power supply (PAS10-35, Kikusui Electronics, Japan). At the cathode, N₂ was supplied as a carrier gas at a constant flow rate of 20 mL min⁻¹. A cold trap (UT-1AS, ASONE Corp., Japan) were installed on both the anode and cathode exhaust lines to condense the water vapor contained in the exhaust gases. The condensed vapor and the water discharged via electro-osmotic drag and back diffusion were collected together as recovered water.

The recovered water was analyzed by attenuated total reflectance Fourier-

transform infrared (ATR-FTIR) spectroscopy (FTIR-4200, JASCO International, Japan). FTIR measurements were performed over the wavenumber range of 400–4000 cm^{-1} at a resolution of 2.0 cm^{-1} with 100 scans. The reference spectrum was recorded in ambient air.

A quadrupole mass spectrometer (QMS, Qulee-HGM 202, Ulvac Inc., Japan) was connected to the exhaust line to measure mass numbers 2 (H_2), 3 (HD), and 4 (D_2). The H/D ratio in the exhaust gas was calculated from the ion currents corresponding to each component obtained by mass spectrometry using the following equation:

$$\frac{\text{H}}{\text{D}} = \frac{i_{\text{H}_2} \times 2 + i_{\text{HD}}}{i_{\text{D}_2} \times 2 + i_{\text{HD}}} \quad (5-3)$$

where i is the ion current. Two types of separation factors were used to evaluate the separation performance. The separation factor α was determined using the following equation, based on the atomic ratio of hydrogen to deuterium (H/D) in the same sample at the inlet and outlet:

$$\alpha = \frac{\frac{[\text{H}]_{\text{out}}}{[\text{D}]_{\text{out}}}}{\frac{[\text{H}]_{\text{in}}}{[\text{D}]_{\text{in}}}} \quad (5-4)$$

where $[\text{L}]$ represents the atomic concentration of hydrogen isotopes, and the subscripts in and out denote the inlet and outlet, respectively. The separation factor β was calculated using the following equation, based on the atomic ratio of hydrogen to deuterium (H/D) in different species discharged from the cell:

$$\beta = \frac{\frac{[H]_{\text{sample}}}{[D]_{\text{sample}}}}{\frac{[H]_{\text{electrolyte}}}{[D]_{\text{electrolyte}}}} \quad (5-5)$$

where the subscripts electrolyte and sample refer to the discharged electrolyte and the discharged sample, respectively.

5.2.2 Mass flow chart

In this study, the recovery rate R was calculated based on a mass balance to verify the validity of the experimental results. The equations used for the mass balance analysis are shown below. The atomic amount of D supplied to the cell as gas, $D_{\text{gas, in}}$, was calculated as follows:

$$D_{\text{gas, in}} = \frac{[D]Qt}{V_{\text{gas}}} \times 2N_A \quad (5-6)$$

where Q is the gas flow rate, t is the measurement time, V_{gas} is the molar volume of the gas, and N_A is Avogadro's constant. The atomic amount of D supplied to the cell as the electrolyte, $D_{\text{aqu, in}}$, was calculated as follows:

$$D_{\text{aqu, in}} = \frac{[D]V_{\text{D, aqu}}}{[H]V_{\text{H, aqu}} + [D]V_{\text{D, aqu}}} \times \frac{Lt}{V_{\text{D, aqu}}} \times 2N_A = \frac{2[D]N_A Lt}{[H]V_{\text{H, aqu}} + [D]V_{\text{D, aqu}}} \quad (5-7)$$

where $V_{\text{H, aqu}}$ and $V_{\text{D, aqu}}$ are the molar volumes of H_2O and D_2O , respectively. L is the flow rate of the electrolyte. The contribution of H_2SO_4 was neglected because its fraction of volume in the solution was approximately 0.005%. The atomic amount of D discharged as gas from the anode, $D_{\text{an, out}}$, was calculated as follows:

$$D_{\text{an, out}} = [\text{D}]t \times \left(\frac{Q}{V_{\text{gas}}} - \frac{IA}{2F} \right) \times 2N_{\text{A}} \quad (5-8)$$

where I is the current density, A is the electrode area, and F is the Faraday constant. Similarly, the atomic amount of D discharged as gas from the cathode, $D_{\text{ca, out}}$, was calculated using the following equation:

$$D_{\text{ca, out}} = [\text{D}]t \times \frac{IA}{2F} \times 2N_{\text{A}} \quad (5-9)$$

After the experiment, the masses of the electrolyte discharged from the cell and the recovered water were measured. The atomic amount of D in the discharged electrolyte, $D_{\text{aqu, out}}$, was calculated using the measured mass W , as follows.

$$D_{\text{aqu, out}} = \frac{[\text{D}]M_{\text{D}}}{[\text{H}]M_{\text{H}} + [\text{D}]M_{\text{D}}} \times \frac{W}{M_{\text{D}}} \times 2N_{\text{A}} = \frac{2[\text{D}]N_{\text{A}}W}{[\text{H}]M_{\text{H}} + [\text{D}]M_{\text{D}}} \quad (5-10)$$

where M_{H} and M_{D} denote the molar masses of H_2O and D_2O , respectively. The atomic amounts of D in the recovered water from the anode and cathode, $D_{\text{aqu, an}}$ and $D_{\text{aqu, ca}}$, were calculated in the same manner as $D_{\text{aqu, out}}$ using Eq. (5-10). From Eqs. (5-6)–(5-10), the recovery rate R was calculated as follows:

$$R = \frac{D_{\text{an, out}} + D_{\text{ca, out}} + D_{\text{aqu, out}} + D_{\text{aqu, an}} + D_{\text{aqu, ca}}}{D_{\text{gas, in}} + D_{\text{aqu, in}}} \times 100 \quad (5-11)$$

5.3 Results and Discussions

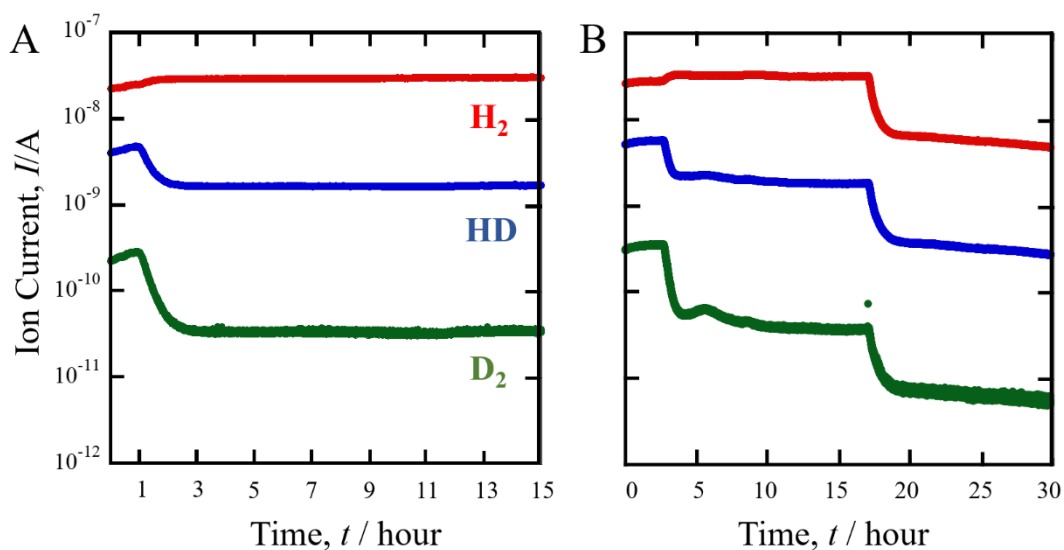


Figure 5-2. Typical QMS data of the exhausted anode and cathode gases during the separation experiment introducing the electrolyte ($H/D = 10$): (A) without ECHP, supplying a mixed H_2/D_2 gas (11.6 mL min^{-1}), and (B) with ECHP operated at 0.10 A cm^{-2} , supplying a mixed H_2/D_2 gas. (red: H_2 , blue: HD, green: D_2)

Figure 5-2 shows typical QMS data for the exhaust gas obtained during the isotope separation experiment and the corresponding H/D ratio in the gas phase (A = without ECHP, B = with ECHP). Figure 5-2A shows the QMS analysis result of the gas discharged from the anode (without ECHP). The vertical axis represents the ion currents, corresponding to the partial pressure of each gaseous species. During the first hour after the start of the measurement, only a mixed H_2/D_2 gas (11.6 mL min^{-1}) was supplied to the cell. When the electrolyte ($H/D=10$) was introduced, the fraction of H_2 increased, whereas those of HD and D_2 decreased. This behavior is attributed to isotope exchange

reactions. VPCE and LPCE occurred between liquid water and the hydrogen gas via water vapor.

Fig. 5-2B shows the QMS analysis results for the gases discharged from the anode and cathode during ECHP operation. During the first 2 hours of the measurement, a mixed H_2/D_2 gas (23 mL min^{-1}) was introduced into the cell. Subsequently, the electrolyte ($\text{H}/\text{D} = 10$) was supplied, and the ECHP was operated at 0.1 A cm^{-2} . The flow rate of the anode exhaust gas under these conditions was identical to that in Fig. 5-2A. As in Fig. 5-2A, the fraction of H_2 increased, while those of HD and D_2 decreased owing to isotope exchange reactions. After confirming the stability of the ion currents over 15 hours of measurement, the gas discharged from the cathode was subsequently analyzed. Since N_2 served as the carrier gas, the partial pressures of the hydrogen species in the cathode exhaust gas were correspondingly lower.

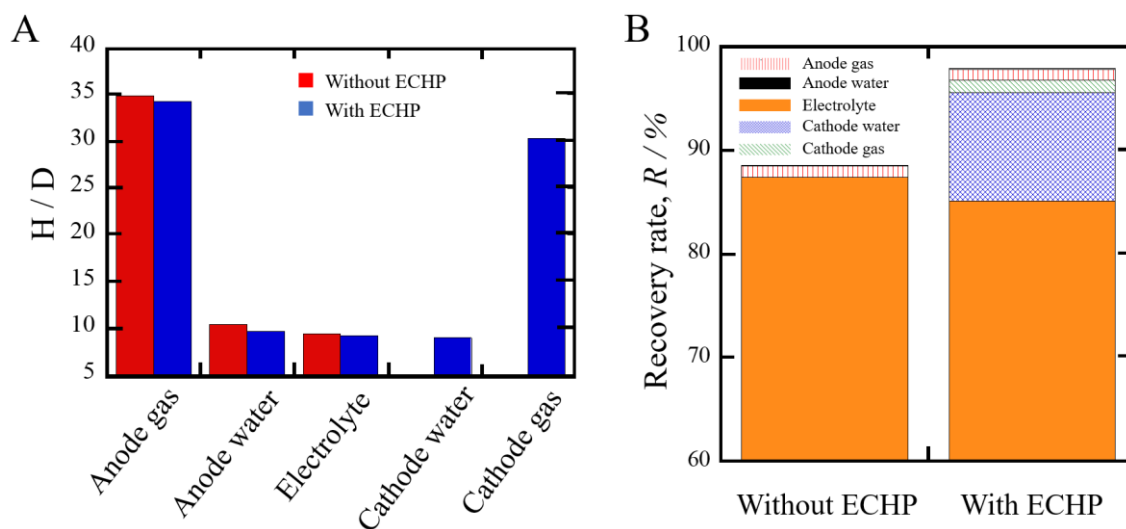


Figure 5-3. A: H/D ratios in each component exhausted from the cell (red: without ECHP, blue: with ECHP). B: Deuterium recovery rate and their distributions calculated from the mass balance without and with ECHP.

Figure 5-3 shows the analytical results of each component and the corresponding mass balance obtained during this measurement. The compositions of the hydrogen gas, recovered water, and electrolyte discharged from the cell were analyzed for both cases without ECHP (red) and with ECHP (blue) (Fig. 5-3A). Without ECHP, the H/D ratio in the hydrogen gas exhausted from the anode was 35, indicating that hydrogen was enriched in the gas phase. The H/D ratios of the recovered water at the anode and the electrolyte were 10.4 and 9.4, respectively. The recovered water at the anode exhibited a higher hydrogen concentration than the electrolyte, suggesting that D was concentrated in the electrolyte. This behavior is attributed to the LPCE process: D transferred to the vapor phase via VPCE was subsequently enriched in the electrolyte through LPCE.

A similar phenomenon was observed during ECHP operation. The H/D ratio of the hydrogen gas exhausted from the anode was 34, indicating that H was enriched in the gas phase. The H/D ratio of the recovered water at the anode was 9.7, which was higher than that of the electrolyte (9.2), indicating a higher H concentration. In all the components—anode hydrogen gas, anode recovered water, and electrolyte—the H/D ratios under ECHP operation were lower than those without ECHP. This is attributed to a larger amount of D being concentrated in the electrolyte during ECHP operation. The H/D ratios of the anode hydrogen gas and the anode recovered water are determined by the isotope exchange reactions of VPCE and LPCE. When the H/D ratio of the electrolyte decreases, the H/D ratio of the anode water vapor in equilibrium with the electrolyte through LPCE decreases. Similarly, when the H/D ratio of the water vapor at the anode decreases, the H/D ratio of the anode hydrogen gas in equilibrium with the anode water vapor through VPCE also decreases.

During ECHP operation, hydrogen gas and recovered water were also produced at the cathode. The H/D ratio of the recovered water at the cathode was 9.0, showing an enrichment of D compared to the electrolyte. The H/D ratio of the cathode hydrogen gas was 30, indicating the production of H-rich gas. These results suggest that a reaction similar to water electrolysis occurs at the cathode. As in water electrolysis, H in the water transported to the cathode preferentially evolved in the gas phase, while the remaining D-enriched water was discharged as recovered water.

Figure 5-3B shows the mass balance for both cases, with and without ECHP. The mass balance was calculated using Eq. (5-11). Without ECHP, 87 % of the supplied D was found in the electrolyte. The amounts of D detected in the anode hydrogen gas and the anode recovered water were 1.1 % and 0.1 %, respectively. In total, 88 % of the

supplied D was recovered.

With ECHP, 85 % of the supplied D was detected in the electrolyte. This slightly lower value compared with the case without ECHP is attributed to the transfer of D to the cathode through electro-osmotic drag. The recovered water at the cathode contained 10 % of D. Overall, 98 % of the supplied D was recovered. Regardless of ECHP operation, the unrecovered D is presumed to remain in residual water inside the cell or in vapor not fully condensed in the cold trap.

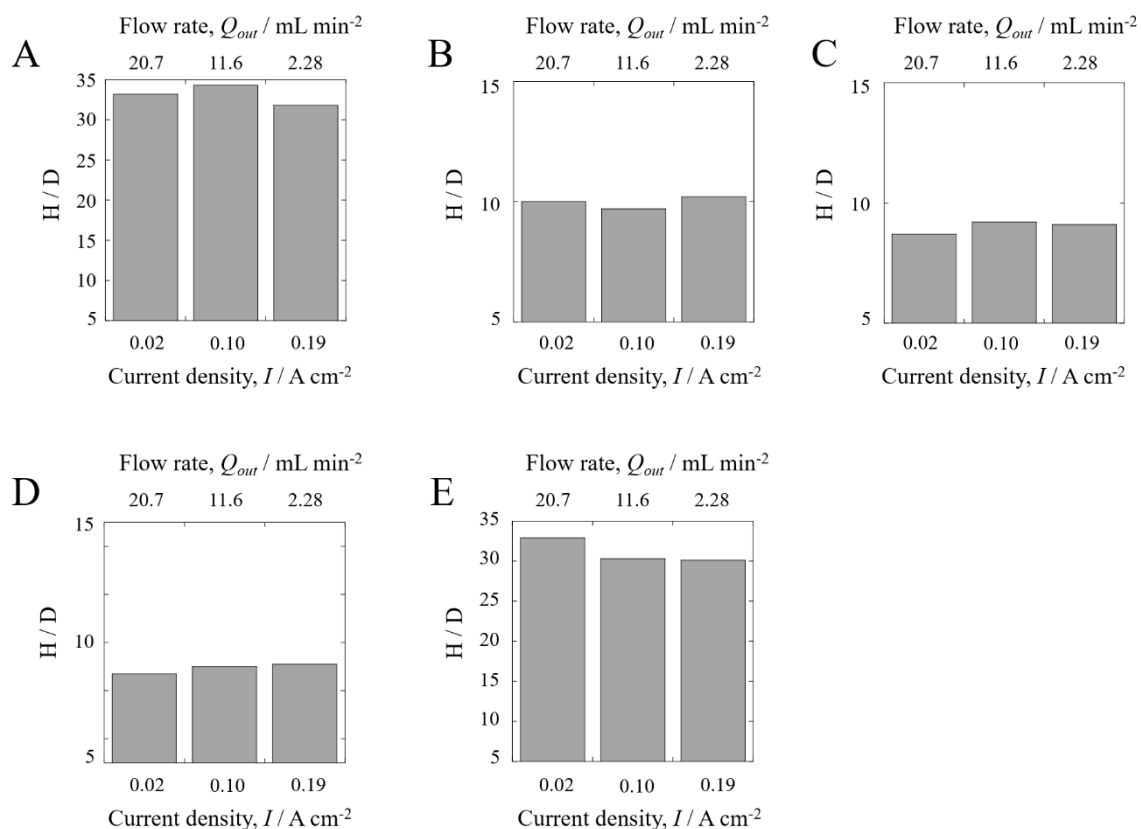


Figure 5-4. H/D ratios in (A) anode gas, (B) anode recovered water, (C) electrolyte, (D) cathode recovered water, and (E) cathode gas during ECHP at various current densities (upper axis: anode exhausted gas flow rate), supplied with a mixed H₂/D₂ gas (22.3 mL min⁻¹) and an electrolyte (H/D = 10).

Figure 5-4 shows the analytical results obtained at various current densities during ECHP operation. In this experiment, a mixed H₂/D₂ gas was supplied to the cell at a constant flow rate of 23 mL min⁻¹. An electrolyte with an H/D ratio of 10 was introduced. Figure 5-4A presents the H/D ratio in the anode hydrogen gas at each current density. The upper axis represents the flow rate of hydrogen gas exhausted from the anode (Q_{out}) under each condition. The H/D ratio ranged from 32 to 34, confirming H enrichment in the gas.

At a current density of 0.1 A cm^{-2} , the H/D ratio was the highest (34), which is attributed to differences in the flooding behavior. At a lower current density (0.02 A cm^{-2}), the smaller electro-osmotic drag allowed greater water transport toward the anode side. The water transported to the anode covered and deactivated the Pt catalyst, suppressing VPCE. At a higher current density (0.19 A cm^{-2}), Q_{out} was low (2.3 mL min^{-1}), resulting in poor removal of water from the anode catalyst surface and suppression of VPCE.

Figure 5-4B shows the H/D ratio of the anode recovered water. In contrast to the anode gas, the H/D ratio was the lowest (9.7) at a current density of 0.10 A cm^{-2} . This difference is attributed to the LPCE process. At current densities of 0.02 and 0.19 A cm^{-2} , a larger amount of water was present in the flow channel, promoting LPCE and increasing the H concentration in the anode vapor. In contrast, at 0.10 A cm^{-2} , the smaller amount of water in the flow channel suppressed LPCE, resulting in a lower H concentration in the anode vapor.

Figure 5-4C shows the H/D ratio and the separation factor α in the electrolyte. The H/D ratio ranged from 8.7 to 9.2 under all conditions, indicating D enrichment in the electrolyte. D was enriched in the electrolyte through LPCE with the anode vapor and through ECHP operation. At a current density of 0.10 A cm^{-2} , the D enrichment via LPCE was smaller, resulting in a higher H/D ratio compared with other conditions.

Figure 5-4D shows the H/D ratio in the cathode recovered water. In contrast to the results for the anode and the electrolyte, the H/D ratio in the cathode recovered water increased with increasing current density. At the cathode, a large amount of water was transported from the electrolyte toward the cathode by electro-osmotic drag. Therefore, at higher current densities, LPCE was more likely to occur than VPCE, whereas at lower current densities, VPCE occurred more efficiently than LPCE.

Figure 5-4E shows the H/D ratio in the cathode gas. In contrast to the cathode recovered water, the H/D ratio in the cathode hydrogen gas decreased with increasing current density. This phenomenon is attributed to the VPCE process. As described in Figure 5-4D, the electro-osmotic drag increased with increasing current density, suppressing VPCE.

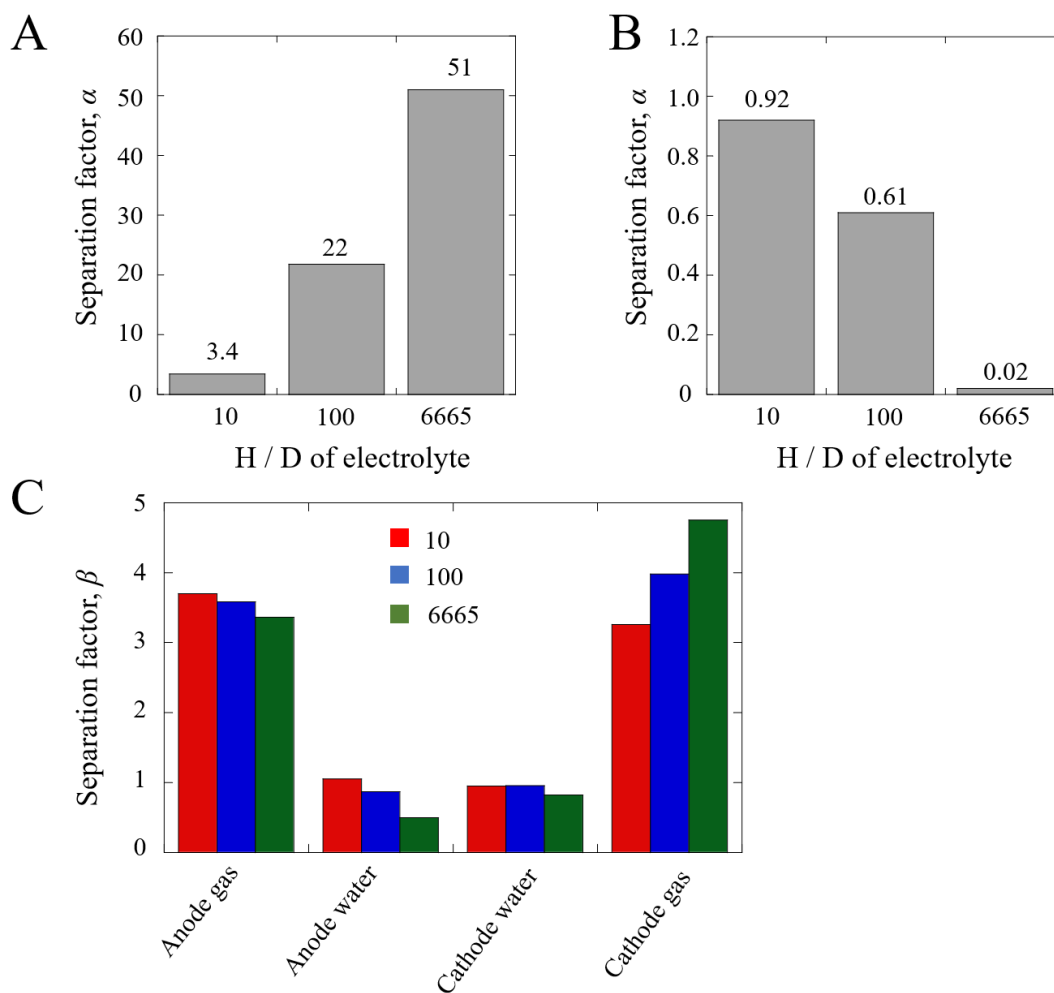


Figure 5-5. Separation factors α for (A) the anode gas and (B) the electrolyte, and (C) separation factors β for each component during ECHP at 0.10 A cm^{-2} using electrolytes with different D concentrations, supplied with a mixed H_2/D_2 gas (22.3 mL min^{-1}).

Figure 5-5 shows the analytical results during ECHP operation using electrolytes with different D concentrations. During these experiments, a mixed H_2/D_2 gas was supplied to the cell at a constant flow rate of 23 mL min^{-1} , and the current density was fixed at 0.10 A cm^{-2} . Figure 5-5A presents the separation factor α for the anode hydrogen gas. α was calculated using Eq. (5-4). An α greater than 1 indicates that H is enriched in the gas phase. A larger α corresponds to a higher separation performance. For the anode gas, α was greater than 1 under all conditions, indicating that H was enriched in the gas phase. When the electrolyte had a lower D concentration, α exceeded 20, demonstrating a high degree of H enrichment. VPCE is an equilibrium reaction that depends on concentration. The separation performance improves with an increasing difference in D concentration between the hydrogen gas and water vapor.

Figure 5-5B shows the separation factor α in the electrolyte. When α is less than 1, it indicates that D is enriched in the electrolyte. A smaller α corresponds to a higher enrichment of D. In all cases, α was less than 1, confirming D was enriched in the electrolyte. α also decreased with decrease in the H/D ratio in the electrolyte. D separated from the anode gas was transported into the electrolyte. Therefore, α for the electrolyte also increased with increasing α for the anode gas.

Figure 5-5C shows the separation factors β for each component during ECHP operation. β was calculated using Eq. (5-5). When β is greater than 1, it indicates that the H concentration is higher than that in the electrolyte. A larger β corresponds to a higher separation performance. For the anode gas, β was greater than 3 under all conditions. The H concentration in the gas phase was higher than that in the electrolyte. When the H/D ratio in the electrolyte was low, β increased and showed the maximum value of 3.7. This value was close to the equilibrium constant K_1 of VPCE (3.5)^[32]. D was efficiently

separated through continuous VPCE occurring in the flow channel. K_1 for VPCE was calculated using the following equation:

$$K_1 = \text{Exp.} \left(\frac{2380}{T^2} - \frac{449.2}{T} + 0.2735 \right) \quad (5-12)$$

where T represents the absolute temperature. Since K_1 represents the equilibrium constant between gas and water vapor, it shows a slightly different value from β .

β of the anode recovered water showed the same trend as that of the anode gas. This tendency was attributed to the difference in the time required for LPCE to reach equilibrium. At an H/D ratio of 10, β was 1.05, which was approximately corresponded to the equilibrium constant K_2 of LPCE (1.08)^[33]. K_2 was calculated using the following equation:

$$K_2 = \text{Exp.} \left(\frac{26398.8}{T^2} - \frac{89.607}{T} + 0.0758 \right) \quad (5-13)$$

A β value close to the equilibrium constant indicates that LPCE had reached equilibrium. In other words, due to the proper occurrence of LPCE, continuous VPCE efficiently enriched H in the gas phase. On the other hand, LPCE may have reached equilibrium at a certain point in the flow channel, beyond which VPCE did not proceed further.

At an H/D ratio of 6665, the β values for the anode vapor were 0.49 and less than 1. The anode vapor had a higher D concentration than the electrolyte. This suggests that the transfer of D from the anode vapor to the liquid water through LPCE was incomplete. It is inferred that VPCE had reached equilibrium at a certain point in the flow channel

and no longer proceeded. Therefore, an improvement in separation performance could be expected by increasing the residence time of water vapor or the amount of liquid water in the flow channel.

The β values for the cathode recovered water were slightly less than 1 under all conditions. This result is attributed to the enrichment of D in the water caused by electrochemical reactions occurring at the cathode as described in Fig. 5-3A. In addition, the increase in the amount of water in the flow channel due to electro-osmotic drag also contributed to this behavior. Since the contact area between the water vapor and liquid water increased, LPCE was promoted, approaching equilibrium.

The β values of the cathode hydrogen gas were greater than 1 under all conditions. The H concentration in the gas phase was higher than that in the electrolyte. Unlike the anode hydrogen gas, β for the cathode hydrogen gas increased with decreasing the H/D ratio in the electrolyte. This difference is attributed to electro-osmotic drag, which increased the amount of water in the flow channel and promotes LPCE. As a result, VPCE also continuously occurred along the flow channel, efficiently transferring D from the hydrogen gas to the electrolyte.

5.4 Conclusions

In this study, D separation was carried out using a modified ECHP cell supplied with a liquid electrolyte. Within the cell, isotope exchange reactions via VPCE and LPCE occurred with the ECHP process. As a result, H was enriched in the hydrogen gas phase, while D was enriched in the electrolyte phase.

ECHP was conducted at different current densities. Flooding was the main focus at both the anode and the cathode. At the anode, flooding occurred when either the electro-osmotic drag or the flow rate of the exhaust gas was low, which suppressed VPCE and promoted LPCE. In contrast, at the cathode, flooding was caused by the electro-osmotic flow. At higher current densities, the increased electro-osmotic flow intensified flooding, suppressing VPCE and enhancing LPCE.

The effect of D concentration in the electrolyte was also investigated. α of the anode exhausted gas reached a maximum value of 51 at low D concentrations in the electrolyte, indicating a strong dependence of isotope exchange on concentration. In addition, β was calculated, where the equilibrium state of LPCE was the main focus. At the anode, when the H/D ratio in the electrolyte was low, the proper occurrence of LPCE promoted VPCE and the enrichment of H in the gas phase. When the H/D ratio in the electrolyte was high, β of the recovered water was 0.49, suggesting that LPCE did not proceed sufficiently. At the cathode, LPCE proceeded effectively under the influence of the electro-osmotic drag, resulting in efficient isotope separation via VPCE.

ECHP can be utilized to enhance processing capacity and to control the flow rates of gases and water vapor. Proper control of vapor flow rates and the amount of liquid water is expected to enhance the separation efficiency. Additional energy savings can be expected through the application of this system to fuel cell reactions.

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Chapter 6 General Conclusions

In this study, hydrogen isotope separation technologies utilizing various electrochemical processes were investigated to realize an efficient fuel cycle in fusion reactors. A PEFC was adopted for extracting hydrogen isotopes from H-rich gas generated during the cryogenic distillation process. The molten salt electrolysis process was employed for extracting hydrogen isotopes from the blanket. As an alternative to the isotopic exchange process in the CECE system, electrochemical hydrogen pumping was introduced. The main findings are as follows:

In Chapter 2, hydrogen isotope separation was performed using a PEFC. A quadrupole mass spectrometer integrated into the gas-recirculation line enabled real-time tracking of gas-phase composition during D separation. Continuous in-cell D separation was achieved, and the separation factor (α) exhibited exponential growth across all inlet concentrations. These results contribute to the realization of energy-efficient hydrogen isotope extraction from H-rich gas discharged from the cryogenic distillation process, using a compact system design.

In Chapter 3, hydrogen isotope separation was performed using a PEFC, now incorporating a gas-recirculation system that reintroduced exhaust gas to the cell and thereby improved hydrogen utilization. By controlling the circulating-gas flow rate and the current density, the apparent separation factor was tunable. Mass-balance calculations resolved the distribution of D within the system. These results demonstrated that the PEFC allows control over both separation performance and processing capacity, enabling it to adapt to variations in the hydrogen gas supply to the CECE process.

In Chapter 4, D separation was carried out in a LiCl–KCl–LiH–LiD molten-salt system. Separation via electrolysis and via isotope-exchange reactions was investigated and compared with aqueous systems. Electrochemical analysis also yielded the diffusion

coefficient of D^- in the molten salt. Whereas electrolysis delivered higher separation performance in aqueous media, isotope exchange was superior in molten salts. This indicates highly active exchange in molten salts and suggests a new route to efficient hydrogen isotope separation. These results indicate the feasibility of tritium extraction from breeding blankets via molten salt electrolysis and can contribute to the simplification of the system configuration.

In Chapter 5, hydrogen isotope separation was achieved by combining electrochemical hydrogen pumping with isotope-exchange reactions. Mass-balance analysis validated the experimental results and clarified D distribution. Isotope exchange enabled effective D separation, while electrochemical hydrogen pumping increased overall throughput. These results present a new alternative featuring a compact system design and high separation efficiency, which can serve as a replacement for the catalytic exchange process in the CECE system.

In summary, through the investigation of various electrochemical methods, including PEFC, molten salt electrolysis, and electrochemical hydrogen pumping, this study anticipates the enhancement of hydrogen isotope separation efficiency in fusion reactors. There are few reports on the application of these technologies to hydrogen isotope separation, and there is significant potential for further development and optimization.

From a background perspective, fusion reactors are one of the key solutions for achieving a large-scale, stable energy supply and a decarbonized society. The hydrogen isotope separation technologies investigated in this study have the potential to contribute to the compact design of fusion reactor facilities. Enhancing the performance of these separation technologies is crucial for reducing construction costs and making efficient

use of limited land, enabling a more compact and cost-effective system design.

The realization of the immense energy source provided by fusion reactors will bring about significant transformations in industries, alongside a reduction in energy costs. The production processes of various products that were previously abandoned due to high energy costs will be revisited, enabling the widespread use of materials with low production volumes in the modern era. As a result, we can expect the enhancement and lightweighting of various products, as well as the widespread adoption of products and services that were previously impossible to produce or utilize.

Furthermore, the realization of fusion reactors holds special significance for Japan. Securing domestic energy sources will render reliance on foreign energy resources obsolete. This will lead to a more stable national economy, accelerating the country's development through the effective use of financial resources that were previously spent on energy imports.

List of Achievements

Papers

1. **Effect of anode gas circulation on deuterium isotope separation by polymer electrolyte fuel cell**

Toranosuke Nago, Koichiro Furusawa, Mikito Ueda, Hisayoshi Matsushima

International Journal of Hydrogen Energy. **50**, 1598–1603 (2024).

2. **Deuterium Isotope Separation using LiCl–KCl–LiH–LiD Molten Salt**

Toranosuke Nago, Yutaro Norikawa, Kenji Harada, Mikito Ueda, Hisayoshi Matsushima,
Toshiyuki Nohira

ECS Advances. **3**, 042502 (2024).

3. **Protium enrichment by polymer electrolyte fuel cell with hydrogen gas circulation**

Toranosuke Nago, Mikito Ueda, Hisayoshi Matsushima

Fusion Engineering and Design. **221**, 115399 (2025).

4. **Effect of Isotopic Exchange Reactions on Deuterium Isotope Separation Using Electrochemical Hydrogen Pump with Liquid Electrolyte**

Toranosuke Nago, Mikito Ueda, Hisayoshi Matsushima

To be submitted

Presentations

5. Deuterium isotope separation by electrolysis in molten LiCl–KCl–LiH–LiD system

Toranosuke Nago, Yutaro Norikawa, Hisayoshi Matsushima, Toshiyuki Nohira, and Mikito Ueda

The 90th Annual Meeting of the Electrochemical Society of Japan (Oral Presentation)

6. Electrolyte Concentration Dependence in Electrochemical CO₂ Separation via Hydrogen Pumping

Sota Kanazawa, Toranosuke Nago, Hisayoshi Matsushima, and Mikito Ueda

The 90th Annual Meeting of the Electrochemical Society of Japan (Oral Presentation)

7. Influence of Liquid Water and Water Vapor on Hydrogen Isotope Separation with a Polymer Electrolyte Fuel Cell

Koichiro Furusawa, Toranosuke Nago, Ibuki Sato, Hisayoshi Matsushima, and Mikito Ueda,

2023 Fall Meeting of the Atomic Energy Society of Japan (Oral Presentation)

8. Effect of Water Vapor on Hydrogen Isotopes Separation by Polymer Electrolyte Fuel Cell

Koichiro Furusawa, Toranosuke Nago, Mikito Ueda, and Hisayoshi Matsushima

244th ECS Meeting (Poster Presentation)

9. Deuterium Isotope Separation By Polymer Electrolyte Fuel Cell with Gas Circulation System

Toranosuke Nago, Koichiro Furusawa, Mikito Ueda, and Hisayoshi Matsushima

244th ECS Meeting (Poster Presentation)

10. Deuterium isotope separation by electrolysis in a molten LiCl–KCl–LiH–LiD system

Toranosuke Nago, Yutaro Norikawa, Hisayoshi Matsushima, Toshiyuki Nohira, and Mikito Ueda

2023 Joint Symposium on Molten Salts (Poster Presentation)

11. Study on tritium separation using water electrolysis and fuel cells

Yui Ishimori, Toranosuke Nago, Ibiki Sato, Hisayoshi Matsushima, and Mikito Ueda

2025 Winter Meeting of the Hokkaido Branch, Chemistry-Related Societies (Oral Presentation)

12. Protium enrichment by polymer electrolyte fuel cell with hydrogen gas circulation

Toranosuke Nago, Mikito Ueda, and Hisayoshi Matsushima

The 92nd Annual Meeting of the Electrochemical Society of Japan (Oral Presentation)

13. Electrochemical hydrogen pumping using liquid electrolytes for deuterium isotope separation

Toranosuke Nago, Mikito Ueda, and Hisayoshi Matsushima

2025 Autumn Meeting of the Electrochemical Society of Japan (Oral Presentation)

14. Research on Tritium Removal via a Hybrid Water Electrolysis–Fuel Cell System

Yui Ishimori, Toranosuke Nago, Ibiku Sato, Hisayoshi Matsushima, and Mikito Ueda

2025 Fall Meeting of the Atomic Energy Society of Japan (Oral Presentation)

15. Deuterium isotope separation using polymer electrolyte fuel cell

Toranosuke Nago, Mikito Ueda, and Hisayoshi Matsushima

14th International Conference on Tritium Science and Technology (Poster Presentation)

Others

16. Effect of water vapor on deuterium separation by a polymer electrolyte fuel cell

Koichiro Furusawa, Toranosuke Nago, Mikito Ueda and Hisayoshi Matsushima

International Journal of Hydrogen Energy. **47**, 36248–36253 (2022).

17. Application of membrane electrode assembly for water hydrogen isotope exchange

Koichiro Furusawa, Toranosuke Nago, Mikito Ueda, Hisayoshi Matsushima

International Journal of Hydrogen Energy. **50**, 629–634 (2024).

Patent

18. 特許第 7615111 号, 分離システム及び分離方法, 2022 年

19. 特開 2024-031641, アルカリ液に溶解した二酸化炭素を放出する方法およびそのための装置、ならびに排ガスから二酸化炭素を回収する方法およびそのためのシステム, 2022 年

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