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Hydrogen isotope separation with an alkaline membrane fuel cell

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Abstract

The separation of deuterium from a hydrogen–deuterium mixture was carried out using an alkaline membrane fuel cell (AMFC) with a Pt catalyst. This novel use of an AMFC to separate deuterium from a mixture of H₂ and D₂ was demonstrated by the production of deuterium-enriched water during power generation by the AMFC. The deuterium separation factor increased with output current (i) to a maximum value of 1.64 attained at $i = 30 \text{ mA cm}^{-2}$.

Keywords

AMFC; CEFC; isotopes separation; deuterium; hydrogen

1. Introduction

The heavy isotopes of hydrogen, deuterium (D) and tritium (T) are materially important in nuclear energy production. In current heavy-water nuclear fission reactors, D is used as a neutron-moderator. Similarly, in nuclear fusion reactors, which are expected to represent the next generation of nuclear power, the reaction of D and T is responsible for the energy production stage.

Because D and T are not directly obtained as individual isotopes, methods to separate them from the more common, lighter isotope, protium, are required. Many researchers have studied various isotope-separation methods, including water distillation [1], chemical exchange [2], water electrolysis [3, 4] and combined electrolysis catalytic exchange (CECE) [5, 6]. The electrolysis method yields the most effective separation but the process consumes enormous amounts of electricity. This has led to a search for other methods that are more energetically efficient.

In an attempt to solve the above problem, we previously proposed a new hydrogen separation system: the combined electrolysis fuel cell (CEFC) process [7]. Here, hydrogen and oxygen were produced by electrolysis and used for power generation by fuel cells. Less electricity was consumed by the separation process owing to the implementation of hydrogen energy recycling. More recent work has reported the hydrogen isotope effect during the anodic reaction in polymer electrolyte fuel cells (PEFCs) [8-10]. However, PEFCs require precious metal catalysts, rendering them expensive and unsuitable for use at the industrial scale.

In contrast, it has been suggested that the development of AMFCs can proceed without using noble metal catalysts due to their faster oxygen reduction kinetics [11-14]. Indeed, work by Piana et al. demonstrated that AMFCs can be operated without the use of any precious metals [15]. Other work has also shown that in alkaline media the kinetics of the oxygen reduction reaction, which is key to the overall process, are faster than those in acidic media, such as when using a cation exchange membrane [16]. In this way, AMFCs could prove more favorable for power generation than PEFCs and we therefore consider AMFCs as a leading candidate for the CEFC system. However, as far as we know, no studies have yet investigated the hydrogen isotope effect for AMFCs. Therefore, this paper focuses on measuring the separation of deuterium using an AMFC and discusses the separation mechanism by drawing comparisons with results from PEFC systems.

2. Experimental

A membrane electrode assembly composed of an anion exchange membrane (A901, Tokuyama Corp., Japan) and two catalytic layers loaded with platinum catalyst was constructed. Both electrodes had an area of 5.0 cm². A 10:1 mixture of H₂ and D₂ was supplied to the anode with gas flow rates of 2.0 and 0.2 mL min⁻¹, respectively. Humidified O₂ was supplied to the cathode at a flow rate of 20 mL min⁻¹. All flow rates were adjusted by a mass flow controller (MC-200SCCM-D, Alicat Corp., USA). The AMFC was operated at 298 K with power generation controlled under constant current mode (0–0.150 A) by a variable resistor unit (PLZ 164WA, Kikusui Electronics Corp., Japan).

The ion current of three gas species ($m = 2, 3$ and 4 representing H₂, HD and D₂, respectively) exhausted from the anode were measured in-situ by a quadrupole mass spectrometer (Q-Mass; Qulee-HGM 202, Ulvac Corp., Japan) with samples taken with and without AMFC operation. Data were recorded for a period of 6 hours until a steady state was attained.

3. Results and Discussion

The first experiment, the results of which are shown in Fig. 1, examined the composition ratio at open circuit potential (OCP) with no power generation to provide a reference point. The first hour of the test involved the analysis of the exhaust gas mixture from the AMFC. After 1 hour, the sampling was changed to analyze the unreacted gas mixture in the Q-mass; however, as Fig. 1 shows, a period of approximately 45 minutes was required to reach a second steady state. Direct sampling of the gases resulted in, compared with those observed from the AMFC anode exhaust, a decrease in the ion current of HD (from 8.4×10^{-10} to 4.0×10^{-11} A) and an increase in that of D₂ (from 1.3×10^{-11} to 8.2×10^{-10} A). The ion current of H₂ showed little change.

The use of AMFC increased the molecular ratio of HD because of the isotope exchange reaction (Eq. 1).



Figure 1 shows that the majority of molecules of D₂ gas that were introduced to the system were converted to HD. Such high catalytic activity might be attributed to the fuel cell's well-designed nanostructure. The same phenomenon was also reported when the fuel cell was operated with a cation exchange membrane (Nafion) [8]. This suggests that the exchange reaction depends on the catalyst rather than the membrane (H⁺ or OH⁻ type).

Figure 2 shows the results obtained by varying the output current density, which was controlled at 20, 25 and 30 mA cm⁻² during a series of every 6-hour experiments. The initial and final values were set to OCP, similar to those in the experiment shown in Fig. 1.

During AMFC operation the ion currents of both HD and D₂ decreased by larger magnitudes as the current (and therefore hydrogen consumption by the oxidation reaction) was increased. In relative terms, the decrease observed for D₂ was larger than that of HD. Compared with the initial values, D₂'s ion current fell approximately 60% to 1.5×10^{-12} A at 30 mA cm⁻², whereas the corresponding decrease in HD was approximately 40%. A period of about 3 hours was required to reach steady state values; this was probably because of the slow replacement of gas in the sample lines owing to the low flow rate of 2 ml min⁻¹. Conversely, the ion current of H₂ appeared to be independent of the power generation process, remaining at a value of 9.0×10^{-9} A throughout the tests. The consumption of HD and D₂ meant that the molar ratio of H₂

slightly increased and supported the thesis that heavier isotopes of hydrogen are preferentially oxidized on Pt surfaces. This isotope effect occurred due to difference of weight or thermodynamic value between protium and deuterium [17].

The deuterium separation factor, α , was calculated by measuring the change in the ratio of protium and deuterium exhausted from the anode, as shown in Eq. 2 [8],

$$\alpha = ([\text{H}]/[\text{D}])_1/([\text{H}]/[\text{D}])_0, \quad (2)$$

where the '0' state represented the ratio observed without power generation and the '1' state represented with power generation. The separation factor was calculated from the ion current of the steady-state conditions shown in Fig. 2.

Using the results presented in Fig. 2 allowed the variation in α with output current to be plotted, as shown in Fig. 3. The value of α was continually greater than 1 signifying a decrease in the concentration of deuterium in the gas phase and a corresponding enrichment in the water phase for all conditions. The separation factor increased linearly with increasing output current and reached 1.6 at $i = 30 \text{ mA cm}^{-2}$. The slope of the line decreased at approximately $i = 20 \text{ mA cm}^{-2}$ with further increases in generated current above this point having a lesser impact on the value of α .

Interestingly, the present result was smaller than the value of α reported for a PEFC system [8]. This might be explained because the systems produce water at different sites. In AMFC, hydrogen gas is supplied to the anode and is oxidized to water by combination with a hydroxide ion (OH^-) that passes through the membrane. That is, the deuterium separation occurs only on the anode side. However, in a PEFC, the gas is dissociated into protons (H^+ or D^+) at the anode and these protons then migrate through the membrane to the cathode where they are reduced to produce water. Thus, for PEFC the isotope effect should be considered during each of the three processes at work: the reactions at the anode and cathode and the migration through the membrane.

Figure 4 shows the AMFC's cell performance. The OCP was initially 1.04 V, which was similar to the reported value [13]. Increasing the output current to 30 mA cm^{-2} decreased the cell voltage to 0.19 V. Although the generation was stable, the voltage observed was lower than that reported previously for an AMFC system [13]. This relatively poor performance may have been caused by the operating temperature of 298 K and the fact that only the cathode side was humidified.

Corresponding to the point of change in the gradient of the relationship between output current and α (Fig. 3), the highest power density was calculated at $i = 20 \text{ mA cm}^{-2}$, which was equivalent to a fuel use of approximately 30%. As also reported

for PEFC systems, the oxygen reduction reaction at the cathode becomes the rate-determining step at high values of current density in the AMFC system [18]. Therefore, the reduction in the production rate of OH^- ions could influence the deuterium separation process.

In summary, this work has shown that an AMFC system with a Pt catalyst can separate hydrogen isotopes and produce deuterium-enriched water. Although the present separation factor was smaller than that reported for a PEFC system, the data are nonetheless useful in supporting the development of non-noble metal catalyzed CEFC processes using alkaline media.

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Figure Captions

Figure 1

Transient behavior of Q-Mass spectrums of mass numbers, m , = 2 (H_2 , red line), 3 (HD, blue line) and 4 (D_2 , green line). A mixture of H_2 (2.0 ml min^{-1}) and D_2 (0.2 ml min^{-1}) was passed through the AMFC for 1 hour and then passed directly to the Q-Mass for 2 hours.

Figure 2

Transient behavior of Q-Mass spectrums of mass numbers, m , = 2 (H_2 , red line), 3 (HD, blue line) and 4 (D_2 , green line) during AMFC operation at several output current densities at 298 K. The arrows signify change of current density.

Figure 3

Variance of deuterium separation factor with the output current density of an AMFC at 298 K.

Figure 4

Voltage–current curve for AMFC using A901 membrane at 298 K.

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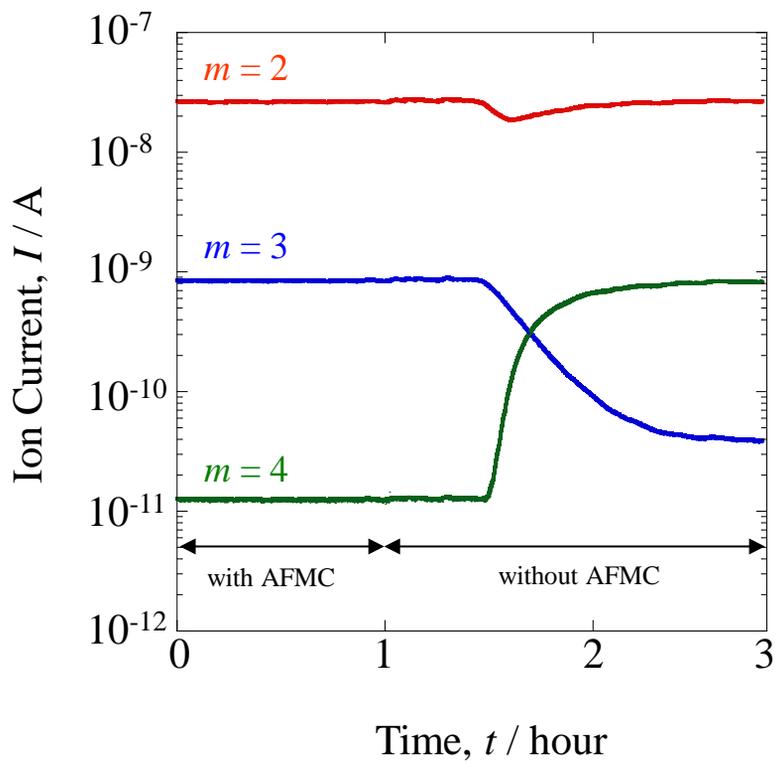


Fig. 1

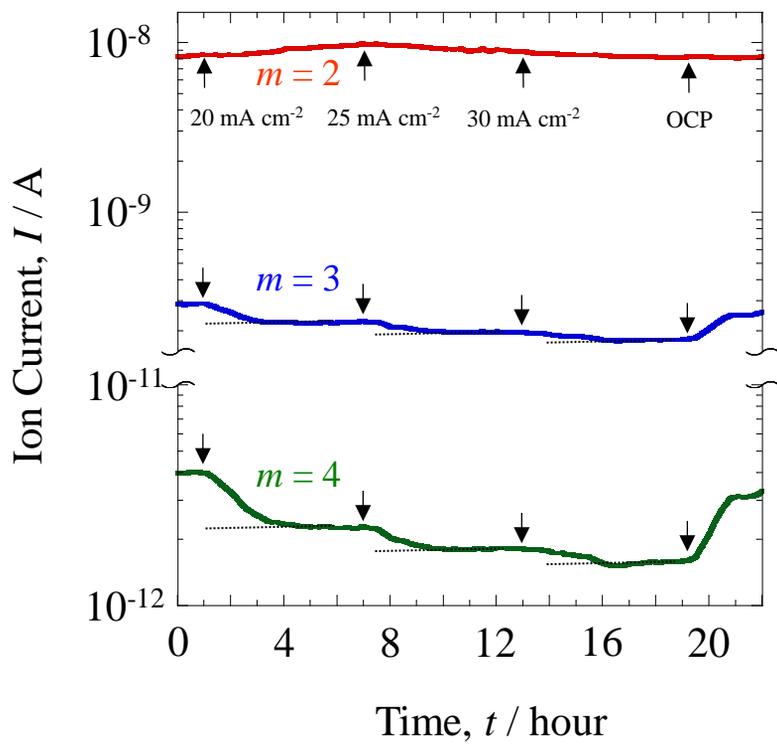


Fig. 2

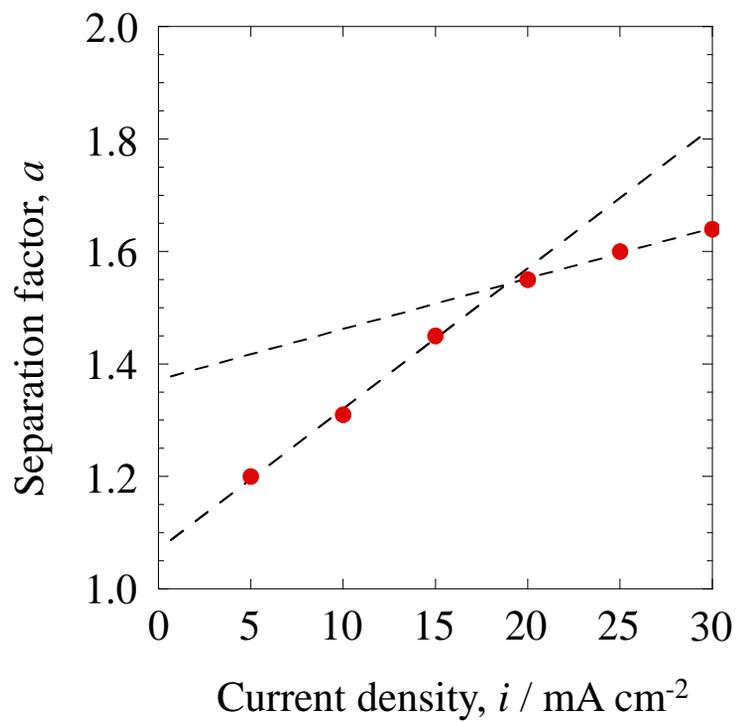


Fig. 3

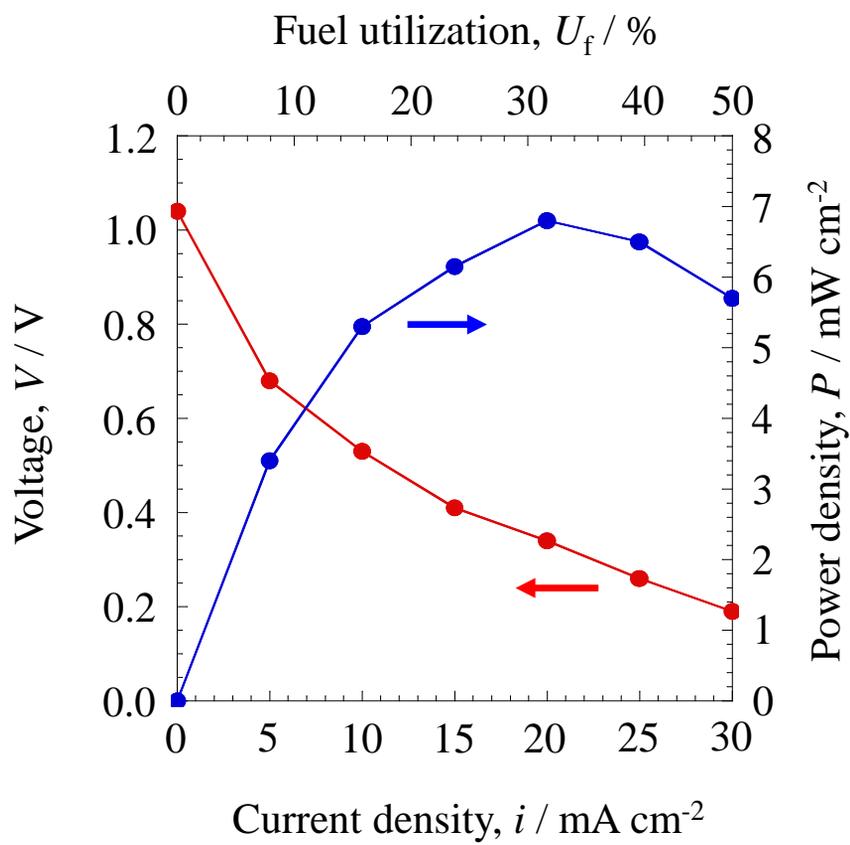


Fig. 4