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CH_4 is decomposed by a low-pressure DC glow discharge, and partial pressures of H_2 and other by-products are measured by the mass spectrometry. The decomposition rate of CH_4 and H_2 conversion rate are calculated from the partial pressure, and the effects of mixed gases with CH_4 on the decomposition characteristics of CH_4 and H_2 conversion rate are investigated. It is found that CH_4 is completely decomposed in the DC glow discharge, and that 80%, 75% and 70% of hydrogen atoms contained in CH_4 are converted into H_2 in CH_4-Ar mixture, pure CH_4 and CH_4-CO_2 mixture, respectively. It is also found that CO, which can be used as fuel, is produced in the DC glow discharge by the decomposition of CO_2 in CH_4-CO_2 mixture.

Keyword : hydrogen production, low pressure glow discharge, greenhouse gas, CO_2 removal, clean energy

1　INTRODUCTION

Global warming due to greenhouse gases is one of the most serious environmental issues in the world. CO_2 and CH_4 are considered to be major cause of the global warming, and it is urgent to reduce the release of those gases in the air and to shift from the consumption of fossil fuel to the utilisation of clean energy like hydrogen.

Since discharge plasma generated by a high voltage application between electrodes contains energetic and highly reactive species, such as electrons, ions, excited molecules, etc., the discharge plasma has been used for material synthesis, decomposition of contaminants, surface modification, etc. using the species. In this work, we develop a method using the energetic and highly reactive species in the discharge plasma for generating hydrogen from a greenhouse gas, CH_4. A low pressure DC glow discharge is generated in CH_4, and products in the glow discharge are investigated by mass spectrometry, and then hydrogen conversion rate from CH_4 is deduced. Further, the influence of CO_2 or Ar additive on hydrogen generation in the glow discharge is investigated. Okazaki et al.[1] reported that about 40% of hydrogen atoms in CH_4 are converted into hydrogen molecules by a barrier discharge with Ni/Al_2O_3 catalysis. In this work, hydrogen conversion efficiency only by discharge plasma is examined.

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2　EXPERIMENTAL APPARATUS AND CONDITIONS

Figure 1 shows the schematic diagram of experimental apparatus. Parallel-plate electrodes of 60 mm diameter and 14 mm separation are placed in a discharge chamber of 155 mm in inner diameter and

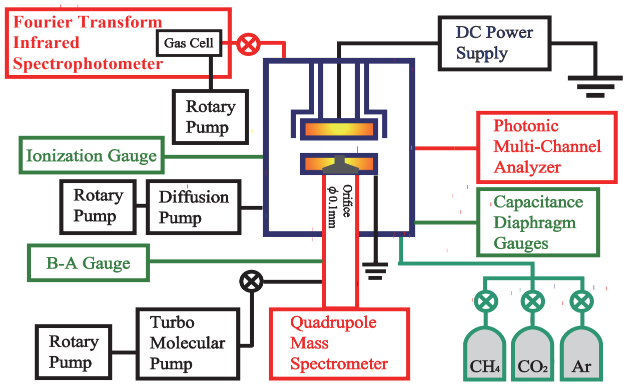


Fig.1 Schematic diagram of experimental apparatus.

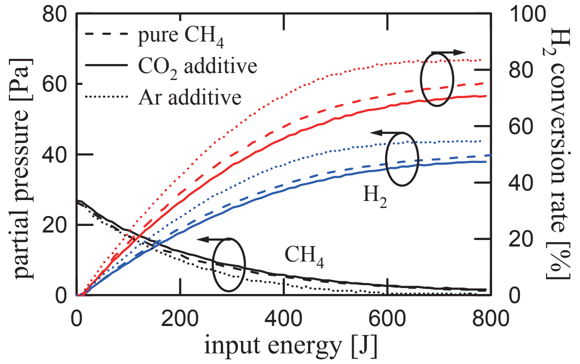


Fig.2 The variations in partial pressures of CH_4 and H_2, and in H_2 conversion rates as a function of input energy.

300 mm in height. The lower electrode and the discharge chamber are earthed, and a negative DC voltage is applied to the upper electrode to generate a glow discharge. Pure CH_4, and CH_4 mixed with CO_2 and Ar are introduced in the discharge chamber, and then a glow discharge is generated with a constant discharge current of 2.5 mA. The initial partial-pressure of CH_4 is kept at the constant value of 26.6 Pa through all experiments, and the initial partial-pressure of CO_2 and Ar, which is added to CH_4, is 26.6 Pa. The purities of CH_4, CO_2 and Ar used in this work are 99.0, 99.9 and 99.999%, respectively.

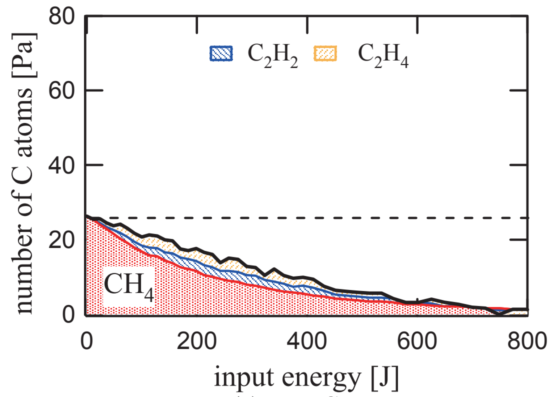
Gas sample is extracted from the glow discharge region through a 0.1 mm diameter orifice fitted at the centre of the lower electrode, and the mass spectra of the gas sample are measured using a Quadrupole Mass Spectrometer (QMS : Anelva M200QAM). The partial pressures of molecules in the sampled gas are deduced from the mass spectra, and then H_2 conversion rate is calculated by the following equation.

$$H_2 \text{ conversion rate} = \frac{[H_2] \times 2}{[CH_4]_0 \times 4} \times 100\% \qquad (1)$$

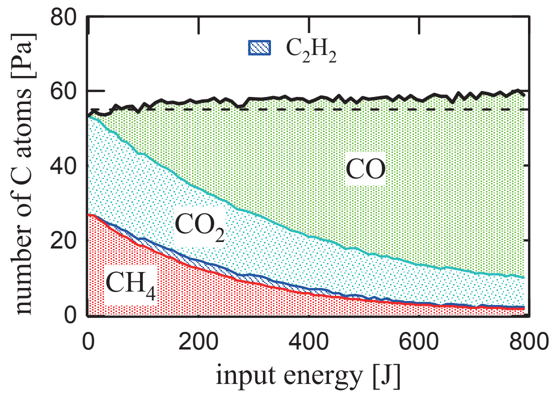
where, $[CH_4]_0$ and $[H_2]$ represent the initial partial-pressure of CH_4 and the partial pressure of hydrogen, respectively. The electrical-energy input (discharge current × applied voltage) to the glow discharge is measured every second.

3 RESULTS AND DISCUSSION

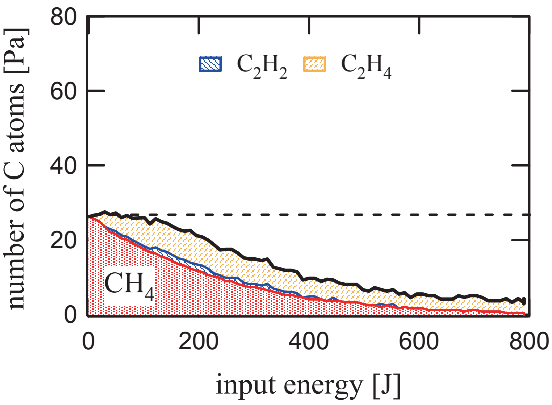
Figure 2 shows the variations in partial pressures of CH_4 and H_2, and that in H_2 conversion rate, as a function of the electrical input energy. There is no significant difference in the variation in the decomposition rate of CH_4 when CO_2 and Ar are added to CH_4. However, the partial pressure of H_2 clearly increases by Ar additive and it decreases slightly by CO_2 additive. The conversion rates deduced by eq.(1)



(a) pure CH_4



(b) CO_2 additive



(c) Ar additive

Fig.3 The variations in mass balance of carbon atoms as functions of input energies.

are 80%, 75% and 70% in CH_4-Ar mixture, pure CH_4 and CH_4-CO_2 mixture, respectively. It is, therefore, found that H_2 conversion from CH_4 is promoted by Ar additive.

The H_2 conversion rates, measured by the same experimental apparatus used here, for $(CH_3)_2CO$, CH_3OH, C_6H_6, C_7H_8 and C_8H_{10} are respectively 65%, 61%, 12%, 13% and 14%; therefore, hydrogen atoms in CH_4 are found to be effectively converted into H_2 from CH_4 in the glow discharge. It is also found that hydrogen conversion rates from CH_4 in the glow discharge are higher than that obtained using the barrier discharge-Ni/Al_2O_3 catalysis reactor[1] and by organic hydrides[2].

Figures 3(a), (b) and (c) show the variations of mass balance for carbon atoms contained in CH_4, CO_2 and by-products (CO, C_2H_2 and C_2H_4) as functions of the input energies. The number of carbon atoms in the unit of Pa is calculated by multiplying the number of carbon atoms in each molecule of CH_4, CO_2 and the by-products by the partial pressures of those molecules. Since the total number of carbon atoms contained in gaseous molecules decreases with the partial pressure of CH_4 when the glow discharge is generated in pure CH_4, the carbon atoms are found to deposit on the electrodes and the wall of the discharge chamber. When the glow discharge is generated in pure CH_4, the discharge tends to be unstable with time.
This can be due to decreasing the secondary electrons by the change of electrode surface condition by the deposition, and increasing breakdown voltage by the reduction of gaseous molecules in the discharge region, which is typical phenomenon in the region below the Paschen minimum.

In CH_4-CO_2 mixture, the carbon atoms in CH_4 and CO_2 are converted into CO, and the total number of carbon atoms in gas molecules does not change with the input energy. This leads that the greenhouse gases, CH_4 and CO_2 are decomposed into H_2 and CO, namely, clean energy resource and combustible material, respectively.

In CH_4-Ar mixture, some of the carbon atoms in CH_4 are converted into C_2H_4, and deposit on the electrodes and the wall of electrode. However, the glow discharge is stably sustained in the residual gas, Ar.

4 CONCLUSIONS

CH_4 is decomposed in a DC glow discharge, and the influence of CO_2 and Ar additive on H_2 generation from CH_4 is investigated in this work. It is found that the highest H_2 conversion rate (80%) is obtained in the glow discharge in CH_4-Ar mixture, and those of 75% and 70% are obtained in pure CH_4 and CH_4-CO_2 mixture, respectively. It is found that those conversion rates are higher than H_2 conversion rates from $(CH_3)_2CO$, CH_3OH, C_6H_6, C_7H_8 and C_8H_{10}. It is also found that CO, which can be used as combustible material, is produced in an artificial greenhouse gas, CH_4-CO_2 mixture.

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