Advanced COx Free Hydrogen Production with Use of Plasma from Hydrocarbon

プラスマを使用した炭化水素からＣＯｘを発生しない新しい水素精製方法

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Abstract:

A highly efficient hydrogen production and purification system with use of dielectric barrier discharge (DBD) type plasma is under development. The produced hydrogen will be fed directly to the fuel cell which produces electricity for the vehicles. Liquefied hydrocarbons are used as the original fuel and decomposed into hydrogen and carbon by plasma discharge reactor. The carbon produced in this process is stored inside the reactor and is taken out later during regular cleanings. Because of no oxygen inside the reactor, no emission of CO_x gas is observed through whole of these processes. At present ~120% of hydrogen compared with residual CH_4 was observed at 120 Wh input energy or 60% at 80 Wh in case of C_3H_8. The decomposition rate is linearly proportional to the input energy. Higher electrode temperature makes better decomposition efficiency. The produced hydrogen molecules numbers are decided only by the input energy in spite of the pressure differences.

I. Introduction

Clean energy source is one of the most important key issues, and the key technologies should be developed urgently. Most of the energy sources in the present world are fossil fuels, However, consumption of the fossil fuels produces large amount of hazardous materials to the environment [1,2].

Hydrogen is expected to be one of the clean energy sources. The hydrogen burning has no major dirty output except just water vapor. Energy conversion efficiency to electricity with use of fuel cell can be expected to reach about ~ 60-80 %. This is one of the best clean energy sources with high conversion efficiency as an energy converter. In the present researches, efficient hydrogen production with use of plasma discharges with COx free system are under development.

Our approach is to use high electric field plasma reactors for decomposing hydrocarbons to produce hydrogen without any carbon chemicals including COx [1-7]. The final target of the present system is to produce hydrogen on vehicle and feed it directly to the fuel cell, so no extra energy such as cooling down and compressing hydrogen in order to put it into a conveyable tank is required. For this purpose, we have tried basic experiments with use of DBD type plasma production technique. All of the discharges were performed in high pressure conditions over 1.5 atmospheric pressures in pure hydrocarbon, which is quite different from the earlier works done by other groups [8].

II. Experimental apparatus and results

Whole experimental system of discharge and detector is shown in Ref.1. The high voltage pulse generator used here has a rise time of about 3 μs, full pulse width varied 5 ~ 30 μs (variable), and repetition rate of 2-4 kHz (variable) with maximum applied voltages 15 kV. In the experiments we use methane (CH_4) or propane (C_3H_8). Each gas is stored in a reaction chamber with a volume of 12 Liter. The discharge electrodes are set inside the chamber. The discharge was continued for a maximum of 3 hours in the present experiments to decompose hydrocarbon gases. This is not the time limit of the present system, but just stopped discharge at each condition. However, it is possible to continues the discharge if we need to take data for long term discharge conditions. The decomposed gases were analyzed with the Gas Chromatograph (Shimadzu GC-2014). The input energy into the discharge area was estimated with use of Lissajous wave form technique, so that the input energy shown here are real energy spent for heating the plasma.

In the decomposition of C_3H_8 or CH_4, other carbon compounds such as C_2-hydrate have been observed, but these are quite small amount, less than 3 % , and we may say that those were not serious amount in the present system.

In this presentation electrode temperature effect

on hydrogen generation is mainly introduced. When the discharge was sustained, the inner electrode

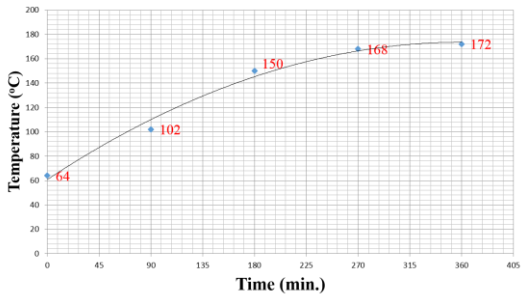
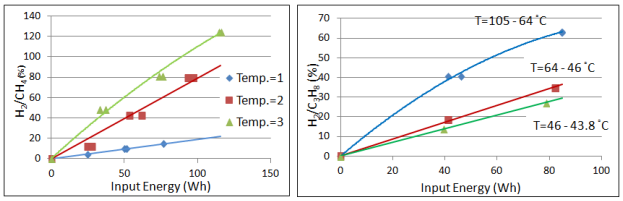


Fig.1. An example of inner electrode temperature vs. discharge time duration.

temperature increases with time as an example shown in Fig. 1. The starting inner electrode temperature in this case was 64°C obtained after the pre-discharges. After finishing 4 experiments the inner electrode temperature becomes 172°C, and the decomposition rate increases with the inner electrode temperature. The experiments were performed repeatedly, and we found that decomposition rate increased almost lineally with the inner electrode temperature. Figure 2 shows



(a) (b)

Fig.2. Decomposition rate as a function of input energy with a parameter of discharge time duration for (a) methane and (b) propane. Here, Temp.=1 in (a) corresponds to the electrode temperature range of 55-100°C, Temp.=2 to100-150°C, and Temp.=3 to 150-165°C.

decomposition efficiency versus the electrode temperature. Typically we conduct the discharge for 90 minutes and at each 90 minutes, we change the methane gas in the chamber with new one. These kinds of experiments were performed for (a) methane and (b) propane. It is also seen that the decomposition rate seems to saturate in both cases in higher temperature.

After taking more data in the present conditions, the temperature effect is arranged into one graph as shown in Fig.3. Here, the decomposition rate of CH_4 or C_3H_8 per unit input energy is measured as a function of inner electrode temperature. This result may depend on the fact that the electrode temperature is low in the case of C_3H_8. The reason of no more electrode temperature increment in C_3H_8 discharges is that the input energy for discharge was not enough for heating the electrode by the limit of discharge power source.

For understanding this mechanism of temperature dependence, we may try to use Saha equation if we can assume that the narrow discharge column area is in a local thermal equilibrium in a constant

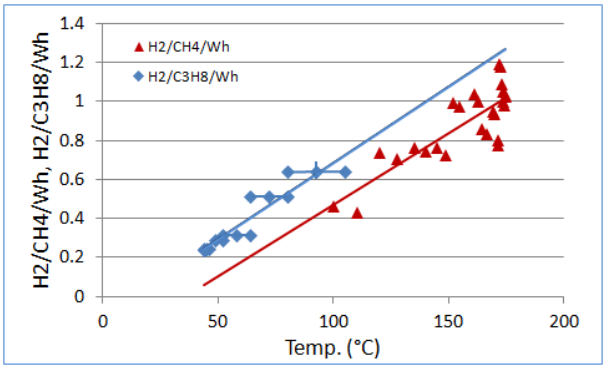


Fig.3. Decomposition rate in unit input decomposition energy as a function of electrode temperature in CH_4 (red) and C_3H_8 (blue) gases.

pressure. However, the temperature dependence estimated from this equation is too large to compare with the experimental results. i.e. when the temperature is very low such as in the present range, it is not possible to compare decomposition rate with that expected amount from Saha equation. Therefore, the observed phenomena cannot be explained by Saha equation, and we are still under consideration for understanding this physical mechanism.

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