Hydrogen Generation from Water with Nonthermal Plasma

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Nonthermal plasma chemical decomposition of water was carried out with two different types of reactors such as ferroelectric packed-bed (FPR) and silent discharge (SDR) to explore the possibility of hydrogen generation in a flow reaction system. When FPR was used, the H_2 yield in this reaction reached 63% at 150 kJ L^{-1} of supplied specific energy density in N_2. On the other hand, the H_2 yield was much lower with SDR than with FPR under the same conditions.

Hydrogen production from different sources has been extensively investigated owing to its future potential as an attractive energy source for fuel cell vehicles, public facilities, and households. Water is one of the cheapest hydrogen sources, and principally three approaches have been developed for the H_2 generation from water: electrolysis, photocatalysis,[1] and mechano-catalysis.[2] However, water decomposition reactions can be carried out only in closed recirculation systems with these methods, and this is one of the major limitations for their practical application. Recently, hydrogen generation from methanol[3] and water[4] has been reported with a dielectric barrier discharge plasma reactor. But reaction-controlling factors have to be unravelled for the optimization of H_2-generating efficiency. Since electron energy up to 12 eV is acquired at shorter residence times of several seconds in nonthermal plasma, it is noteworthy to examine the scope of hydrogen-forming reactions with nonthermal plasma from the viewpoint of its extended application to diverse chemical processes associated with hydrogen utilization.

In the present work, we have studied the H_2 generation behavior from water in nonthermal plasma, focusing on the effect of plasma-generating methods and the factors governing the reaction efficiencies. The reaction mechanism is also discussed on the basis of the background gas effect.

The schematics of ferroelectric packed-bed (FPR) and silent discharge (SDR) reactors used in this research were described in detail elsewhere.[5,6] With FPR, gas flow rate ranged from 10 to 1500 mL min^{-1} (residence time 3 to 443 s). On the other hand, gas flow rate was fixed at 50 mL min^{-1} (residence time 3 s) with SDR. The both reactors employed AC power supply at 50 Hz and the maximum voltage of 7.8 kV was applied for both the reactors. No breakdowns occurred during operations within their maximum voltages.

Distilled water was supplied to the reactors by humidified gases prepared in a water-bubbling type device in a thermostatic bath. The water vapor concentration was determined by a dew point hygrometer, and its contents were controlled within the range of 1.0–2.5%. Water was decomposed in N_2, Ar, Air, and O_2 at an atmospheric pressure by using a conventional mass flow reaction system. The products were analyzed by a TCD–GC with a packed column of Molecular Sieve 13X, and the amount of the H_2 generated was measured by using a calibration curve separately prepared.

In this paper, H_2 yield [eq (1)] is plotted against specific energy density (SED) given by eq (2), where "Power" denotes the plug-in power.

$$H_2 \text{ yield (mol\%)} = 100 \times [H_2 \text{ concentration (ppm)}]/[\text{initial concentration of } H_2O \text{ (ppm)}] \quad (1)$$

$$\text{SED (kJ } L^{-1}) = \text{Power (kW)}/[\text{Flow rate (L } min^{-1})/60] \quad (2)$$

Figure 1 shows the effect of gas flow rate on the H_2 yield in N_2 at the water concentration of 1.0% with FPR. With an increase in SED, the H_2 yield gradually increases at different flow rates. The H_2 yield up to 29% is obtained at 30 kJ L^{-1} of SED when the flow rate is 50 mL min^{-1}. Moreover, the H_2 yield in this reaction reaches 63% at 150 kJ L^{-1} of SED when the flow rate is 10 mL min^{-1}. An interesting trend is observed that higher H_2 yields are obtained at higher flow rates, i.e., shorter residence times at fixed SEDs. This kind of trend is quite opposite to those observed in the decomposition of volatile organic compounds, which are homolytically decomposed and oxidized to CO_2.[7] These facts can be ascribed to the occurrence of backward reactions of H_2 and oxygen species such as O and O_2. The molar ratios of $[H_2]/[O_2]$ ranged from 2.3 to 7.4 with FPR. Separate experiments on the water formation from H_2 and O_2 suggest that a part of O_2 reacts with H_2, but its concentration is very small in the cases where $[H_2]/[O_2]$ is higher than the stoichiometric ratio. Since O_2 balance is poor in the water decomposition, oxygen atoms might be trapped on the surface of $BaTiO_3$ and/or migrated into its lattice structure.

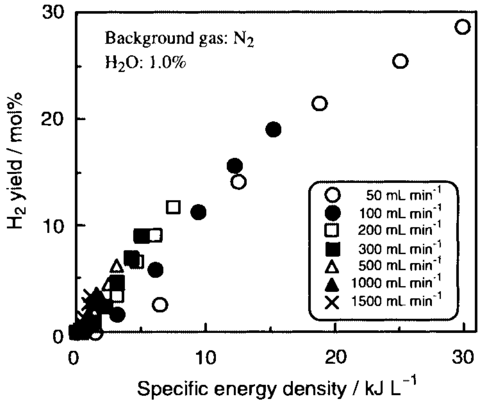

Figure 1. Effect of gas flow rate on the H_2 yield in N_2 with FPR.

The effect of water concentration on the H_2 yield in N_2 with FPR was further examined at 100 mL min^{-1} of gas flow rate. The H_2 yield gradually increased at different water concentrations with an increase in SED. When SED was fixed at 15 kJ L^{-1}, H_2 yield decreased from 19.0% to 11.9% with the increase in the water concentration from 1.0% to 2.5%. The

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absolute amount of H_2 increased with water content in N_2, and the rate for H_2 formation leveled off at 13 μmol min^{-1} with the water concentration of around 2.0%. The maximum H_2 yield highly depended on gas flow rate and input power under our operating conditions (Figure 1), but the reasonably highest water concentration should be ca. 2.0%.

Figure 2 shows the effects of background gas and reactor on the H_2 yield at 1.0% of water concentration. The gas flow rates for FPR and SDR are fixed at 100 mL min^{-1} and 50 mL min^{-1}, respectively. With FPR, the H_2 yield under the same conditions decreases in the order: Ar > N_2 > Air ≈ O_2. The facts that higher H_2 yields are obtained in Ar than in N_2 at the fixed SEDs can be ascribed to the more efficient energy transfer to H_2O from Ar ($^1P_1{}^0$) (11.83 eV) than from N_2 ($a^1\Pi_g$) (8.59 eV). The transition from N_2 ($X^1\Sigma_g{}^+$) to N_2 ($a^1\Pi_g$) by electric dipole is forbidden and N_2 excitation is expected to be less efficient than that of Ar. O_2 and air were a much less effective background gases. It is clear from these data that O_2 suppresses H_2 generation from water. It seems that O_2 and the active oxygen species generated from O_2 rapidly react with H or H_2. Another interpretation is that the dissipation of energetic electrons by O_2 lowers the efficiency of H_2 generation.[7]

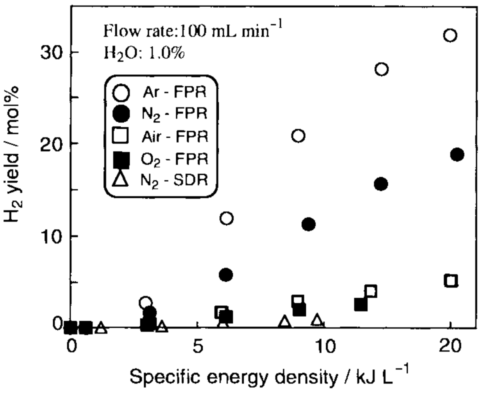

Figure 2. Effects of reactor and background gas on the H_2 yield.

Suib and coworkers have reported the water splitting with a dielectric barrier discharge plasma reactor.[4] Their highest H_2-generating rate (3.4 μmol min^{-1}) has been obtained in Ar at 2.3% of water concentration and 10 mL min^{-1} of gas flow rate with the reactor of Au-coated copper rod as inner electrode (Au-tubular PACT reactor). On the other hand, the H_2 generation rate with FPR ranged from 20 μmol min^{-1} to 54 μmol min^{-1} in Ar at 2.0% of water concentration in the gas flow rate range of 100 to 1000 mL min^{-1}. These data clearly show that FPR is a potential reactor to achieve high H_2-generating efficiency even in the absence of precious metal catalyst.

With SDR in N_2, H_2 yield reaches 1.0% at 9.7 kJ L^{-1} of SED. This efficiency is much lower than with FPR under the same conditions. In addition, the H_2 yield in N_2 with SDR is lower than those in air and O_2 with FPR. Tanabe and coworkers have reported almost the comparable efficiencies of H_2 generation from water with the same type of dielectric barrier discharge plasma reactor in Ar.[3] FPR and SDR have shown the comparable performances in the decomposition of trichloroethylene, bromomethane, and tetrafluoromethane in N_2,[8] suggesting that almost the same plasma intensity is obtained in both the reactors. These data suggest that $BaTiO_3$ does not act as a catalyst in the cleavage of chemical bonds. Therefore, the reactor-dependent H_2 yield observed in this reaction offers a corroboration that higher electron temperatures are obtained in FPR than in SDR[9] and the Au-tubular PACT reactor.[4]

We have shown here the effects of reactor and background gas on the H_2 generation from water in nonthermal plasma. Approximately 63% of H_2 yield is obtained as maximum in the water decomposition in N_2 with FPR. The efficiency of H_2 generation is decreased by gaseous oxygen. The optimized water content is about 2.0% in N_2. SDR has shown the lower performance compared with FPR, suggesting the different electron temperatures in both the reactors at the same input energy densities.

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