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Characteristics of Methane Destruction Using a Pulsed Corona Discharge at Atmospheric Pressure

MISHRA Lekha Nath, SHIBATA Kanetoshi[1], ITO Hiroaki, YUGAMI Noboru and NISHIDA Yashushi

Energy and Environmental Science, Graduate School of Engineering, Utsunomiya University, Utsunomiya 321-8585, Japan

[1]Kanto Polytechnic College, Oyama 323-0813, Japan

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Abstract

Experiments are performed to improve a pulsed corona discharge system for methane destruction at atmospheric pressure. The corona discharge is energized by 6–12 μs wide voltage pulses (0.3–7 kV) at a repetition frequency of 1.050 kHz. The characteristic of methane destruction is observed by a mass spectrometer. We have found that methane destruction depends on the parameters such as: pulse width, input pulse voltage, repetition frequency, discharge current and discharge time. The effects of argon gas on methane destruction were also observed. The structural geometry of the soot, resulting from discharge process, is observed by transmission electron microscope. The main aim of this study is to show that the discharge could help as for the production of hydrogen and carbon nanotubes.

Keywords:

pulse corona, gas discharge, mass spectrometer, electron transmission microscopy (TEM), carbon nanotubes (CNTs), hydrogen.

1. Introduction

The world needs for a consumption of low price energy in which it increases day per day. Some studies predict that the global energy consumption will at least be triple in the next 30 years [1]. Consumption of energy depends evidently on the increase in population and economic situation. The environmental contaminations, such as carbon dioxide production by day to day technologies led to an anxious level, [2,3], that is why refinement or filtering methods have to be developed. We believe that the future source of energy will be the controlled thermonuclear fusion for producing electric power, but it is very far to be economically feasible in present world. The hydrogen fuel, is believed to be an alternative means for near future, because it is the most abundant element on the earth (more than 75% of the environmental elements), and renewable.

Recently, non-equilibrium plasmas source have been extensively studied as a possible way to initiate the reaction of methane for producing the various products, such as methanol and higher hydrocarbons for being useful in industrial applications [4]. A number of researchers are also interested in finding a way to improve synthesis gas production from methane by using the electric discharge plasma [5]. Considerable research efforts have been made on conversion of methane using pulsed barrier discharge into more useful chemicals including synthesis gas, gaseous and liquid hydrocarbons [6,7]. Even from the earlier days, corona discharge processes have played an important role in many industrial applications, such as electrostatic precipitation, electro photography, static control in semiconductor manufacture, ionization instrument, generation of ozone and destruction of toxic compounds [7]. But its application as a pulsed power supply refers to recent years.

On the other hand, CNTs [7-9] have been demonstrated as enable components of various electronic and chemical-mechanical devices functional on the molecular scale. Among these devices are chemical force sensors, gas detectors, field emission displays andso on. To develop these devices into manufacturable products and to gain control of device assembly in the molecular level a practical technique for in situ nanotube growth is needed.

It is worth mentioning here that there are no such related works dealing with the production of hydrogen and CNTs using brush electrode in pulsed corona discharge. Hence, keeping this point of view, a new technique has been developed in our laboratory for the conversion of methane to hydrogen and carbon at atmospheric pressure and ambient temperature. The main reason for choosing this method, is based on its potential to operate at atmospheric pressure, with an electric discharge, operating relatively at low power and to secure a suitable energy for activating the methane molecules.

Corresponding author's e-mail: mishra@plasma.ees.utsunomiya-u.ac.jp

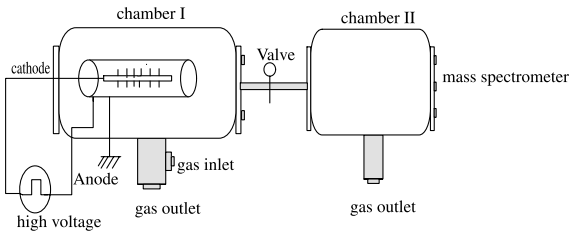

Fig. 1 Experimental Setup.

The present paper is organized as follows. In Sec. **2**, the experimental setup is introduced, Sec. **3** gives the results and its discussions, and the paper is concluded in Sec. **4**.

2. Experimental set up

The experimental set up is shown in Fig. 1. The corona discharge was performed in the chamber I (ϕ 150 mm × 360 mm), called the discharge chamber. This discharge chamber was connected with a narrow stainless steel tube (ϕ 7 mm × 1,500 mm) to the Chamber II (ϕ 150 mm × 300 mm) through a needle valve. This chamber II, called the detection chamber, was fitted to a mass spectrometer analyzer head (model Pfeiffer vacuum Prisma^{TM} 80 quadrapole mass Spectrometer QMS 200). The vacuum system in the discharge chamber side consisted of one 1,200 l/s diffusion pump backed by one 300 l/min rotary pump. In the detection chamber side, it consisted of one 550 l/min Turbo Molecular pump backed by one 300 l/min rotary pump. The base pressure of both chamber were kept below 10^{-7} Torr. After completion of evacuating process, the methane gas was introduced into the discharge chamber for increasing the pressure of chamber to 1 atmosphere. When the corona discharge is finished, the needle valve between the chambers was adjusted to maintain the required operating pressure range for a mass spectrometer. The operating pressure of mass spectrometer is less than 0.4×10^{-4} Torr. The structural geometry of CNTs were observed by TEM.

The pulsed discharge reactor used in this work was done by using a high voltage pulse power supply. A four channel digital storage oscilloscope was used to record voltage waveforms through a voltage divider. The discharge current through 1 kΩ resistor connected in series with grounded electrode was used for the calculation of the pulse energy and the discharge power. Plasma -chemical reactions were carried out in a gas reactor, placed in the discharge chamber, made of stainless steel mesh (ϕ 26 mm × 200 mm) and with two different metallic electrodes inserted inside it, i.e (i) brush electrode made of iron (ϕ 6 mm × 200 mm), and (ii) nickel electrode (ϕ 5 mm × 200 mm). The inner electrode and the outer mesh electrode were separated from each other with the help of ceramic insulator avoiding the electrical connection. The high voltage pulse was supplied to the inner electrode and the outer electrode was grounded with connecting wire. In the case of brush electrode, a number of brush-like needles made of stainless steel (ϕ 1 mm × 3 mm) were placed on it with 1 cm gap between each other as shown Fig. 1.

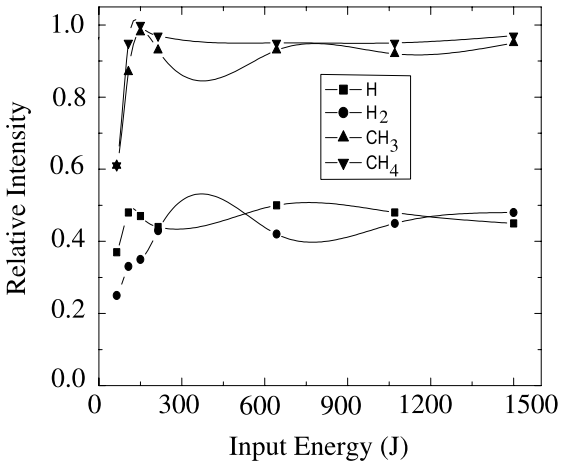

Fig. 2 Relative intensity of different molecules and radicals with a variation of input energy.

3. Experimental results and discussions

When an electric field (DC, AC or pulse) is applied to electrodes, the energetic electrons transfer their energy to gas molecules by collision, leading to excitation, attachment, dissociation, or ionization of molecules.

Figure 2 shows the relative intensity of molecules and radicals as a function of energy, at constant frequency (1.050 kHz) and pulse width of order of 10 μs during five minutes. However, discharge current varies from 5.8 mA to 68 mA. For example, for 150 J energy, the amount of current is found to be 15.2 mA. In this case, a brush electrode (6 mm diameter and 200 mm length) is used for discharging of methane. This figure infers that the relative intensity increases rapidly up to 300 J, and after then it gradually changes up to 1500 J. This result indicates that at low input energy, the production rate of hydrogen is more than that of high input energy consumption. In this case, the radicals such as CH_3 and H produced by plasma from source gas, will undergo chain reaction leading to re-formation of methane and hydrogen gas.

Figure 3 shows the variation of intensities of hydrogen and methane molecule with a variation of discharge time. Here, 10 μs duration of pulse voltage 7 kV with a repetition frequency of 1.050 kHz is applied to the electrodes in an atmospheric pressure. We have found that for longer discharge time, the intensity of hydrogen is higher than that of shorter time. Conversely, by increasing the discharge time, the intensity of methane decreases linearly. We note that the discharge time is one of the key factor for producing hydrogen gas as well as CNTs.

Figure 4 shows the variation of discharge current corresponding to different input voltages, in presence and absence of argon gas. The discharge currents (I_d) were found to be in the range of 5.8–68.0 mA and 7.0–90.0 mA for methane and Argon-methane plasma respectively, at discharge voltages of 0.3–7 kV. Hence, this result infers that the discharge current increases in the presence of argon. Although the argon gas is an inert, the decomposition in a discharge state would have a certain influence on energy distribution of

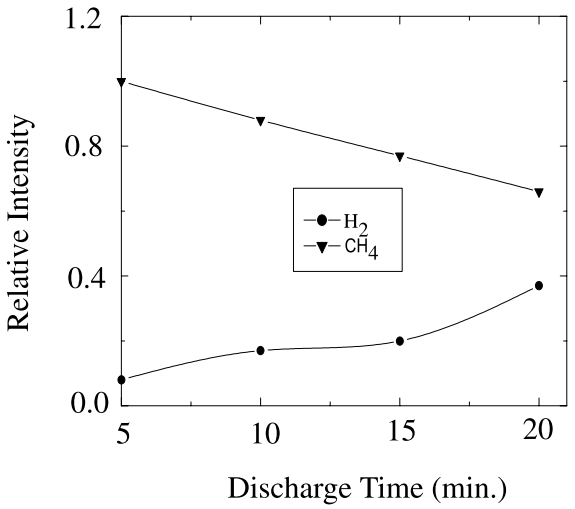

Fig. 3 Relative intensity of hydrogen and methane molecules with a variation of discharge time.

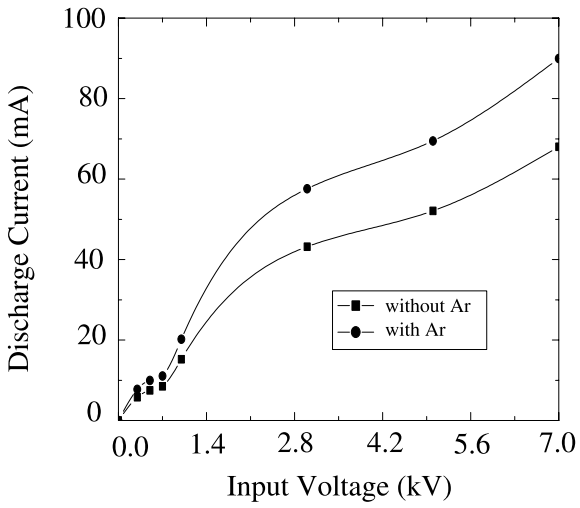

Fig. 4 Discharge current as functions of input voltage with/ without mixing argon.

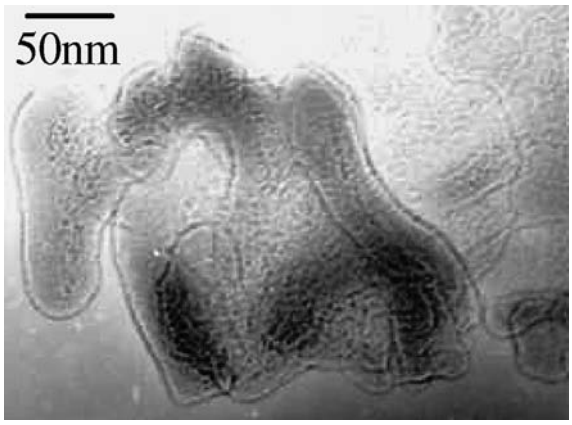

Fig. 5 Typical morphology of CNTs observed by TEM. Scale bar 50 nm.

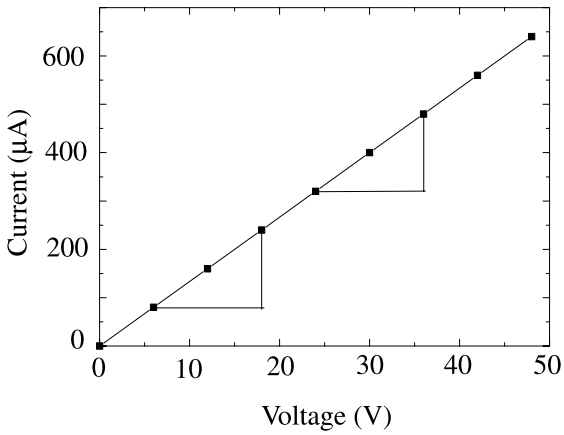

Fig. 6 Typical I-V characteristics of CNTs, measured by using four probe method.

electrons too, which helps the production of various active species during the formation of plasmas. More specifically, the injection of argon atoms into the input gas, enhances the rate of CH_4 conversion to its radicals. In this sense, the argon gas acts apparently as a catalizer. For this purpose, the optimal relative pressure of argon to methane was chosen as 1:760.

Figure 5 shows the TEM picture of the CNTs of the soot, collected from nickel electrode with 5 mm diameter and 200 mm length. The figure shows different bundle of bent tubes. In general, the apparent shape of the tubes are quite similar to that of CNTs produced by arc-evaporation method [10,11]. The growth process of CNTs is unique [12] since carbon is the only elemental material that forms hollow tubes and that may be due to the strong surface energy anisotropy of graphite basal planes compared to other lattice planes. However, the individual tube apparently, had greater tendency to produce the 'ropes' or aligned bundles.

Figure 6 shows the I-V characteristics of CNTs. In this case, four probe-measurements were made to determine the voltage drop across a short length (15 mm) of cathode. We have found the resistivity of CNTs nearly 0.15 Ω cm at ambient pressure and temperature of 299 K. For calculating its resistivity, a corresponding resistance (i.e.75 Ω) is calculated from a slope of I-V curves and a cross section area (i.e. 0.307 mm^2) of deposited soot on the cathode is measured by using a micrometer screw gauge. Experimentally, it is found that the resistivities of CNTs at 300 K varied by up to six orders of magnitude, from 5×10^{-6} to 6 Ω cm [13]. Our result also lies within this range, which helps to proof the morphology of soot inCNTs.

Under pulse corona plasma production, the activation and conversion of methane could be realized via collision of methane molecule with energetic electrons.

$$CH_4 + e \rightarrow CH_3^* + H^* . \qquad (1)$$

This reaction will very likely be followed by the formation of H_2 through the reaction of another molecule of methane with H-radical

$$CH_4 + H^* \rightarrow CH_3^* + H_2 \,. \qquad (2)$$

When argon gas is introduced into methane, its internal energy produced by the dissociative recombination (RD) reaction via the following equation, may enhance the further dissociation.

$$Ar + e \rightarrow Ar^* \rightarrow Ar^+ + e \rightarrow Ar + h\nu \qquad (3)$$

where h is the Plank's constant and ν is the frequency of photo-radiation.

4. Conclusion

We have investigated the characteristics of the production of hydrogen and CNTs by the decomposition of methane inside the reactor using pulse corona discharge under conditions of room temperature and atmospheric pressure. The development of dissociationof methane with corona discharge under several conditions have been observed. We have noticed that the key radicals such as CH_3 and H produced by pulse corona plasma from source gas, will undergo chain reaction leading to efficient formation of hydrogen gas as well. We have found the external diameter and resistivity of CNTs around 50 nm and 0.15 Ω cm respectively. The main results obtained from the present experiments could be quite useful for the production of hydrogen, CNTs, and future industrial applications.

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References

[1] C.A. Dahl and L.M. Donald, Energy Sources **20**, 875 (1998).
[2] G. Isenberg, Journals of Power Sources **84**, 214 (1999).
[3] I. Diner, Energy Sources **20**, 427 (1998).
[4] J. Huang and S. Suib, J. Phys. Chem. **97**, 9403 (1993).
[5] L. Zhou, B. Xue, U. Kogelschatz and B. Eliasson, Energy and Fuels **12**, 1191 (1998).
[6] M. Okumoto *et al.*, IEEE Ind. Applicat. **37**, 1618 (2001).
[7] T. Kishida *et al.*, Thermal Science and Engineering **7**, 1 (1999).
[8] J.S. Chang, P.A. Lawless and T. Yamamoto, IEEE Trans. Plasma Sci. **19**, 1152 (1991).
[9] S. Iijima, P.M. Ajayan and T. Ichihashi, Phys. Rev. Lett. **69**, 3100 (1992).
[10] N. Agraint, J.G. Rodrigo and S. Vierira, Phys. Rev. B **47**, 12345 (1993).
[11] Y. Zhang and H. Dai, Appl. Phys. Lett. **77**, 3013 (2000).
[12] S. Iijima, Phys. Rev. Lett. **56**, 354 (1991).
[13] T.W. Ebbesen, Ann. Rev. Mater. Sci. **24**, 235 (1994).