PULSED DISCHARGE PLASMAS IN SUPERCRITICAL CARBON DIOXIDE *

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Abstract

In recent years, several studies about electrical discharge plasma in supercritical carbon dioxide (CO_2) have been carried out. One of the unique characteristics of supercritical fluid is a large density fluctuation near the critical point that can result in marked dramatic changes of thermal conductivity. Therefore, the electrical discharge plasma produced in supercritical fluid has unique features and reactions unlike those of normal plasma produced in gas phase. In our experiments, two types of large volume plasma, namely the pulsed streamer discharge and the pulsed arc discharge have been generated in a supercritical CO_2. It was found that the characteristic of the pulsed discharge plasma in supercritical CO_2 depends on the change of the CO_2 density near the critical region.

I. INTRODUCTION

Recently, the supercritical fluid is greatly considered as the substitute of the organic solvent used in foodstuffs, medicine and also in chemical reaction technology due to its benign property to environment [1, 2]. Supercritical fluids have unique tunable properties like diffusivity, density, thermal conductivity and mass transfer rate, which can be adjusted continuously by changing temperature and /or pressure. Specially, in the chemical reaction field, supercritical fluid is effectively used to enhance the reaction rate with the control of reaction path such as prevention of the catalyst degradation evolving poisoning material, radical reaction and ion reaction at high temperature. In water medium and at atmospheric condition, discharge plasma was successfully produced and actively used to treat aquatic harmful living organisms, environmental contaminant and also for recycling of building construction materials [3, 4, 5, 6]. Discharge plasma in supercritical fluid has various active chemical effects those might be very interesting and peculiar which would indicate a new horizon to this field.

A large volume of pulsed discharge plasma was successfully produced in supercritical CO_2 at 8 MPa [7]. Specially, near the critical region of CO_2 (31.1ä and 7.38 MPa), a large fluctuation of its density is observed that can results in some dramatic change of thermal conductivity. Supercritical carbon dioxide is considered as reaction medium because it is nontoxic, non corrosive, inflammable and not explosive.

The objectives of our works are to study the potentiality of supercritical CO_2 as a unique medium for plasma formation as well as the characteristics of pulsed discharge plasma.

Fig. 1 shows a typical photographs of the arc discharge (thermal plasma) produced by our experimental apparatus at 0.1 to 8.0 MPa and at 60ä . For instance, the light emitted from discharge plasma directly indicates its chemical activity.

In supercritical CO_2, it is observed that the discharge plasma is much brighter than that in gas phase. It has been already reported that the micrometer-scale discharge plasma in supercritical CO_2 can be generated with very lower voltage than predicted by Paschen's law, but the mechanism for this phenomenon remains unclear [8].

Figure 1. Pressure dependency of arc discharge in CO_2

II. EXPERIMENTAL APPROACH

Fig. 2 shows the schematic diagram of the supercritical plasma reactor (AKICO Co., Japan) provided an inspection window through which continuous monitoring is performed. Reactor vessel is made of stainless steel: SUS316 having compressive strength of 30 MPa and the total volume of reaction cell of 1,300 ml. Carbon dioxide was pumped with the syringe pump (THAR SE100X,

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ISCO Inc., USA) to the cell. The pump head was cooled at about 8ä by flowing cooling liquid through cooler. A thermocouple and a backpressure regulator controlled the temperature and the pressure of the reaction cell. The experimental pressure was changed from 0.1 to 20 MPa by introducing carbon dioxide at constant experimental temperature. The pulse transformer (winding ratio 1:3) was connected to a Blumlein type Pulse Forming Network (B-PFN) consist of 7 stages, which has a capacitor (1.7 nF) and an inductor (0.2 μH). A high voltage probe (EP100K, Pulse Electronic Engineering Co. Ltd., Japan) was used to measure the voltage. The current was measured by a current transformer (4997, Pearson Electronics, Inc., USA), which was connected to a digital oscilloscope. During experiment, B-PFN charging voltage was constant at 17.5 kV and 13 kV for the cases of pulsed arc discharge and streamer discharge, respectively, by using DC power source (PS/EW40R15, GLASSMAN HIGH VOLTAGE, INC., USA). The point to plane electrode was employed and the gap distance of electrode was fixed at 10mm.

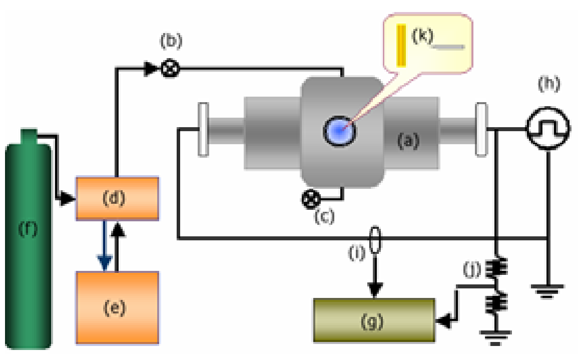

Figure 2. Schematic diagram of the experimental setup, and indices mean as follow; (a) SCF cell, (b) CO_2 inlet, (c) CO_2 outlet, (d) Syringe pump, (e) Cooling system, (f) CO_2 cylinder, (g) Digital oscilloscope, (h) B-PFN DC power source, (i) Current transformer, (j) High voltage probe, and (k) Point to plane electrode.

III. RESULT AND DISCUSSION

Two types of pulsed discharge such as arc discharge and streamer discharge were produced in supercritical CO_2 by applying pulse voltage. The experimental conditions are shown in Table 1.

Table 1. Experimental conditions

Discharge type	Arc discharge		Streamer discharge
Charging voltage	17.5 kV		13 kV
Temperature	32.5ä	100ä	37ä
Pressure	From 0.1 to 20 MPa		From 0.1 to 10 MPa
Electrode gap	10 mm		10 mm
Pulsed width	260 ns		195 ns

A. Arc discharge

Fig. 3 shows the dependence of the peak voltage on the pressure in cell at temperature of 32.5ä and 100ä .

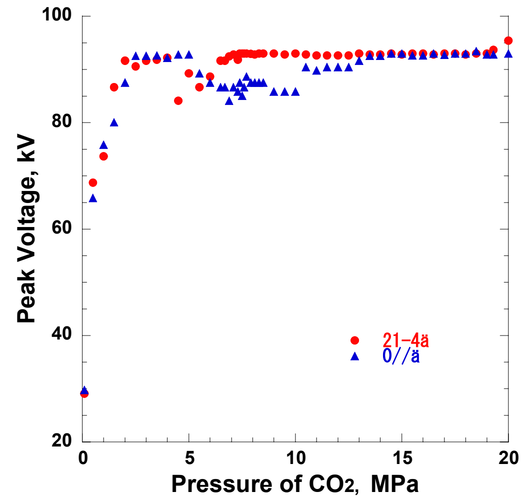

Figure 3. Characteristic of peak voltage at different pressures and temperatures.

Fig. 3 shows that the peak voltage is almost constant at the vicinity of 2 MPa followed rapidly increase, and decreases at the vicinity of 5-7 MPa. The peak voltage is almost again constant after around 10 MPa. This effect may be due to the output voltage of B-PFN did not reach at the design value and was saturated with about 90kV.

Ito and Terashima [8] reported that a rapid decrease of the breakdown voltage happens in the supercritical region using the electrode gap of the micrometer scale. Similar tendency was observed in our experiment but it was not so remarkable. In general, the clustering phenomenon [1, 2] may be considered to explain the competitive effect of the intermolecular interaction of the solvents (effect of the microscopic) and the swinging in the vicinity of a critical point (effect of the macroscopic) on breakdown. Because of the index that relates to fluctuation is the isothermal compressibility k_T and it is specifiable as follows:

$$k_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T ,$$

where V, P and T show the volume of fluid, pressure and absolute temperature, respectively. G stands for Gibbs's free energy.

The density fluctuation F_d is obtained from the relationship of that spatial fluctuation of the molecules number $\Delta N^2 = \langle N^2 \rangle - \langle N \rangle^2$, the isothermal compressibility k_T and Boltzmann's constant k_B [9]:

$$F_d = \frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = \frac{\langle N \rangle k_T k_B T}{V} .$$

Therefore, from the equation of states, and density $\Delta\rho^2$, it is easily seen that the following relations hold:

$$\frac{\langle(\Delta\rho)^2\rangle}{\langle\rho\rangle^2}=\frac{k_T k_B T}{V}$$

Figs. 4(a) and 4(b) show the pressure dependency of "Time delay from the voltage impression to the dielectric breakdown: T_{Delay}" in the point-plane electrode set up in supercritical CO_2 on "Density of carbon dioxide: N_{CO2}".

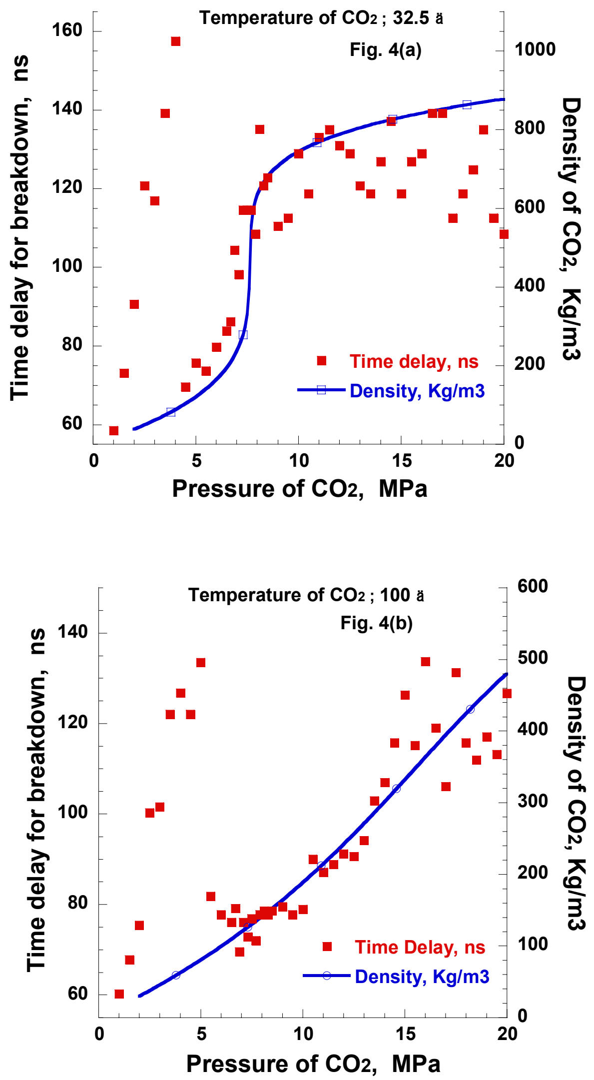

Figure 4. Characteristics of time delay for breakdown and of density of CO_2 at different pressure and at temperature of (a) 32.5ä and (b) 100ä .

The T_{Delay} is defined as Full Width at Half Maximum (FWHM) of applied voltage. The solid lines in Fig. 4 (a) and (b) indicate the variation of CO_2 density with pressure at 32.5ä and 100ä , respectively, is calculated from the equations of stats. It reveals that the time delay gradually increases near critical point where the large density fluctuation of CO_2 is usually observed this may be due to which a local channeling between the electron and cluster is formed.

B. Streamer discharge

For the production of streamer discharge, the charging voltage to the generator was controlled so as not to occur the arc discharge and applied voltage to the electrode was 13 kV of peak while the gap between the point and plane electrode was 10 mm. The temperature of reaction cell was kept at 37ä . Photographs of the streamer discharge were taken by using a digital single lens reflex camera (D30, Canon, Japan) through the inspection window of reaction cell. The operating conditions of the camera were the diaphragm F22, exposure time 3s (4 shots integrated) and ISO sensitivity 200. Under our experimental condition (0.1-10 MPa), the waveform of voltage during the production of streamer discharge was almost unchanged and the pulse width and the peak voltage were 195ns and 69kV, respectively.

Figure 5. Photograph of the streamer discharge plasma at pressure of 9.5MPa and at temperature of 37ä .

Fig. 5 shows the integration photograph of the pulsed streamer discharge at 9MPa. It was observed that the brightness and thickness of electrical discharge channels increase with the increase in pressure and the brightest one obtained at 9.5 MPa shown in Fig. 5 except at near critical pressure, 7.5 MPa. This effect may be because of the higher input energy at 9.5 MPa and other causes such as thermal conductivity.

IV. SUMMARY

Discharge plasmas (arc discharge, streamer discharge) were produced both in gaseous CO_2 and in supercritical

CO_2. Time delay of breakdown voltage and peak voltage were measured at 32.5ä and 100ä for arc discharge and at 37ä for steamer discharge within the pressure ranges of 0.1 to 20 MPa. It is concluded that from near critical conditions the time delay for breakdown voltage gradually increased with pressure, though there was fluctuation before critical pressure. A greater discrepancy of the time delay for breakdown was observed near this critical point due to the abrupt change of the density of CO_2. The brightest and thickest streamer discharge plasma was produced at 9.5 MPa. So we think the density of CO_2 is vital parameter for the plasma production in supercritical fluids.

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