Plasma Production in Pressurized Carbon Dioxide up to Supercritical Conditions

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Supercritical carbon dioxide is great importance in industrial uses as the extracting solvent of various useful ingredients, a reaction solvent and a reaction catalyst since it has unique characteristics such as high diffusivity(like a gas) and high solubility (like a liquid). On the other hand, electric discharge plasma also has higher chemical reactivity. Therefore, the combination of SC CO_2 and electric discharge plasma may offer the possibility of a new horizon in the future reaction fields. This report deals with the effect of the polarity on dc breakdown voltage characteristics of a point-to-plane gap in supercritical CO_2 that is required to design a plasma reactor.

In the experiments, the CO_2 state was controlled within the gas, liquid, and supercritical phases. The experimental results showed that it was found that negative polarity is desired condition for the dc plasma reactor since an active corona supplying rich chemical radicals appears in supercritical CO_2 under such condition.

Keywords: Supercritical carbon dioxide, corona discharge, electrical breakdown, breakdown mechanism, plasma reactor

1. Introduction

Supercritical fluid (SCF) has received increasing importance in a variety of fields due to its high diffusivity (like gas) with improved mass transfer rates and high solubility (like liquid), and the operation can be manipulated by changing temperature and pressure. Carbon dioxide (CO_2) is mostly used as SCF because of its low critical temperature 304.1 K and low critical pressure 7.38 MPa, having significant physical as well as transport properties. Those properties of carbon dioxide make it widely used as an extracting solvent of various useful ingredients, reaction solvent and reaction catalyst [1, 2]. On the other hand, electric discharges have well known properties of high reactivity and high chemical activity. Over the past few decades, a considerable number of studies have been conducted on the research of electric discharge contributing to an environmental problem such as the decompositions of harmful gases, removal of toxic compounds namely dioxin [3-5]. However, very few attempts have been made about the reaction of the plasma production in SCFs. Several studied have been made on the plasma production in supercritical carbon dioxide (SC CO_2) [6, 7]. The research of discharge phenomena in SCFs is an undeveloped field, and the prebreakdown phenomena are not well explained. Therefore, it is an important and attractive job to study of electric discharge plasma production in SCFs, and possibly to offer significant and new ideas in future industrial fields.

The objective of this work is to study the prebreakdown phenomena and breakdown characteristic in CO_2 medium at the experimental conditions from atmospheric to supercritical condition in order to develop a new chemical reactor that can be used for the production of discharge plasma in SC CO_2.

2. Thermodynamic State of CO_2

Figure 1 was obtained from the numerical calculations of the physical properties of CO_2 using the equation of state [8], and shows the different phases of CO_2 with the parameters such as density, pressure and temperature. The figure contains some density isotherm lines and regions. The isotherms below the critical temperature and pressure in lower density region are termed as saturated gas lines and those of in higher density region are saturated liquid lines. In the higher density region, the liquid phase is divided into two regions such as higher pressurized liquid region located above the critical pressure (P>Pc) and lower pressurized liquid region located below the critical pressure (P<Pc).

This experiment was carried out at 298 K and 313 K. The density isotherm at 298 K indicates that the density of

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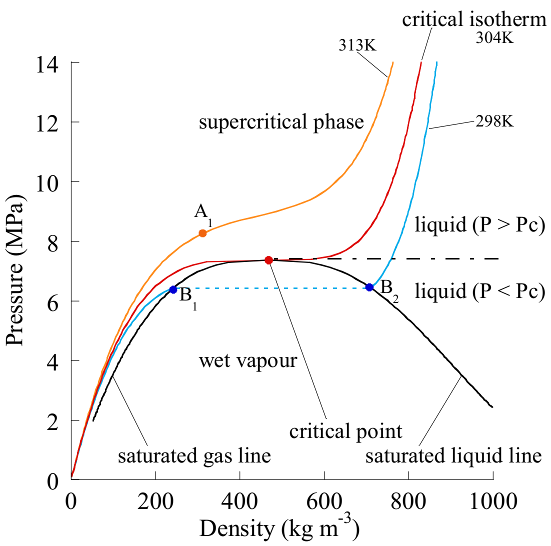

Fig. 1. CO_2 pressure-density diagram

CO_2 increases with increase in pressure from gas to liquid phase, and that of at 313 K the density increases from gas to supercritical phase. The figure also illustrates how the density at different regions such as lower pressured liquid, higher pressured liquid and SCF regions of CO_2 medium changes while it is locally heated at the tip of needle during the production of discharge plasma. In the region of lower pressurized liquid, the state at the tip of a point seems to shift in the direction where the density of CO_2 decreases with the Joule's heat from electric discharge plasma. In other words, lower pressurized liquid phase seems to move into gas phase through wet vapor region where the gas and liquid molecules are in fog condition. On the other hand, in the region of higher pressurized liquid, the same tendency is observed, but the higher pressurized liquid phase moves to SCF phase. This point of view deserves careful attention.

3. Experimental Apparatus

A schematic diagram of the experimental setup is shown in Figure 2. The test reactor is made of stainless steel: SUS316 having compressive strength of 30MPa, the maximum temperature of 573 K and the total volume of reaction cell of 1,300mL. Power lead is introduced through the center of long bushing made of peak resin, and the annular space is sealed off with double o-rings. Liquid CO_2 from a cylinder with a siphon attachment was passed through a cooling head of high-pressure pump to the test reactor. A thermocouple and a backpressure regulator controlled the temperature and the pressure of the test reactor, respectively. After attaining the experimental temperature and pressure, it was kept for a night for steady state of carbon dioxide medium in test reactor. The experimental temperatures were 298 K and 313 K. At constant temperature, the experiment was performed at different pressures in descending direction. The negative/positive dc voltage from a high voltage stable dc power supply was applied to needle electrode at a rate of applied voltage 2.5 kV/s. The signal of corona light intensity measured by photo multiplier tube (PMT) goes into the oscilloscope of the shield room.

The relation of breakdown voltage (BDV) to each pressure was converted to the relation of BDV vs. corresponding density because the ionization phenomenon in media is deeply related to mean free path that is inversely proportional to density of medium, it was numerically calculated by using the equation of state [8] at each experimental pressure. That is, the experimental results for BDVs were shown in respect with the density changes of CO_2.

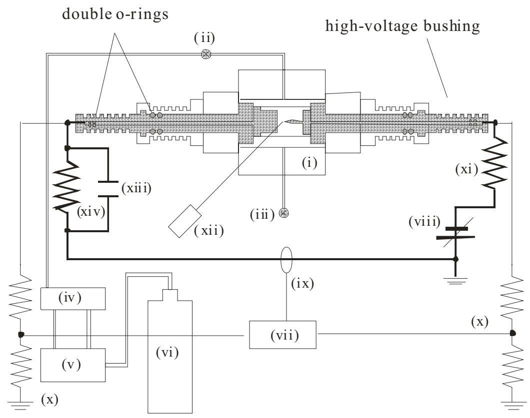

Fig. 2. Schematic diagram of the experimental setup: (i) test cell, (ii) CO_2 inlet, (iii) CO_2 outlet, (iv) syringe pump, (v) cooling system, (vi) CO_2 container, (vii) digital oscilloscope, (viii) dc power source, (ix) current transformer, (x) high voltage probe, (xi) damping resistor, 2 MΩ (xii) photomultiplier (xiii) capacitor, 17×10^{-3} μF and (xiv) damping resistor, 2 MΩ

4. Results and Discussion

4.1 Pre-breakdown phenomena

Figure 3a shows the typical negative corona onset voltage V_C and breakdown voltage V_B in supercritical phase at 313 K. The discharge light intensity I_{ph} and the applied voltage V_{app} were obtained by additional experiments using a short gap of about 80 μm and a high increase rate of voltage.

The corona light intensity is increased with the applied voltage. Once an electric discharge form shifts to arc from corona discharge, simultaneously with a dielectric breakdown, luminescence intensity is rapidly increasing and is surpassing the measuring range of an oscilloscope. In our experimental condition, negative corona discharge has been observed in both supercritical and liquid phases, but it has not been so stable in gas phase. On the other hand, positive corona discharge has not been observed in any phases shown in Figure 3b.

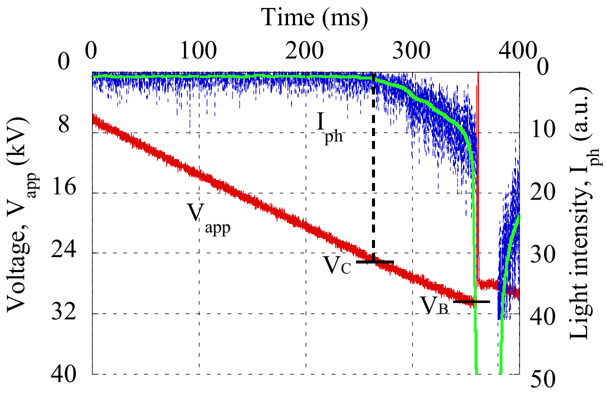

Fig. 3a. Typical negative corona onset and breakdown voltages in supercritical phase at 313 K

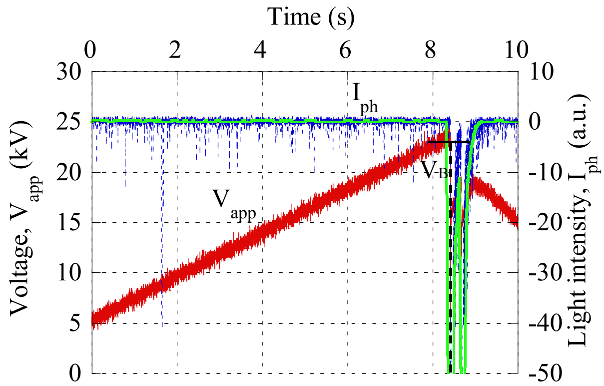

Fig. 3b. Typical positive corona onset and breakdown voltages in supercritical phase at 313 K

4.2 Breakdown Characteristics

BDVs for both polarities are measured as a function of density as shown in Figure **4,** where the corona onset voltages (COV) are also plotted. In the figure, the average of the five measured BDVs and their deviation are illustrated by an open symbol and vertical bar. The followings are noted from the experiments under the conditions of d = 250 µm, r = 80 µm, and T=313 K and of d = 250 µm and r = 120 µm and T=298 K.

4.2.1 Gas phase

The density region of the CO_2 gas phase at 298 K and 313 K is less than 240 kg m^{-3} (Figure 1). The negative BDV is lower than the positive BDV at a given gas density. The slope of the BDV changes with density and polarity. With a negative polarity, the characteristics consist of a convex upward curve in the low density region and a convex downward curve in the high density region, and with positive polarity, the BDV changes with density in a similar manner as negative polarity at 298 K but at 313 K it shows a convex upward curve in all density regions. It could be argued that the negative BDV increases significantly near the saturation state at 298 K and the sub-supercritical state at 313 K, but in contrast with this, the positive BDV tends to show complete saturation at 313 K as shown in Figure 4a.

In all experiments, the measured BDV tends to scatter widely in the liquid and supercritical phases and the deviation for positive BDVs is much larger than for negative BDV. It should be noted that the lowest BDV for positive polarity is somewhat close to the negative BDV in gas. Therefore, we believe that corona discharge might occur in the gas at positive polarity but the light emission is too weak to be detected by the photomultiplier measurement system. Since the corona observation system in this study needs to be improved, we will deal with the BDV characteristics in the following.

The drastic increases in the negative BDV near saturation at 298 K and the sub-supercritical state at 313 K in Figure 4 may be explained by eletrostriction. When a high voltage is applied to a non-uniform field gap in saturation or sub-supercritical gases, the gases in the region of the highest electric field will condense by eletrostriction and BDV is rapidly increasing.

4.2.2 Liquid phase

In the case of liquid phase, the density region is in the range more than 700 kg m^{-3} at 298 K. Both positive and negative BDV increases with density. This increasing rate of negative BDV is larger than positive one.

Negative breakdown occurs after the preceding corona discharge, as stated Section3, and the corona discharge happen the density near the tip declining. Therefore, the breakdown mechanism of the liquid can be classified into two categories: bubble-triggered breakdown in pressures lower than the critical pressure; non bubble-triggered breakdown in pressures higher than the critical pressure.

4.2.3 Supercritical phase

Finally, in the case of supercritical phase, the density region is in range more than 240 kg m^{-3} at 313 K. Negative breakdown occurs after the preceding corona discharge, like a liquid phase, and the negative BDV increases with density. However, the positive average BDV is almost independent on the density. The strong density dependence of negative BDV is probably related to the formation of a low-density region due to electron injection from the cathode that will suppress breakdown through the higher density region surrounding the low-density region and trigger a corona discharge. The corona discharge in the low-density region then produces a corona stabilization effect, i.e., that is the strong density dependence of negative BDV.

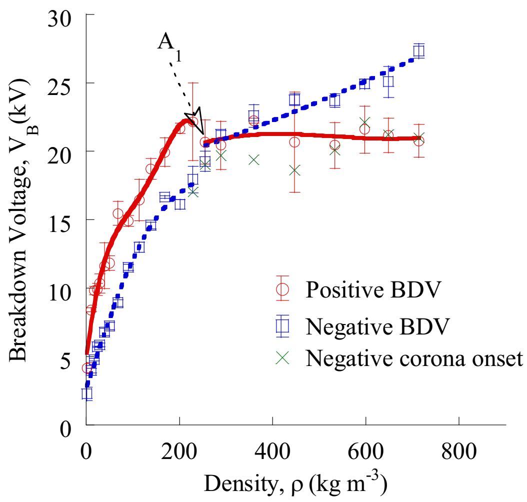

Fig. 4a. Dependence of BDV on CO_2 density; *T*: 313 K, *d*: 250 μm, *r*: 80 μm

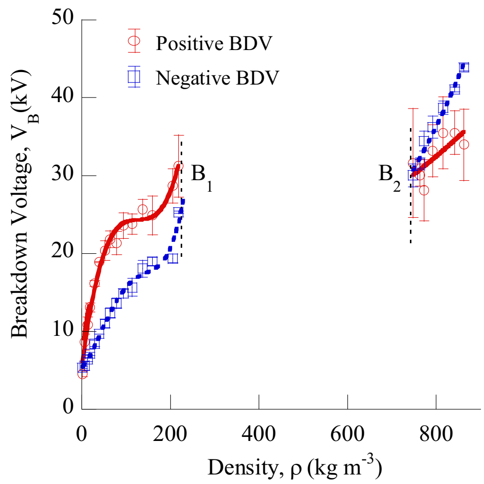

Fig. 4b. Dependence of BDV on CO_2 density; *T*: 298 K, *d*: 250 μm, *r*: 120 μm

5. Summary

The breakdown phenomena and breakdown voltage characteristics of positive and negative dc discharges were investigated in carbon dioxide medium using needle to plane electrode. The following results were obtained:

In the gas phase, positive BDV is higher than negative BDV and seems to be affected by the electrostriction effect in the higher density region near the saturation or sub-supercritical phase. The lowest value of positive BDV at a given density is sometimes close to that for negative BDV. It is believed that positive corona discharge might appear before breakdown although measurements with a photomultiplier were not able to detect any light emission from the corona.

In the liquid phase, negative BDV is higher than positive BDV because of negative corona stability effect. The breakdown mechanism in lower-pressure liquid for negative discharge can be explained by the bubble-triggered effect that is not applicable for the higher-pressure liquid as well as supercritical phase.

In the supercritical phase, BDV is almost constant. In terms of corona discharge, negative discharges in SC CO_2 with a higher density are better for a plasma reactor than positive discharges.

Breakdown voltages are fluctuated significantly at the same experimental conditions in the case of positive discharge, whereas no such fluctuation is observed in the case of negative discharge.

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