Negative DC Corona Discharges in Supercritical Carbon Dioxide

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ABSTRACT

In our previous work, positive dc discharge plasmas have been measured and analyzed. In present studies, the measurements for breakdown voltages were made with point-plane electrodes for high-pressure carbon dioxide (CO_2) up to supercritical conditions under negative DC applied voltage. Negative dc corona (glow discharge) is Trichel pulses. Corona pulses, whether positive or negative, are streamers: each pulse is a streamer. The results exhibit a dramatic phenomenon: corona discharge can be generated, and corona discharge area is formed from onset to spark breakdown with a very low voltage at critical point and in its close vicinity, where no corona discharge exists in normal high pressure gas. An explanation is probably because of the unique characteristic anomaly of large fluctuations in the density and energy at critical point and in its close vicinity, where the extensive unstable clusters are formed, and the mean free path of electrons are increased.

INTRODUCTION

The investigation of corona discharge (discharge plasma) in supercritical fluids (SCFs) is of few and of interest. Corona discharge (or discharge plasma) studies have been undertaken for many years, not only because of the scientific interest in corona mechanisms but also because of their practical engineering importance [1-4]. However, presently only a trial generation of discharge plasma in SC CO_2 was performed with a micrometer scale gap and platinum coplanar film electrodes produced with lithography technique [5], obviously the explanation is very limited and some phenomenon still remain unclear. In the present work, SC CO_2 was used as a medium for corona discharge generation because it is nontoxic, not corrosive, inflammable and not explosive, as environmentally acceptable solvents for chemical reactions. Furthermore, its critical temperature of 304K is closed to the ambient temperature. By experiments, the breakdown voltages in very high pressure CO_2 up to the SCF environment using 0.5-1.0mm gap point-plane electrodes have been measured. The measured results show a bizarre situation for CO_2 breakdown voltages, which is much lower in near the supercritical point than the measured in the normal high pressure gas. Therefore, an ionized plasma state can be formed in the vicinity of the critical point with very low applied voltage; more reasonable explanations and discussions are made in Section 3. The discharge plasma generated in SCFs is one of non-thermal plasmas that demonstrated promising results due to its capability of simultaneous treatment of various pollutants, easy maintenance and integration with the exist systems.

EXPERIMENTS

The schematic diagram of the experimental equipment (AKICO, CO.) used for plasma generation in SC CO_2 is shown in Figure1. CO_2 is initially cooled and compressed to the desired pressure by a high- pressure pump, then pumped into the SCF cell, which is a 1300ml cylindrical stainless steel optical chamber with high pressure glass windows (max. pressure 30MPa). In the cell, the CO_2 can be heated by heaters, and pressure and temperature were monitored by using a sensor and thermocouple, and controlled within the accuracy of ±0.05MPa and ±1K, respectively. A point-plate electrode configuration was employed to produce discharge plasma under positive dc applied voltage, and the oscilloscope to monitor voltage and current. The detailed experimental conditions are as follows:

Fluid: CO_2
Temperature: 37.0□
Pressure: 0.1 to 15 MPa
Electrode: Point - Plane
Gap: 0.5 - 1 mm
Negative DC Voltage: 0 to 40 kV

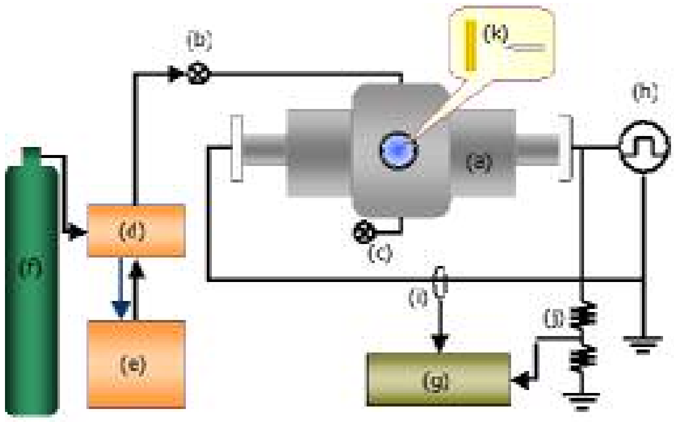

Figure 1. Schematic diagram of the experimental setup, and indices mean as follow; (a) SCF cell, (b) CO_2 inlet, (c) CO_2 outlet, (d) Syringe pump, (e) Cooling system, (f) CO_2 cylinder, (g) Digital oscilloscope, (h) Negative DC power source, (i) Current transformer, (j) High voltage probe, and (k) Point to plane electrode.

RESULTS AND DISCUSSION

The photograph of negative dc corona discharge in SC CO_2 condition (critical point: 7.38MPa and 304K) is shown in Figure 2, and Figure 3 shows typical breakdown voltage and current waveform, the current reached maximum when breakdown happened. The dc breakdown voltages were obtained by the above methods for CO_2 pressures ranging from 0.1 to 15Mpa using 0.5-1.0mm gap point-plane electrodes, these results were shown in Figure 4, one can see the breakdown voltages increased with increasing pressures for the different electrode gaps. However, a dramatic drop happened at near the critical point, thus as seen in Figure 2, corona discharge can be generated under a low applied voltage.

Figure 2. DC corona discharges

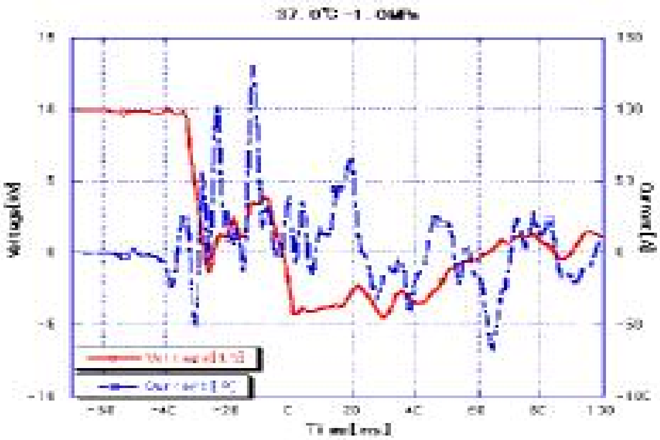

Figure 3. Typical breakdown voltage and current waveform

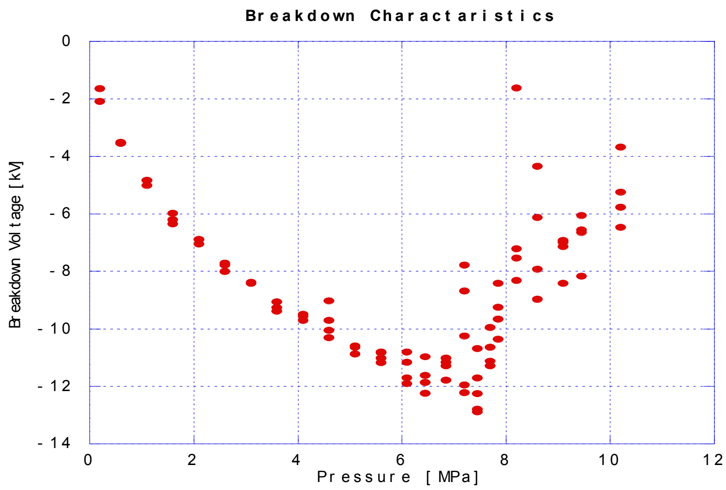

Figure 4. Breakdown voltages in SC CO_2

The negative dc corona only gives pulses briefly at the onset voltage, the burst pulses will either join together, becoming a regularly pulsating negative glow covering the active electrode, or the largest will develop into negative streamers, which are plasma filaments that carry their own ionization region ahead and propagate rapidly towards the anode. Correspondingly, negative dc corona (glow discharge) is Trichel pulses. Corona pulses, whether positive or negative, are streamers: each pulse is a streamer. If the streamer gets big enough then complete breakdown across the gap occurs. Since this is a 'short circuit' of the gap, the current will rise until it is the circuit's short-circuit current and thus an arc discharge is formed, as observed in Figure 2.

The atomic, molecular, electronic, ionic, and photon collision processes in CO_2 and at the electrodes can be involved in the various mechanisms of breakdown. Basically, five ionization processes are of importance in understanding how corona and breakdown occur:

(1) Ionization of molecules by high-energy particles*

$$\frac{1}{2}mv^2 + (CO_2)_n \Rightarrow (CO_2)^+_n + e;$$

(2) Ionization of molecules by electron impact

$$(CO_2)_n + e \Rightarrow (CO_2)^+_n + e + e;$$

(3) Re-combination of ions and electrons on impact

$$(CO_2)^+_n + e \Rightarrow (CO_2)_n + \text{energy};$$

(4) Photo-ionization, or the ionization of molecules by photon impact

$$\text{photon} + (CO_2)_n \Rightarrow (CO_2)^+_n + e;$$

(5) Negative ion formation by electron attachment

$$e + (CO_2)_n \Rightarrow (CO_2)^-_n;$$

Because of process (1), electrons are produced randomly throughout the gas and, because of process (2), in high-field regions, these electrons may increase in number and develop into avalanches. Because of process (3), electrons and positive ions in avalanches may recombine to produce photons. Because of process (4), more electrons may be produced ahead of the avalanche, which can cause the development of a streamer. However, because of process (5), free electrons are removed which may slow or even stop the growth of avalanches. We should also be aware of electron emission at the negative electrode (or cathode) due to high fields (specifically 'field-enhanced thermionic emission') and photon impact on the cathode (or 'photo-emission'). At very high fields, electron emission can initiate the breakdown process. Photo-emission is one of the positive feedback factors causing streamers.

The electrical breakdown strength of CO_2 increases with pressure. As the pressure increases the mean free path (mfp) of the electrons decreases, it becomes more difficult for electrons to gain sufficient energy for ionization, and so a higher electric field is required in order that the electrons may gain sufficient kinetic energy between collisions to cause ionization. However, the lowering of breakdown strengths at near critical point in SC CO_2 under high pressures can be attributed to the formation of extensive clusters in SC CO_2 condition. The clustering phenomenon or local density enhancement is regarded as a fundamental feature in SCFs, the cluster formation generally influences the solution structure and affects transport properties such as mass transfer coefficients, thus the gap increases between molecules at high pressures, electron mfp increases, avalanche can develops into streamer.

On the other hand, the extensive density inhomogeneities, or larger density fluctuations, caused unstable clusters in SC conditions. The cluster is different from that in solids and liquids. The member molecules are bound to each other with relatively weak intermolecular forces such as van der Waals forces and the lifetime of an average cluster is much shorter than in solids and liquids. In certain SC CO_2 condition, an electron can not only cause ionization of CO_2 molecules by collision but also attach to CO_2 molecules to form a negative ion (see the ionization processes (2) and (5) above), which may result in a local change of the dielectric constant or the conductivity, and a distortion of the localized effective electric field. Meanwhile, the ionization potential decreases with increasing of the number of molecules in the clusters, the ionization coefficient α is much bigger than the attachment coefficient η, and thus avalanches can develop into streamer, further spark paths were formed and leading to breakdown with a lower voltage.

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* These high-energy particles are due to either 'cosmic rays' (or 'cosmic radiation') or natural radioactivity.

SCFs have densities approaching those of liquids together with the mass transport properties of gases. This combination gives them unique properties as solvents for chemical processes. In particular, complete miscibility of gases and substrates can be achieved at relatively high concentrations. Computer simulation methods, Monte Carlo and molecular dynamics (MD) are powerful tools and provide a possibility for studying the dynamic properties such as clustering formation, motion and distribution in SCFs at the molecular level. In particular, the clusters affect ionization mechanism about electron collision, recombination and attachment.

CONCLUSION

Measurements have been experimentally made of breakdown voltages using a point-plate electrode system in SC CO_2 for a range of high pressures. The experimental results exhibit a dramatic phenomenon: a larger trough of breakdown voltage exists in near the critical point in SC CO_2 condition, and show that the discharge plasmas can be generated with a low of applied voltage. The explanations were given based on some clustering theory, the cluster formation generally influences the solution structure and affects transport properties such as mass transfer coefficients, thus the gap increases between molecules at high pressures, electron mfp increases, the electrons may gain sufficient kinetic energy between collisions to cause ionization. On the other hand, the ionization potential decreases with increasing of the number of molecules in the clusters.

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