Enhanced conversion of CO_2 by atmospheric pressure dielectric barrier discharge with different electrode configurations

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Abstract: The CO_2 decomposition performance of a dielectric barrier discharge using different electrode configurations is investigated. The effects of dielectric barrier materials and electrode configurations with and without copper mesh electrode on CO_2 conversion are investigated experimentally. The results show that the use of a dielectric barrier with a higher relative dielectric constant and the electrode setup with copper mesh can significantly improve the CO_2 conversion, which provides a reference for improving the reactor design.

Keywords: CO_2 decomposition, dielectric barrier discharge, electrode configurations

1. Introduction

Dielectric barrier discharge (DBD) under atmospheric pressure has received wide attention in a considerable number of industrial fields due to its advantages of simple structure, moderate operating conditions and distinctly non-equilibrium characteristic [1]. The temperature of heavy particles in the plasma formed by DBD can be close to room temperature and the electrons have relatively high energies, typically in the range of 1-10 eV, which is sufficient to break most chemical bonds. Therefore, DBD is extremely suitable for the conversion of compounds with high chemical stability, such as CO_2 decomposition [2]. Previous studies on the chemical kinetics of CO_2 decomposition have shown that stepwise vibrational dissociation by electron impact is a more efficient solution than direct dissociation by electron impact [3]. However, a typical plasma system formed by DBD has a high electron energy of about several eV, which is not beneficial for stepwise vibrational dissociation of CO_2 molecules and causes lower conversion rates and energy efficiencies.

In order to achieve efficient conversion of CO_2, it is important to regulate the structure and operating parameters of DBD reactor to form suitable discharge conditions. Previous studies on operating parameters, such as applied voltage, frequency, gas flow rate, and structural parameters of DBD reactor such as dielectric thickness, discharge gap distance and length, etc. have supplied plenty of valuable information about CO_2 decomposition by DBD [4]. The selection of dielectric materials is a key factor for DBD reactor design and there are many experimental results about the influence of dielectric materials on CO_2 decomposition, which show that different relative dielectric permittivities have certain effects on CO_2 conversion and energy efficiency [5]. It is found that higher CO_2 conversion can be obtained by using dielectric materials with higher relative permittivity but CO_2 conversion does not necessarily increase with the increase of the relative permittivity of dielectric material, so the selection of dielectric materials needs to be further combined with DBD reactor design to enhance CO_2 conversion.

In addition, capacitance is a crucial parameter of DBD reactor which has effect on the discharge characteristics of a reactor [6]. The capacitance of DBD reactor is not only associated with the structural parameters of a reactor, but also with the dielectric material selection. Hence, the main objective of this study is how to effectively combine the reactor design with the dielectric material selection to improve CO_2 decomposition. A comparative experimental study on CO_2 decomposition in a double-layer dielectric reactor and a new reactor with copper mesh inserted in the middle of the double-layer reactor as an electrode using different dielectric materials is conducted, and the effect of various parameters on CO_2 conversion is analyzed by combining the discharge characteristics of the two reactors.

2. Experimental

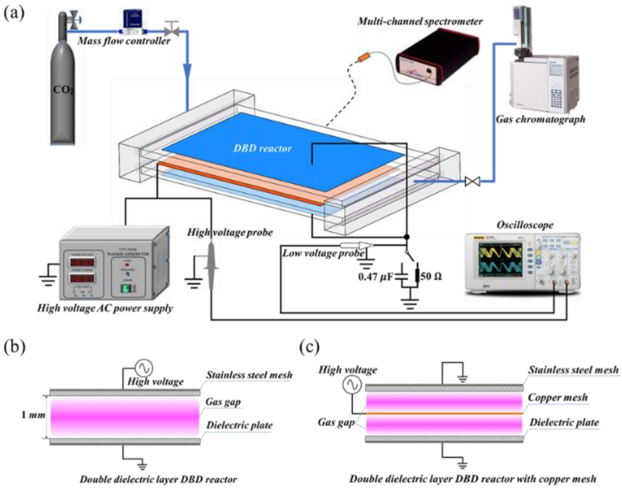

Fig. 1. Schematic of (a) experimental setup, (b) double dielectric layer DBD reactor and (c) double dielectric DBD reactor with copper mesh.

As shown in Fig. 1 (a), the discharge power of DBD reactor is energized by a high voltage AC power supply (CTP-2000K) and the output voltage frequency is set to 7 kHz at all conditions. A high voltage probe (Tektronix P6015A) is used to measure the applied voltage of DBD reactor. An external resistor (50 Ω) and a capacitor (0.47 μF) are in series with DBD reactor to monitor the total current and charge by a low voltage probe (Tektronix P2220). All electrical signals are recorded by a four-channel digital oscilloscope (Tektronix MDO3034). The plasma optical emission from the gas gap of DBD reactor is collected and analyzed by a multi-channel spectrometer (Avantes, AvaSpec-ULS4096CL). CO_2 (99.995% purity) is used as the feed gas with a flow rate of 10–50 sccm. After passing through DBD reactor, the gas is analyzed by a gas chromatograph (Zhejiang Fuli, GC9790Plus) equipped with a thermal conductivity detector (TCD). To evaluate the performance of plasma processing, the CO_2 conversion is defined as follows

$$CO_2\ conversion(\%) = \frac{CO_2\ converted\ (mol/s)}{CO_2\ input\ (mol/s)} \times 100\% \quad (1)$$

The specific energy input (SEI) and energy efficiency (η) is defined to evaluate the energy cost of CO_2 decomposition

$$SEI(kJ/L) = \frac{average\ discharge\ power\ (W)}{CO_2\ flow\ rate\ (sccm)} \times 60(s/min) \quad (2)$$

$$\eta(\%) = \frac{\Delta H\ (kJ/mol) \times CO_2\ conversion(\%)}{22.4(L/mol) \times SEI(kJ/L)} \quad (3)$$

Here, ΔH represents the reaction enthalpy (283 kJ/mol) of pure CO_2 decomposition.

Two kinds of DBD reactor structure are used in this study as shown in Fig. 1 (b) and (c). One structure is the conventional double dielectric planar reactor, using stainless steel mesh with a length of 85 mm and width of 40 mm as electrodes. The thickness of the two dielectric plates is set to 2 mm and the discharge gap distance is set to 1 mm. The geometry of another DBD reactor is the same as the main body of the double dielectric layer reactor, the main difference is that a piece of copper mesh (400 mesh) with dimensions of 85 mm length and 40 mm width is inserted in the middle of double dielectric layer reactor as a high voltage electrode, and the two electrodes on the other side of the dielectric layers are both grounded. In this case, the gap distance on both sides of the copper mesh electrode is 0.5 mm, respectively.

Table 1. Physical properties of two dielectric barrier materials and dielectric capacitances of reactors.

Dielectric material	Chemical composition	Relative permittivity (ε_r)	Dielectric capacitance of double layer reactor (pF)	Dielectric capacitance of double layer reactor with copper mesh (pF)
Alumina	Al_2O_3 99.70% Na_2O 0.15% SiO_2 0.10%	9.6	72	288
Zirconia	ZrO_2 96.5% MgO 0.51% CaO 0.10%	25	188	752

The geometrically determined dielectric capacitance of DBD reactor C_{diel} obtained in this study using two kinds of dielectric barrier materials (alumina or zirconia) in combination with the electrode setup is given in Table 1. In the subsequent experiments, we use four DBD reactors with different capacitances composed of different dielectric materials and different electrode configurations to investigate their effects on CO_2 decomposition.

Figure 2 (a) shows a typical Q-V plot for DBD. The slope of AB and CD corresponds to the total capacitance of DBD reactor C_{cell}, which is composed of the dielectric capacitance C_{diel} and the gap capacitance C_{gap}. The slope of AD and BC represents the effective dielectric capacitance ζ_{diel} and should be equal to C_{diel} for a fully discharge bridged gap [6], [7]. An alternative equivalent circuit model proposed by Peeters *et al*. is used here, as shown in Fig. 2 (b) [7]. As the discharge in DBD reactor gap here is a case of partial surface discharging, the electrical parameters related to discharge can be obtained more accurately by using this circuit model.

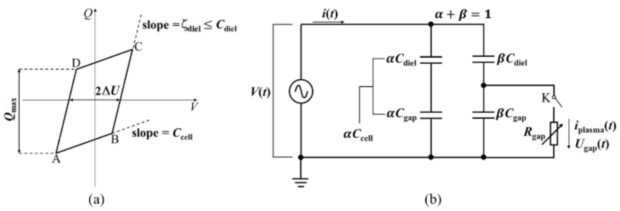

Fig. 2. (a) a typical Q–V plot of DBD and (b) equivalent circuit of a DBD reactor.

3. Results and discussion

A comparison of the conversion rate and energy efficiency obtained for CO_2 decomposition in a double dielectric layer reactor with alumina or zirconia plates as dielectric layers, respectively (identified as Double Al_2O_3, and Double ZrO_2) and in a double dielectric reactor with copper mesh electrode inserted between the corresponding double dielectric layers (identified as Al_2O_3-Cu-Al_2O_3 and ZrO_2-Cu-ZrO_2) is presented in Fig. 3.

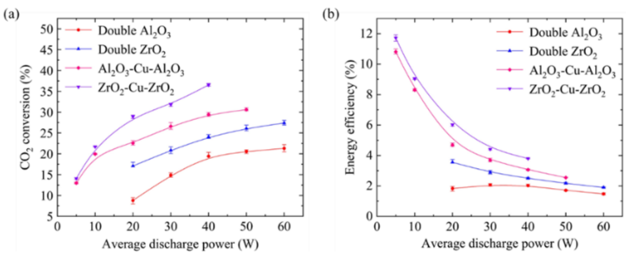

Fig. 3. (a) CO_2 conversion and (b) energy efficiency as a function of discharge power for different DBD reactors (CO_2 flow rate of 20 sccm).

As can be seen from Fig. 3 (a), corresponding to the same reactor structure, the reactor composed of ZrO_2 with higher relative permittivity presents a higher CO_2

conversion than that of the Al_2O_3 reactor. The CO_2 conversion of the double-dielectric layer reactor with copper mesh are much higher than that of the double-dielectric layer reactor without copper mesh. For the ZrO_2-Cu-ZrO_2 reactor, CO_2 conversion is as high as 36% at a discharge power of 40 W and a CO_2 flow rate of 20 sccm. Energy efficiency of CO_2 decomposition corresponding to different discharge powers is given in Fig. 3 (b). In general, the energy efficiency decreases with increasing discharge power, and the energy efficiencies of the double-dielectric layer reactor with copper mesh electrode are higher and can reach more than 10% at lower power levels.

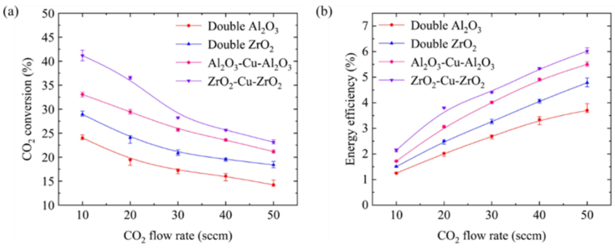

Fig. 4. (a) CO_2 conversion and (b) energy efficiency as a function of CO_2 flow rate for different DBD reactors (discharge power of 40 W).

The variation of CO_2 conversion and energy efficiency with CO_2 flow rate for different DBD reactors is given in Fig. 4. It is seen that CO_2 conversion increases and energy efficiency decreases as CO_2 flow rate decreases for different DBD reactors. Over the entire gas flow rate variation range, CO_2 conversion and energy efficiency of the reactor composed of ZrO_2 are higher than those of the Al_2O_3 reactor. The performance of the double-dielectric layer reactor with copper mesh electrode is better than that of the double-dielectric layer reactor without copper mesh. For the ZrO_2-Cu-ZrO_2 reactor, CO_2 conversion is higher than 40% at a discharge power of 40 W and a CO_2 flow rate of 10 sccm.

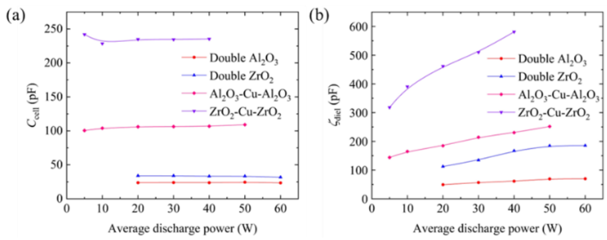

Fig. 5. (a) cell capacitance, (b) effective dielectric capacitance as a function of discharge power extracted from the Q–V plots for different DBD reactors (CO_2 flow rate of 20 sccm).

Figure 5 shows the reactor capacitance C_{cell} as well as the effective dielectric capacitance ζ_{diel} obtained from the Q-V plots for different DBD reactors. For the ZrO_2-Cu-ZrO_2 reactor, the C_{cell} value is more than twice that of the Al_2O_3-Cu-Al_2O_3 reactor and is more than five times higher than that of the ZrO_2-ZrO_2 or Al_2O_3-Al_2O_3 reactor. Although the double dielectric layer reactor also shows the higher dielectric permittivity, the larger reactor capacitance C_{cell}, the use of double dielectric layer with copper mesh configuration has a more obvious effect on the capacitance of DBD reactor. From the effective dielectric capacitance ζ_{diel} given in Fig. 5 (b), it appears that for all the reactors with different electrode configurations, the ζ_{diel} for the ZrO_2-Cu-ZrO_2 reactor are much higher than the other reactors and the ζ_{diel} increase with the increase of the discharge power. Combined with Fig. 3 and Fig. 4, it is seen that increasing the reactor capacitance helps to improve CO_2 conversion and energy efficiency.

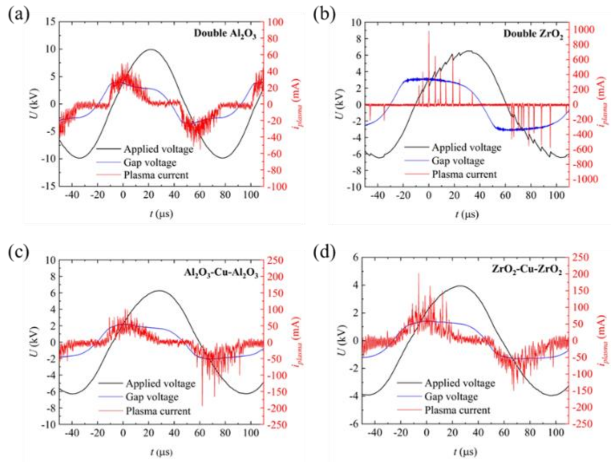

Fig. 6. Comparison of applied voltage $V(t)$, gap voltage $U_{gap}(t)$ and plasma conduction current $i_{plasma}(t)$ waveforms for the reactor of (a) Al_2O_3-Al_2O_3, (b) ZrO_2-ZrO_2, (c) Al_2O_3-Cu-Al_2O_3, and (d) ZrO_2-Cu-ZrO_2 (discharge power of 40 W, CO_2 flow rate of 20 sccm).

The applied voltage of DBD reactor $V(t)$, gap voltage $U_{gap}(t)$, and plasma conduction current $i_{plasma}(t)$ waveforms is shown in Fig. 6. As can be seen from the conduction current waveforms of different DBD reactors, the discharge is characterized by multiple current pulses per half-cycle, and the duration of these current pulses is extremely short, typically less than one microsecond. This is usually considered as a sign of filamentary discharge. It can be found that the reactor with copper mesh electrode has a lower applied voltage than the reactor without copper mesh electrode. Similarly, the gap voltage during the active discharge phase of the reactor with copper mesh electrode is lower than that of the reactor without copper mesh electrode. The presence of multiple current pulses in the reactors has a good synchronization with the gap voltage, that is, when the gap voltage reaches a certain threshold, a considerable number of discharge current pulses start to appear, then the gap voltage seems to enter a plateau area with less variation.

The filamentary discharge is characterized by plenty of micro-discharge processes formed in the gas gap. As shown in Fig. 7, the main parameters describing the characteristics of the micro-discharge process can be extracted from the conduction current waveforms in Fig. 6.

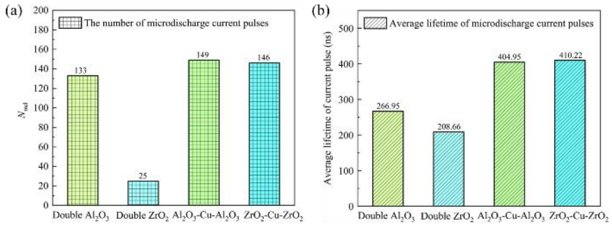

Fig. 7. (a) Number (b) average lifetime of micro-discharge current pulses per cycle for different DBD reactors (discharge power of 40 W, CO_2 flow rate of 20 sccm).

It can be seen from Fig. 7 (a) that the number of micro-discharge current pulses of the double-dielectric layer reactor with copper mesh electrode is bigger than that of the double-dielectric layer reactor without copper mesh electrode. As shown in Fig. 7 (b), The micro-discharge current pulse duration of the double dielectric reactor with copper mesh electrode is much higher than that of the reactor without copper mesh electrode. Combined with the number of current pulses given in Fig. 7 (a), it shows that the use of copper mesh as the electrode greatly improves the discharge uniformity in discharge time and space, which is beneficial to the conversion of CO_2.

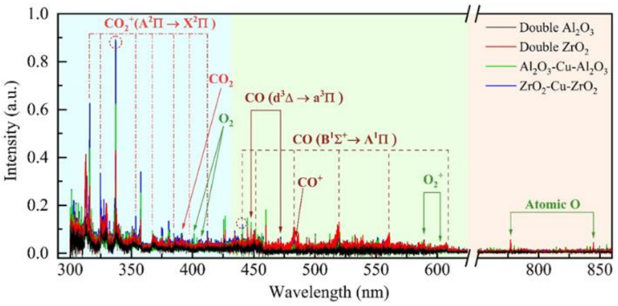

Fig. 8. Optical emission spectra of CO_2 discharge in different DBD reactors (discharge power of 40 W, CO_2 flow rate of 20 sccm).

Figure 8 shows the optical emission spectra of CO_2 discharge in different DBD reactors. It can be seen that the optical emission spectra of the plasma discharge between 300 nm and 850 nm contains Fox, Duffendack and Barker (FDB, $A^2\Pi \rightarrow X^2\Pi$) bands of the CO_2^+, (Ångström system, $B^1\Sigma^+ \rightarrow A^1\Pi$ and triplet system, $d^3\Delta \rightarrow a^3\Pi$) bands of excited CO molecules, excited CO_2 molecules (391.2 nm, $^1B_2 \rightarrow X^1\Sigma^+$), excited oxygen molecules (400.5 nm, 406.5 nm), excited O_2^+ (588.3 nm, 602.6 nm), and excited oxygen atom (777.2 nm, 845.0 nm). The FDB bands of CO_2^+ have the highest emission intensity, while the two characteristic bands of CO have the second highest emission intensity, so the emission intensity of these bands can be used for further analysis of the ionization and dissociation processes of CO_2.

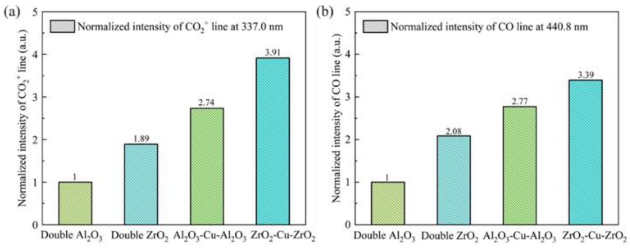

Fig. 9. Comparison of normalized spectral line intensity of (a) CO_2^+ and (b) excited CO molecules in different DBD reactors (discharge power of 40 W, CO_2 flow rate of 20 sccm).

We extract two spectral lines from Fig. 8, 337.0 nm as well as 440.8 nm, and conduct a normalized comparison of their emission intensities, as shown in Fig. 9. As can be seen from the figure, the use of dielectrics with higher relative permittivity and double-dielectric layer with copper mesh electrode both result in enhanced CO_2^+ as well as CO spectral line intensity, which is also a reflection of enhanced discharge efficiency of CO_2 system.

4. Conclusion

In this study, the performance of different electrode configurations, dielectric barrier materials of DBD reactors for CO_2 decomposition is investigated experimentally. The results indicate that the use of a reasonable combination of reactors with high relative permittivity as well as reactors with copper mesh electrode can increase the reactor capacitance, and substantially improve the conversion rate and energy efficiency of CO_2 decomposition. The analysis of micro-discharge characteristics shows that the use of double-dielectric layer reactor with copper mesh electrode can increase the number and duration of micro-discharge current pulses considerably. Optical emission spectra analysis of CO_2 plasma shows that the combination of using high relative permittivity dielectric material as well as reactor with copper mesh electrode can effectively improve the discharge efficiency of CO_2.

5. Acknowledgments

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6. References

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