Effects of discharge parameters on carbon dioxide conversion in TiO₂ packed dielectric barrier discharge at atmospheric pressure

Ang Li^{1,2} · Yuxiang Pei¹ · Xiaoping Tao¹ · Zhongping Wang¹

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Abstract

A cylindrical dielectric barrier discharge reactor packed with TiO₂ is developed to convert undiluted carbon dioxide (CO₂) into CO and O₂ at atmospheric pressure. Basing on linear regulation of instruments, a series of typical discharge parameters have been electrically controlled and measured in an attempt to find the maximum CO₂ conversion and the best energy coupling. It is discovered that CO₂ conversion has a stronger correlation with apply voltage, and further research manifested that lowering feed gas flow and increasing discharge frequency contribute to higher CO₂ conversion within our controllable range. After comprehensive analysis of these trends and results of subsequent experiments, the maximum CO₂ conversion of 12.72% is achieved at the voltage of 22 kV, with 9.09 kHz frequency and 20 ml/min flow rate, and the highest energy efficiency of 15.80% is achieved at the voltage of 22 kV, with 8.47 kHz frequency and 20 ml/min flow rate.

Keywords Dielectric barrier discharge (DBD) · Plasma-catalysis · CO₂ conversion · Energy efficiency

1 Introduction

As the problems of climate change and global warming is drawing close attention, efficient decomposition of massive CO₂ emission has become an immediate need. From 2005 to 2012, the cumulative increase in CO₂ emissions was 5703 million tons in Beijing's service sectors [1]. Efforts have been made to deal with this global challenge, carbon capture and storage (CCS) and carbon capture and utilization (CCU) are the main measures to reduce CO₂ from the terminal end. However, as CO₂ corresponds to a particularly stable oxidized state of carbon, its reduction is not spontaneous and requires significant energy input [2]. Among the alternative processes for CO₂ decomposition, non-thermal plasma (NTP) can dissociate stable molecules at temperatures as low as room temperature, which makes it a promising technology in the conversion and utilization of CO₂ [3]. The typical non-thermal plasma discharge appears to be uniform and stable, but in fact it

has a large number of discharge channels, known as filamentary microdischarges, forming in the gap. Various NTP configurations have been tested for the decomposition of CO₂, and dielectric barrier discharge (DBD) is among them. DBD is a nonequilibrium ac-driven gas discharge with the presence of insulating medium in the discharge space. The presence of medium blocks the formation of channels so that the discharge system does not create a spark or arc. The integration of plasma and solid catalysts has great potential to generate a synergistic effect, which can activate the catalysts at low temperatures and improve their activity and stability, resulting in the remarkable enhancement of reactant conversion, selectivity and yield of target products, as well as the energy efficiency of the plasma process [4–6].

Different non-conductive materials have been introduced into the plasma system to further improve the conversion of CO₂ and energy efficiency of the plasma process. Mei et al. [4] introduced the plasma with photocatalysts,

✉ Xiaoping Tao, taoxp@ustc.edu.cn | ¹School of Physical Sciences, University of Science and Technology of China, Hefei 230026, China. ²Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, China.

the combination of BaTiO_3 and TiO_2 , which manifested a synergistic effect and significantly enhances the conversion of CO_2 . Yu et al. [7] used a series of materials including aluminum oxide, perovskite, silica gel and quartz, of which CaTiO_3 showed the highest conversion at the same input power. The eye-catching performance of CeO_2 reminds us to pay more attention on rare-earth elements in Deb-jyoti Ray and Ch. Subrahmanyam's research [8]. There are many factors that could affect the performance of DBD reactors. Despite factors like input power or applied voltage, relevant research results have shown that packing methods [9], reactor design [10], type of diluent gas [11, 12] also have a significant effect on the performance of DBD reactors.

In present work, research is focused on CO_2 conversion and energy efficiency. In the experiment, the cylindrical DBD reactor is packed with TiO_2 powder. TiO_2 is chosen for its rich nature, such as relatively high dielectric constant, photocatalytic property, and outstanding performance in some relevant researches [13–15]. TiO_2 plays the role of a fundamental catalyst in this research field and we chose it for its typicality. We hope to study the decomposition and energy utilization of CO_2 at room temperature and atmospheric pressure, with the change of applied voltage, frequency, flow rate and input power, in order to find the best energy coupling and conversion under the optimum discharge conditions. This letter reports the effect of flow rate, applied voltage and frequency on CO_2 conversion and energy efficiency.

2 Experimental

2.1 Experimental set-up

A schematic diagram of our experimental set-up has been shown in Fig. 1. DBD discharge and gas decomposition is achieved through a cylindrical quartz tube with 22 mm inner diameter and 25 mm outer diameter, which serves as the main structure of the reactor. Fixed around the quartz tube is a seamless steel pipe with 34 mm outer diameter, serving as the external electrode. Running through the whole reactor is a stainless steel rod, on which is drilled several 4 mm holes to let gas in, acting as the inner electrode. The diameter of the rod is 15 mm, so the discharge gap equals 8 mm. The total length of the tube is 250 mm and the axial symmetry is maintained in the process. The external electrode is grounded by a capacitor (2.02 μF) so as to get the charge quantity. A high voltage source (CTP-2000K Plasma Generator) is connected to the inner electrode, and the real-time supply voltage as well as current is displayed on its screen. As is depicted in the schematic, the

Fig. 1 Experimental set-up

Fig. 2 SEM image of TiO_2 powder

space around the tube is filled with cooling liquid, which is driven to circulate by an electrical pump.

2.2 Reaction materials

The discharge tube is fully packed with TiO_2 , and in this way the discharge volume is strongly reduced, leading to a modification of discharge mode from filamentary discharges to predominantly surface discharges [16]. However, electric field strength could be increased and actions could be processed more sufficiently for the large surface area of the powder. We choose TiO_2 (AR, powder, Tianjin Zhiyuan Chemical Reagent Co., Ltd.) as packing material, of which the dielectric constant is 85. The powder is dry pressed, sieved through mesh and then packed in. The Scanning electron microscopy (SEM) image for TiO_2 nanoparticles obtained at 10.0 kV is presented in Fig. 2. It can clearly be seen that the crystallite size is about 154 nm. After pressing TiO_2 powder into the reactor, the cross-section schematic is shown in Fig. 3. The gas fluid spreads out the powder through the reactor.

Fig. 3 Cross-section schematic

Bottled CO_2 is served as the undiluted gas provider, from which CO_2 passes through the pressure relief valve into the MFC (Sevenstar, D07-7B, 50 ml/min), so a constant CO_2 flow is achieved. Consider that the MFC is calibrated by N_2 , a coefficient of 0.737 is meant to multiply with the value displayed on indicator to get the real flow rate.

2.3 Measuring methods

In order to control the flow, a flow readout box (Sevenstar, D08-2E) works as a display instrument of MFC. By rotating the knob, we could get a stable CO_2 input flow during the discharge process, and cleaning mode is used at the end of each measurement to sweep out the residual gas, which means the valve within MFC opens and a relatively large flow (about 50 ml/min) is put through the gas circuit. After applying a voltage, the conversion process is starting to go on. While the gas is passing through the AC electric field, a high voltage probe delivers waveforms back to the oscilloscope (Agilent, 54622A), which could help control input voltage as well as frequency. The Lissajous figure can be achieved by connecting the other channel to the capacitor to calculate the discharge power.

Each discharge process continues for 5 min, and then the mixed gases that have run through the tube are imported by a polyethylene pipe (3 mm diameter) to the chromatography (FL9790, molecular sieve TDX-01) for analyzing the discharge production, after which waste gases are exhausted. Hydrogen (H_2) plays the role of carrier gas, which pushes other gases into GC and would not be detected by GC, enables the detection of other gases, shown as peaks in display screen. Specific gas type could be changed by modes selection. Stable column pressure proves steady carrier gas flow. Once the chromatograms are formed, the areas of different peaks can be calculated to ascertain the proportions of each gas. The gas identifications could be distinguished through their typical times

to form the peaks. CO_2 is typically peaked at 9.37 min and carbon monoxide (CO) is at 1.79 min. CO_2 conversion could be made sure through the areas of peaks before and after 5 min discharge. Some other parameters are obtained through the following relations.

2.4 Parameters

In the DBD reactor, the core reaction is [17]

Where ΔH is the reaction enthalpy of CO_2 splitting.

The power injecting into the discharge plasma is given by [18]

$$P = \frac{1}{T} \int_0^T V I dt = f C \oint V dV \quad (2)$$

which could be achieved by calculating the area of Lissajous figure. Fitting algorithm is applied to get the approximate value.

The relation to get CO_2 conversion is

$$\text{CO}_2 \text{ conversion (\%)} = \frac{\text{CO}_2 \text{ converted (mol/min)}}{\text{CO}_2 \text{ input (mol/min)}} \quad (3)$$

SIE is an important physical quantity which means specific input energy

$$\text{SIE (kJ/L)} = \frac{\text{Discharge power (W)}}{\text{CO}_2 \text{ flow rate (ml/s)}} \quad (4)$$

SER means specific energy requirement

$$\text{SER (eV per molecule)} = \frac{\text{SIE (eV per molecule)}}{\text{CO}_2 \text{ conversion (\%)}} \quad (5)$$

Relations of energy efficiency in two different units are listed as follows [8]

$$\text{Energy efficiency (\%)} = \frac{\Delta H \text{ (eV per molecule)}}{\text{SER (eV per molecule)}} \quad (6)$$

$$\text{Energy efficiency (mmol/kJ)} = \frac{\text{CO}_2 \text{ converted (mol/s)}}{\text{discharge power (W)}} \quad (7)$$

3 Results and discussion

3.1 Typical discharge waveform

The applied voltage and the discharge current signals at the same peak applied voltage were recorded on the oscilloscope. The channel 1 of the oscilloscope measures the voltage between the outer electrode and inner electrode,

Fig. 4 Typical discharge waveforms

Fig. 5 Typical Lissajous figure

while the channel 2 gets the current data from the capacitor. Figure 4 represents the discharge voltage-current waveforms as a function of time at the peak applied voltage of 8 kV. At each frequency, when the voltage is low, the waveform basically shows a sine wave. When the voltage gradually increases to form micro-discharge, the current waveform becomes sharp.

The typical Lissajous figure is achieved under a frequency of 8.06 kHz and peak-to-peak voltage of 16 kV, as shown in Fig. 5. The power injecting into the discharge plasma can be calculated in Eq. 2. When the voltage is low, it presents a nearly elliptical pattern. As the voltage increases, the ellipse expands continuously and shows a parallelogram trend, that is, the discharge power increases continuously. By adjusting frequencies (8.06 kHz, 8.47 kHz, 9.09 kHz), the relation of discharge power and applied voltage could be indicated in Fig. 6. In this experiment, the flow rate was constant at 20 ml/min. The frequency is measured with the oscilloscope which has discrete display values, and finer tuning is expected with advanced instruments. In those frequencies typical Lissajous figure could be achieved without obvious distortion, which means a higher conversion rate could be expected. According to

Fig. 6 Discharge power as a function of voltage for various frequency

Fig. 7 CO₂ conversion as a function of voltage at different flow rate (frequency: 8.06 kHz)

the Eq. 4, SIE (specific input energy) also showed the same trend. This phenomenon tells us that discharge power increases together with the applied voltage within a certain range.

3.2 Effect of flow rate on conversion

Figure 7 presents the relations of voltage and conversion at a fixed frequency (8.06 kHz) with the change of flow. It can be seen from the figure that for a constant flow, increase of the voltage contributes to CO₂ conversion. As is seen from the figure, the conversion under each voltage reduces as the flow rate increases. Therefore, the proper

reduction of flow rate could increase conversion within a range. This result is comparable with Koen Van Laer's work [19]. We understand this phenomenon in a way that at a lower flow rate, the discharge process is carried out more completely. With a longer retention time, there's more chance for electrons to collide with CO₂ molecules, which plays a crucial role in molecules ionization. But too low flow rate is inappropriate for the experiment due to air-resistor in the DBD reactor. In the follow-on experiments, the flow rate of 20 ml/min is chosen.

3.3 Effect of frequency on conversion

According to previous experiment, the flow rate is controlled at 20 ml/min, which is relatively low so as to get a higher conversion. With the use of plasma generator, the discharge frequency in range can be continuously regulated. Figure 8 manifests the relations of applied voltage and conversion at different frequency (8.06 kHz, 8.47 kHz, 9.09 kHz). A maximum CO₂ conversion of 12.72% is achieved at the discharge frequency of 9.09 kHz and the applied voltage of 22 kV. For a constant frequency, with the increase of applied voltage, CO₂ conversion is improved. This attributes to the cause that the higher the applied voltage is, the more energetic electrons we get, and it gets more chance for it to form activity groups.

In the three curves of different frequencies, the conversion increase coordinately with frequency. This lead us to the question that does it make sense to continue increasing the frequency? It makes sense in a way, but at a higher frequency, if we want to attain the same applied voltage, a higher input power is required, and this is not cost-effective [6].

Fig. 8 CO₂ conversion as a function of voltage at different frequency

3.4 Effect of frequency, voltage and flow rate on energy efficiency

In order to get the energy efficiency, specific energy requirement (SER) is calculated and shown in Fig. 9a. According to Eq. 6, energy efficiency is calculated and shown in Fig. 9b. Relations shown in Fig. 9 indicate that energy efficiency is inversely proportional to SER. The relations also indicate that energy efficiency is positively related to conversion but inversely proportionate to discharge power, and our previous experiments showed that conversion and discharge power is positively related to applied voltage when other parameters are fixed. But Fig. 9b gives us an insight that energy efficiency is also positively related to applied voltage, and this suggests that conversion is more tightly related to applied voltage than discharge power. This works in concert with Fig. 7. The highest energy efficiency 15.80% is achieved at the

Fig. 9 **a** Relationship between SER and voltage for different frequency. **b** Relationship between energy efficiency and voltage for different frequency

Fig. 10 Relationship between energy efficiency and voltage for different flow rate

frequency of 8.47 kHz, the flow rate of 20 ml/min and the applied voltage of 22 kV. Clearly, a trade-off effect exists between the conversion of CO₂ and efficiency of the plasma process [10]. Therefore, in order to enhance conversion and energy efficiency, other parameters and methods like bead size [19], synergy of plasma-catalysis [9], dilution of gas [20, 21] and barrier thickness [22] could be taken into account.

Then the frequency is fixed at 8.06 kHz, and the flow rate is changed from 15 ml/min to 45 ml/min. After calculating all the parameters, Fig. 10 can be gotten, which shows the relations between applied voltage, flow rate and energy efficiency, manifesting a similarity to Fig. 7. Energy efficiency is presented in two units. As it has been shown in the experiment, if the flow rate is changed (from 15 ml/min to 45 ml/min) when other variables are fixed, no observable changes could be detected from the Lissajous figure and discharge waveforms. The phenomenon in a way is that gases distribute little to the system's distributed capacitance, for the cylindrical capacitance comes in the form of $2\pi\epsilon L/\ln(R_1/R_2)$, (ϵ : dielectric constant of medium gas; L : length of the tube; R_1 , R_2 : outer and inner diameter of the tube), of which the ratio R_1/R_2 stays constant. The reactor is set in ordinary pressure and it suggests that the total quantity of gas molecules is essentially unchanged. As a result, ϵ stays unchanged regardless of other variations. That leads to the direct ratio of energy efficiency to CO₂ conversion.

4 Conclusion

In this study, a DBD reactor packed with TiO₂ powder dielectric has been designed and tested to study the decomposition and energy utilization of CO₂. With the change of applied voltage, frequency, flow rate and input power, CO₂ conversion and energy efficiency were be experimental measured.

Applied voltage is served as a key variable in the research. All the experimental results show that discharge power, conversion and energy efficiency are positively correlated with applied voltage, and conversion is more tightly related to applied voltage than discharge power. This underlines the importance of applied voltage and leads us to pay attention to the enhancement of withstand voltage. Through optimizing discharge conditions, the maximum CO₂ conversion and the highest energy efficiency can reach 12.72% (Voltage = 22 kV; Frequency = 9.09 kHz; Flow rate = 20 ml/min) and 15.80% (Voltage = 22 kV; Frequency = 8.47 kHz; Flow rate = 20 ml/min). The conversion is lower than some existing DBD devices, but the energy efficiency stays in the common range, compared to the partially packed device (CO₂ conversion around 25%, energy efficiency 0.4 mmol/kJ) [4] and the one with screw type inner electrode (CO₂ conversion 27.2%, energy efficiency 10.4%) [10]. One possible reason for the low conversion rate is the limited applied voltage, which could only reach 22.0 kV in our experimental range. Higher voltage would make permanent damage to the quartz tube, and thicker tube could suffer a wider range so is expected to exhibit higher performance in the follow-up experiments. However, as is expected, keeping increasing applied voltage would not show positive effect constantly, and the turning point would be of much value to researchers. The positive effect of mixing N₂ on CO₂ conversion [23] is also under investigation, and data comparison is supposed to be revealed in later works.

In addition, the relation of frequency and CO₂ conversion is unimodal. It is monotonically increasing within a range, but is going down in our qualitative observation. From the view of flow rate, the proper reduction of flow rate could increase conversion, but it has no effect on discharge power. More relations are to be investigated in order to find the effective parameters which contributes remarkably to the conversion process.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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