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Enhanced CO_2 decomposition via metallic foamed electrode packed in self-cooling DBD plasma device

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Abstract

A self-cooling dielectric barrier discharge reactor, packed with foamed Cu and Ni mesh and operated at ambient conditions, was used for the composition of CO_2 into CO and O_2. The influences of power, frequency, and other discharge characteristics were investigated in order to have a better understanding of the effect of the packing materials on CO_2 decomposition. It is found that porous foamed Cu and Ni not only played a role as the carrier of energy transformation and electrode distributed in discharge gaps but also promoted the equilibrium shifting toward the product side to yield more CO by consuming some part of O_2 and O radicals generated from the decomposition of CO_2. The maximum CO_2 decomposition rates of 48.6% and 49.2% and the maximum energy efficiency of 9.71% and 10.18% were obtained in the foamed Ni and Cu mesh, respectively.

Keywords: dielectric barrier discharge, CO_2 decomposition, metallic foamed materials, energy efficiency

(Some figures may appear in colour only in the online journal)

1. Introduction

The emission of carbon dioxide as a result of the combustion of fossil fuels is the main cause of global warming. Though CO_2 capture and storage (CCS) and the reduction of CO_2 are well-known routes, it would be better to consider CO_2 as a raw material for new reactions, such as reforming of methane for syngas production, CO_2 hydrogenation for synthesis of methanol, methane, formaldehyde, dimethyl ether, etc [1, 2]. In addition, CO_2 can be directly decomposed into CO and O_2, since CO is more reactive than CO_2 and can be used in various catalysis processes such as the Fischer–Tropsch process and other value-added feedstock [3, 4]. This offers an effective way for utilization of low value CO_2 and while reducing CO_2 emissions substantially.

Nowadays, dielectric barrier discharge (DBD) plasma has been proved to be a new approach for the degradation of CO_2 in many studies found in the literature, e.g. [5]. CO_2 cannot be efficiently activated and decomposed in a conventional thermal or catalytic process due to its high chemical stability. With the characteristics of low cost, non-equilibrium, and the unique capacity to initiate both chemical and physical reactions [6, 7], DBD plasma is a promising selection for the classical thermal and catalytic route for gas purification at ambient conditions due to the presence of a large quantity of energetic electrons with a mean electron energy of 1–10 eV. The energy is high enough to break down the chemical bonds of insert molecules, like CO_2, and generate a large amount of reactive species for chemical reactions. This species can make

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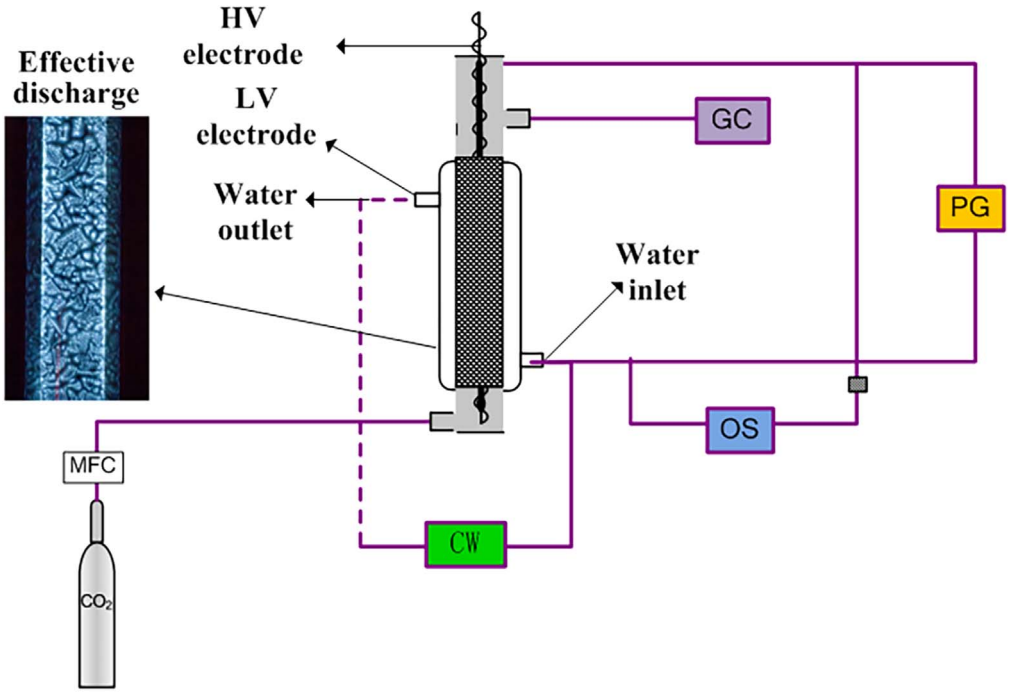

Figure 1. Experimental setup for CO_2 decomposition in the self-cooling DBD reactor.

thermodynamic unfavorable chemical reactions occur in a mild operating environment [8]. DBD plasma is a hot spot in environmental clean-up, greenhouse gas reform, and so on since it can be combined with a catalyst to improve the selectivity and yield of target products [9]. It has many advantages for CO_2 decomposition: it operates at atmospheric pressure and low temperatures, and has a simple construction which can be easily scaled up in industrial applications, and it has been demonstrated in the production of O_3. Moreover, it can be easily switched on and off [10].

Packing materials were applied to assist DBD plasma with the aim of promoting the CO_2 decomposition. Packing of $Ca_{0.8}Si_{0.3}TiO_3$ had significant growth in CO_2 conversion compared with SiO_2 and Al_2O_3 due to the great difference in permittivity [11]. Packing of $CaTiO_3$ improved the discharge characteristics of CO_2 decomposition with a maximum conversion of 12.6% [12]. Packing of $BaTiO_3$ in the discharge process increased the average electric energy and mean electron energy [8]. $BaTiO_3$ performed better than TiO_2 and glass in CO_2 conversion when a synergistic effect occurred between the plasma and photo-catalysts, and the maximum conversion reached 38.3% [13]. A micro reactor packed with CaO achieved a higher CO_2 conversion of 41.7% and an energy efficiency of 5.7% among materials, like Al_2O_3, MgO, and quartz, but the CO_2 capture abilities of CaO may influence the results [14]. The highest CO_2 decomposition rate of 42% as far as we know was reported in a ZrO_2 packed DBD reactor, with the corresponding energy efficiency of 4.7% [15].

The highest CO_2 decomposition rate in this work reached 48.6% and 49.2% with the packing materials of porous foamed Ni and Cu mesh, which was different from normal packing, like the spherical particles, used in many of the studies found in the literature. A pronounced improvement of CO_2 decomposition rate and energy efficiency was obtained with the introduction of porous foamed Cu mesh and Ni mesh. Indeed, it is neither the highest obtainable CO_2 decomposition rate nor the highest energy efficiency that should be focused on, but the combination of both of them. This result is promising in the field of CO_2 decomposition with DBD plasma. Therefore, the effect can be further improved by changing different operating parameters and packing materials, and may have great potential in the utilization of CO_2 in the future.

2. Experimental setup

Figure 1 is a schematic diagram of the experimental setup which was similar to our previous setup [16]. It includes three parts: the reaction system consisting of a plasma generator (CTP-2000K, Nanjing Suman) and a self-cooling DBD plasma reactor (made of Pyrex glass) for the discharge and CO_2 decomposition; the measurement system employing a voltage probe (P6015A, Tektronix), a current monitor (A622, Tektronix), and an oscilloscope (TDS3054B, Tektronix) for measuring the discharge parameter; the analysis system containing gas chromatography (GC-2014C, SHIMADZU) for determining the composition of the exhaust gas which comes from the plasma reactor.

The plasma reactor was composed of a double coaxial glass cylinder which was 200 mm in length with a discharge gap of 4 mm. Pure CO_2 (99.9%) was chosen as the feed gas and the gas flow rate was controlled by a mass flow controller (D08-4C/ZM, Beijing Sevenstar).

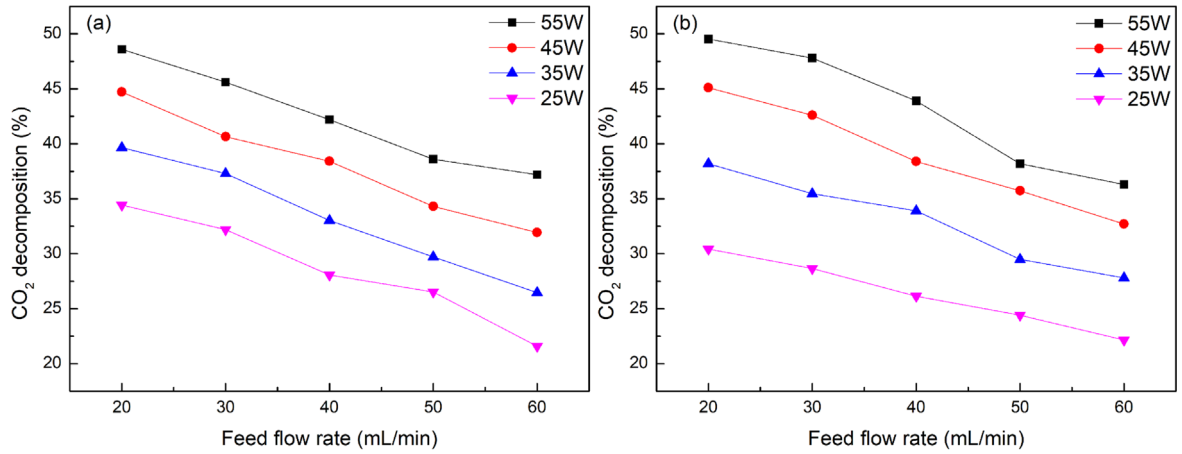

Figure 2. Effect of discharge power and feed flow rate on CO_2 decomposition (frequency = 9 kHz): (a) foamed Ni mesh packed reactor, (b) foamed Cu packed mesh reactor.

In this work, porous foamed Cu and foamed Ni meshes were applied, which were distributed widely in the discharge zone of the DBD reactor, both a size of 1–3 cm^3.

To measure the performance of the plasma process, the specific input energy (SIE), CO_2 conversion, selectivity toward CO were defined as follows:

$$CO_2 \text{ decomposition rate } (\%) = \frac{CO_2 \text{ converted}}{CO_2 \text{ input}} \times 100\% \quad (1)$$

$$CO \text{ selectivity } (\%) = \frac{CO \text{ formed}}{CO_2 \text{ converted}} \times 100\%. \quad (2)$$

SIE is the energy consumption per milliliter of gas flow, and P is the discharge power.

$$P(W) = f\int_0^T U\mathrm{d}Q = f\int_0^T U\mathrm{d}u \quad (3)$$

$$\mathrm{SIE} = \frac{60 \times P}{F}. \quad (4)$$

Energy efficiency (η):

$$\eta(\%) = \frac{\Delta H \times CO_2 \text{ decomposed}}{\mathrm{SIE} \times 24.5} \times 100\% \quad (5)$$

where ΔH is the enthalpy of the reaction, $\Delta H = 283\ \mathrm{kJ\ mol^{-1}}$, and the molar volume was $24.5\ \mathrm{l\ mol^{-1}}$.

3. Results and discussion

3.1. Effect of packing materials on CO_2 decomposition

Metallic oxides such as CaO, TiO_2, ZrO_2, and so on have been applied to CO_2 decomposition in many of the studies reported in the literature [13–15]. According to associated reports, foamed Cu and Ni meshes have not been applied for this aim before. The CO_2 decomposition rate in the porous foamed Ni and Cu mesh packed reactor was investigated with different discharge powers and the results are displayed in figure 2. We also conducted the experiment with different feed flow rates at a fixed discharge power, as shown in figure 2. It was proven that the feed flow rate was also an important factor influencing the CO_2 decomposition.

The general observation is that the CO_2 decomposition rate will be obtained with a higher discharge power but lower feed flow rate, especially in the presence of foamed Ni and Cu meshes. A higher discharge power means more sufficient energy injected into the reactor for the activation and decomposition of CO_2, and a lower feed flow rate implies a longer residence time of reactants. All of these lead to a higher energy density and hence higher CO_2 decomposition. The performance of packing materials further strengthened the electric field, and gave birth to more energetic electrons due to their good properties to conduct conductive properties, leading to an increase in the average electron density and number of microdischarge. The maximum CO_2 decomposition rates of 49.2% and 48.6% were achieved at the CO_2 flow rate of $20\ \mathrm{ml\ min^{-1}}$, with a maximum discharge power of 55 W in the foamed Cu and Ni meshes, respectively. The performance is attributed to the good conductive properties of the porous foamed Ni and Cu meshes.

The porous foamed Cu and Ni meshes applied here acted as many electrodes which were distributed in the discharge gap due to their good conductive properties. This special characteristic has many advantages. Foamed materials played a role as a carrier of energy transformation so that the energy transformation to CO_2 was more efficient and more energy was used for the decomposition of CO_2. In addition, many micro electrodes distributed in the discharge gap made the microdischarge occur more widely and evenly when the potential was applied. The microdischarge provided more chemical reaction channels. Apart from this, more CO_2 was exposed to the surface of the Ni and Cu materials for their porous structure. The strong and widespread microdischarge initiated on the surface of the packing materials enhanced the chance of collision between CO_2 molecules and energetic electrons, or other active particles, and promoted the decomposition of CO_2. The effect of the materials can be

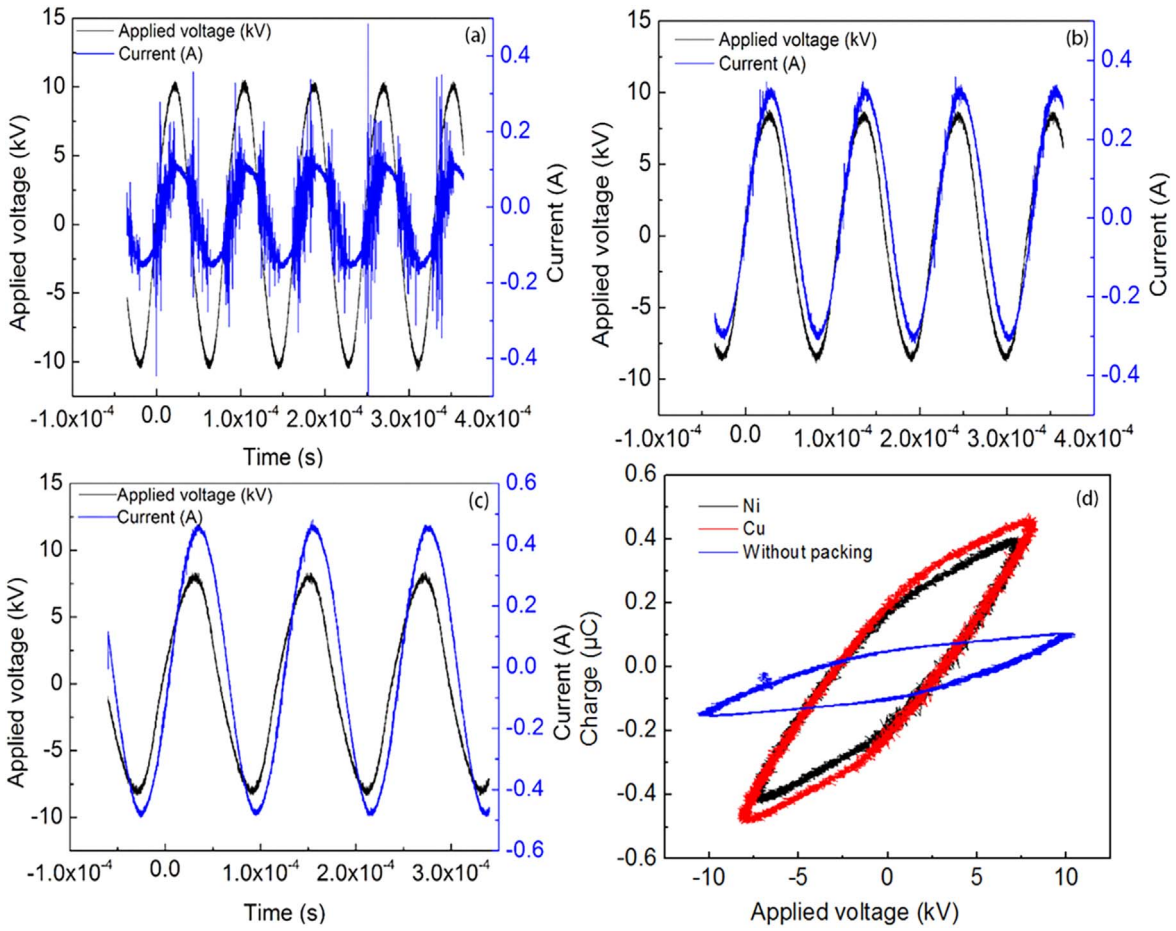

Figure 3. Discharge characteristics of CO_2 discharge in the DBD reactor (flow rate = 20 ml min^{-1}, P = 55 W): (a) non-packed reactor, (b) foamed Ni and (c) foamed Cu mesh packed reactor, (d) Lissajous figure of unpacked reactor and packed reactor.

proved by the number and amplitude of the current pulses which increased as a result of the increasing discharge power, suggesting that more chemical reaction channels and reactive species were produced for CO_2 decomposition [17].

It has been found that CO_2 can be activated on transition metal catalysts [18] and adsorbed on transition metal surfaces. Otherwise, it is reported that CO_2 has a chemisorption over the surface of Ni [19]. So it is not difficult to speculate that foamed Ni and Cu mesh will activate more CO_2 molecules for decomposition due to the chemisorption on their surface. The recombination of O radicals to O_2 takes precedence over the combination of CO and O radicals on various solid surfaces at low temperatures [20–22], and our results are in good agreement with this finding.

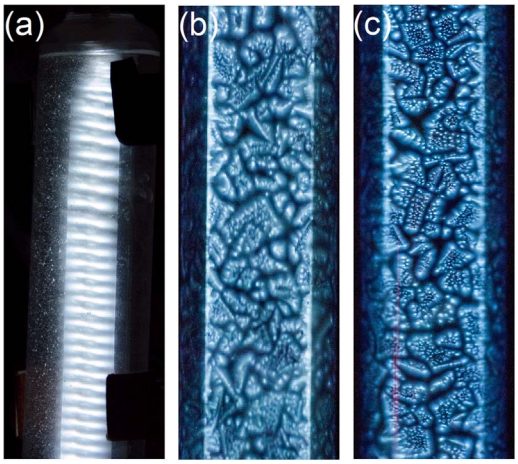

Figure 4. Images of CO_2 discharge in the self-cooling DBD reactor (flow rate = 20 ml min^{-1}, P = 55 W). (a) Unpacked reactor, (b) foamed Ni mesh packed reactor, (c) foamed Cu mesh packed reactor.

3.2. Discharge characteristics of the CO_2 discharge

It can be noted from the Q–V curve that the foamed Ni and Cu mesh packing was significantly different from that of the unpacked reactor. The spikes of the voltage/charge were different at different operating conditions and this resulted in various discharge behaviors as shown in the characteristics for the formation of the microdischarge in DBD reactor [23]. As can be seen from figure 3, notably, that there were much less filamentary discharges in the reactor filled with foamed Cu and Ni meshes than in the unpacked reactor.

This means that the discharge mode changed from a filamentary discharge to a mode of surface discharge combined with filament discharge. Then, it can be noted that the amplitude for the charge and applied voltage of the foamed

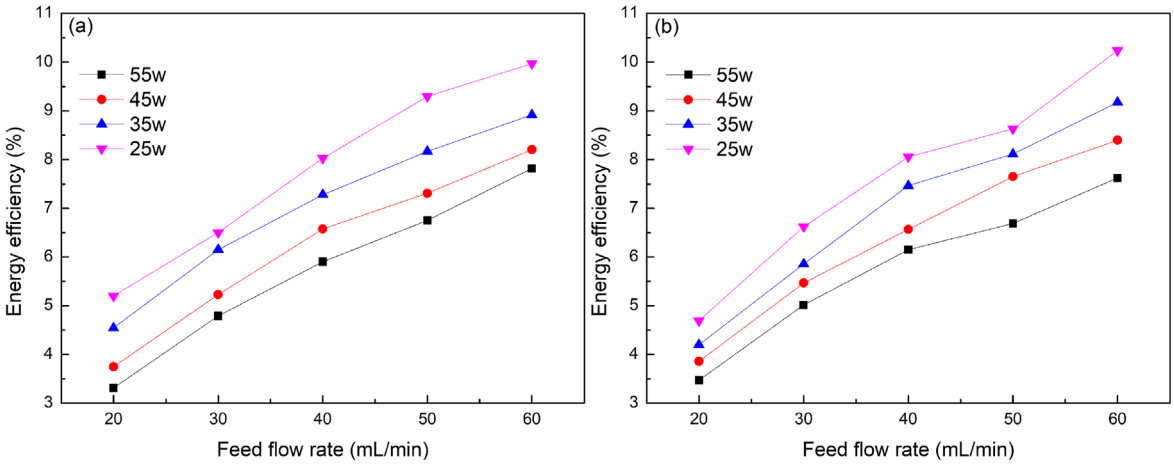

Figure 5. Pictures of CO_2 discharge in the self-cooling DBD reactor (frequency = 9 kHz). (a) Foamed Ni mesh packed reactor, (b) foamed Cu mesh packed reactor.

Cu and Ni mesh packed DBD reactor is higher than that of the unpacked reactor at the same discharge power. It may demonstrate that the micro discharges generated in the case of porous foamed Ni and Cu mesh were stronger. More intensive plasma generation in the presence of foamed Cu and Ni mesh can create a large amount of high energy species to decompose CO_2, and such a difference can also explain the difference in CO_2 decomposition. The Lissajous figure of the CO_2 discharge, varying under different conditions, is presented in figure 3(d). The shape of the figures changes with the change of packing materials which was due to the change in dielectric strength [24]. It displays the transferred charge and applied voltage in the discharge.

Images of the CO_2 discharge during the process are displayed in figure 4. The widely distributed and intensive microdischarge on the surface of the porous foamed Ni and Cu mesh was observed, which is an important reflect of the discharge process. As a result, multiple materials provided different discharge behaviors, improving the formation of the microdischarge [25]. It should be mentioned that the electrical conductivity of the packing materials or electrode materials may also contribute to the high CO_2 decomposition.

3.3. Energy efficiency

Energy efficiency matters much in the practical application of non-thermal plasma in the decomposition of CO_2. As indicated in the formula (5) in the experimental section, the energy efficiency in the plasma system is defined by both the gas flow rate and discharge power. The feed flow rate and discharge power are the main parameters which affect the energy efficiency [26]. A higher feed flow rate leads to lower CO_2 decomposition but is more energy efficient. It is estimated that an energy efficiency of 52% would be needed for the CO_2 decomposition to compensate for the CO_2 production by the fossil fuel combustion in the conductive properties production [27]. van Laer and Bogaerts obtained an energy efficiency of 9.6%, which corresponds to a CO_2 conversion of only 10%, in a ZrO_2 packed DBD reactor [15]. The maximum energy efficiency with pure AC obtained up to now was 15.3%, with a CO_2 conversion of only 22% [3]. The CO_2 decomposition and energy efficiency of the discharge process cannot get to the maximum values simultaneously at the same plasma operating conditions, therefore, a balance between CO_2 decomposition rate and energy efficiency is important for CO_2 decomposition. Thus, the energy efficiency as a function of gas flow rate and discharge power was conducted in this work.

A maximum CO_2 decomposition rate reached to 49.2% with 55 W of discharge power in the foamed Cu mesh packed reactor, at a flow rate of 20 ml min^{-1}. As can be seen from figure 5, the corresponding energy efficiency was 3.8%, and it was 1.8 times higher than that of the unpacked reactor under this condition. However, the highest energy efficiency obtained was 10.18%, with a corresponding CO_2 decomposition rate of 22.2%, which was obtained at the highest flow rate 60 ml min^{-1} and with the discharge power of 25 W. The introduction of porous foamed Ni and Cu mesh in the self-cooling DBD reactor greatly improved the CO_2 decomposition rate and energy efficiency. A packed-bed DBD reactor can not only generate higher maximum decomposition or energy efficiency, but can also provide better combined values of them.

3.4. Energy dispersive x-ray (EDX) analysis of the packing materials

Figure 6 shows the EDX of the porous foamed Ni and Cu mesh before and after the reaction. It is clear that the oxygen element was detected in addition to consistent elements of foamed Ni and Cu mesh before the reaction. It can be concluded that some of Ni and Cu were oxidized during the reaction due to the formation of oxygen in the process, so the CO_2 decomposition rate decreased gradually with the increasing reaction time, because some part of the O_2 and O radicals were consumed for the oxidization of Cu and Ni during the reaction. The improvement in CO_2 decomposition might be correlated with the consumption of the generated O_2

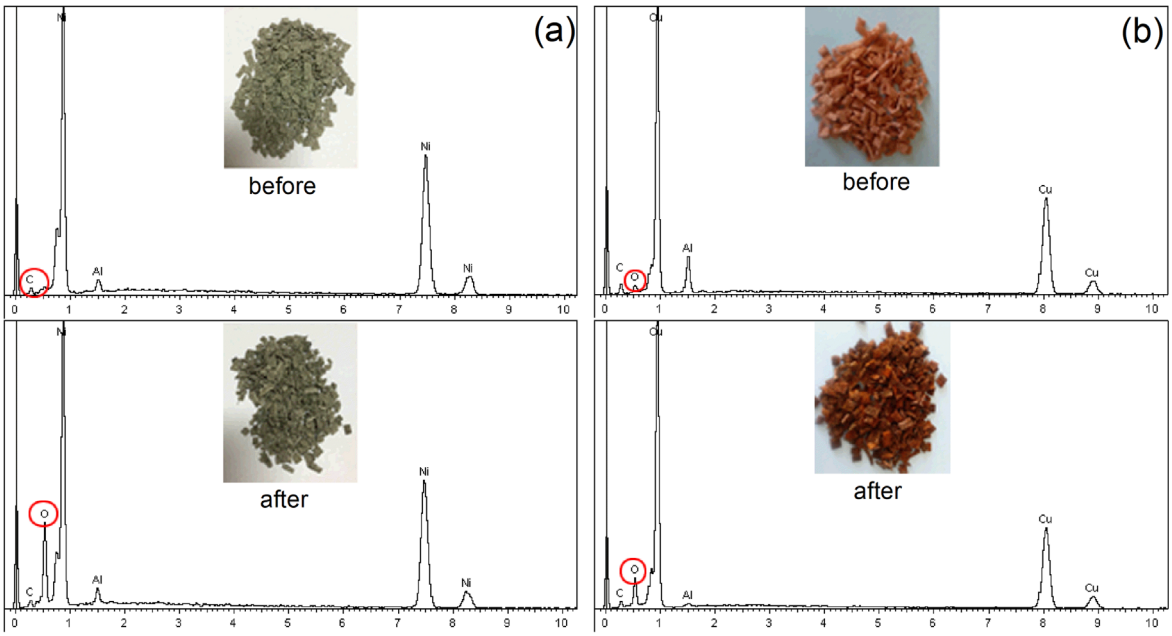

Figure 6. EDX analysis of foamed (a) Ni and foamed (b) Cu before and after the reaction.

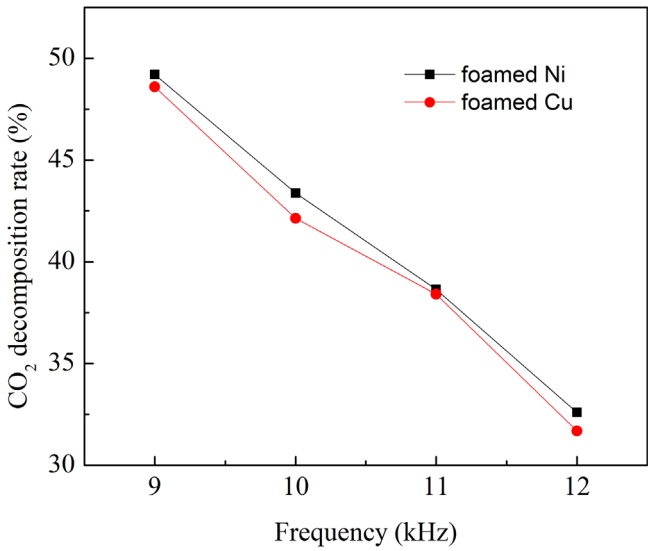

Figure 7. CO_2 decomposition rate at different frequencies (P = 55 W, flow rate = 20 ml min^{-1}).

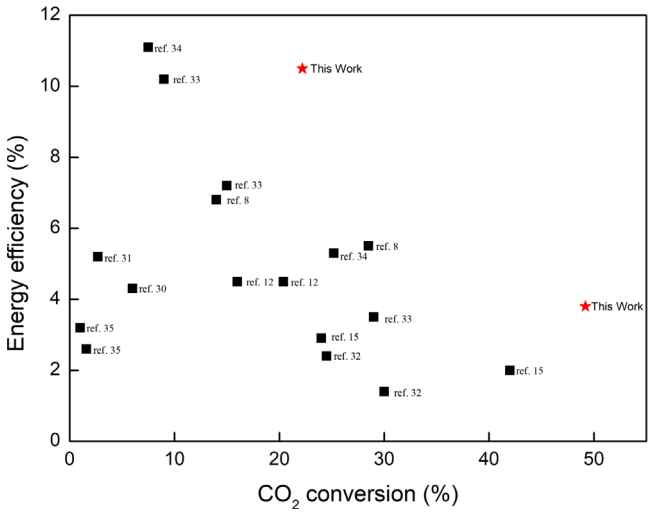

Figure 8. Comparison of CO_2 conversion and energy efficiency values obtained in this work with the best available data in the literature for a DBD reactor used for pure CO_2 splitting.

or O radicals, because the transfer of O_2 molecules and O radicals is conducive for the equilibrium shifting toward the product side to yield more CO.

3.5. Effect of frequency

In the self-cooling DBD reactor, the influence of frequency on the CO_2 decomposition was unelectable. As shown in figure 7 below, the CO_2 decomposition rate decreased as the frequency increased from 9–11 kHz in the foamed Ni and Cu mesh packed reactor. The decreased CO_2 decomposition rate may lie in the reduced density of electrons because of the increased discharge frequency. Changes in the frequency from 9–11 kHz lead to a significant decline in the CO_2 decomposition rate with the same input power, increasing the discharge frequency lowered the discharge current apparently, hence the density of electrons.

The plasma in filamentary regime (high frequency) had a different electron energy distribution function from less regime-glow regime (low frequency). This explained the decline in the rate of decomposition of CO_2. At lower frequencies, more electrons which are capable of breaking of the C=O bond were generated. This is in agreement with the result that the decline in frequency leads to an increase in the CO_2 conversion and energy efficiency [28]. For a constant power, the applied voltage

reduction is the result of the increase in frequency. This means that the electric field is weakened during discharge process. In relation to that is the decline in the average energy of electrons, so that less electrons are able to take part in the CO_2 dissociation process. The cause of the drop in voltage has been studied by Valdivia-Barrientos [29].

3.6. Comparison with other results reported in the literature

Figure 8 shows a comparison of our work with other results in the literature. It is the combination of high CO_2 conversion and high energy efficiency which matters for further application and packing materials play a key role. With the help of good conductive properties, it is easy to achieve high CO_2 conversion or energy efficiency when packing porous foamed Ni and Cu mesh. These new materials and its conductive properties can be further improved by studying different operating parameters or working with catalysts, and may have great potential in the utilization of CO_2 in the future.

4. Conclusions

Direct CO_2 decomposition into CO and O_2 in a self-cooling DBD reactor was investigated in the presence of porous foamed Ni and Cu mesh. What stands out is the durability of CO_2 decomposition in presence of packing materials, which not only provided a great increase to CO_2 decomposition, but also can be recycled several times without decreasing CO_2 decomposition. In comparison with the CO_2 decomposition in an unpacked reactor, the CO_2 decomposition rate and energy efficiency were greatly improved twofold in the presence of packing foamed Ni and Cu mesh, due to their electric conductivity that can make widely distributed micro discharges. Consequently, an intense electric field would be generated around each contact site of the discharge space. Foamed Ni and Cu mesh acted as an energy carrier for the transfer of electron and reactive species to CO_2 decomposition, and yielded high CO_2 decomposition of 48.6% and 49.2%, with the maximum energy efficiency of 9.71% and 10.18%, respectively.

Acknowledgments

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