[Research Note]

Effects of Sound-wave Irradiation on Decomposition of Carbon Dioxide in DC-pulse Discharge Field

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The effects of sound-wave irradiation were investigated on the decomposition of carbon dioxide in a discharge plasma. Discharge plasma supplies high local energy levels, as charged medium particles, so chemical reactions ungoverned by thermodynamics can occur. However, the discharge space is extremely confined, which restricts the conversion rate. This study investigated the combination of plasma and sound-wave irradiation, which increases the vibration motion of the medium. A streamer was observed to expand into a fan shape on irradiation of sound waves. The expansion of the discharge space was positively correlated with the magnitude of the sound. Accordingly, the effects of sound-wave irradiation on the direct decomposition of carbon dioxide were evaluated. The decomposition rate of carbon dioxide (r_{CO_2}) increased with sound pressure at the closed end of the sound tube, and r_{CO_2} at 1.8 kPa approximately increased to approximately twice that for no sound-wave irradiation. This increase in r_{CO2} resulted from the improvement in the reaction probability due to expansion of the discharge space and increased vibration of the charged particles.

Keywords
Discharge plasma, Sound wave, Carbon dioxide, Decomposition, DC pulse discharge, Energy efficiency

1. Introduction

Carbon dioxide is an important greenhouse effect gas involved in global warming, so the development of processing technologies is highly desirable. Additionally, carbon monoxide is a useful chemical raw material which can be formed by the direct decomposition of carbon dioxide ($CO_2 \rightarrow CO + 0.5O_2$), so highly efficient on-site production would be extremely valuable technology. However, the thermodynamics of direct decomposition of carbon dioxide require high temperatures, so catalytic reaction is unlikely. Therefore, methods which develop high local energies such as discharge plasma fields have been investigated[1)~3)]. Plasma-catalyst compound systems, in particular, have received considerable attention from the viewpoint of reaction efficiency[4),5)]. Sound-wave irradiation of various gas flows has shown that the combination of plasma, which involves conversion of medium to charged particles, and sound, which is the propagation of the vibration motion of the medium, causes expansion of the discharge space, and that the degree of the expansion depends on the magnitude of the sound[6)].

We have investigated the plasma-sound wave combined system as a control method for chemical reactions in plasma generated by DC-pulse discharge. Since either vibration speed of the medium particles and/or sound pressure can be controlled in the present system, a higher collision probability can be expected under atmospheric pressure than under increased total pressure or CO_2 supply pressure without sound-wave irradiation. The present study evaluated the effects of sound-wave irradiation on the acceleration of the decomposition of carbon dioxide in a DC discharge field.

2. Experimental Apparatus and Method

2. 1. Sound-wave Irradiation Type DC-pulse Discharge Reactor

The sound-wave irradiation type DC-pulse discharge reactor is shown in **Fig. 1**. The reactor consisted of a sound source for irradiation of frequency-controlled sound waves, an acrylic sound tube (30 mm I.D.,

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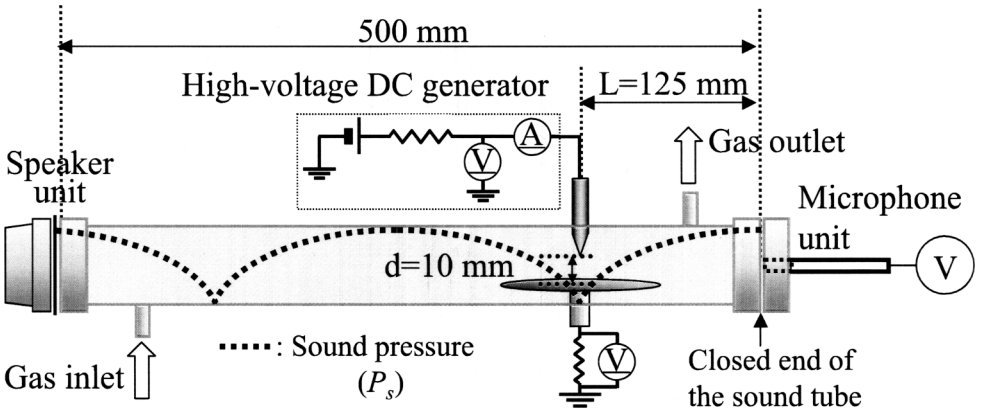

Fig. 1 Sound-wave Irradiation Type DC-pulse Discharge Reactor

500 mm length) in which the stationary wave is formed, and a high-voltage DC power source. The electrical discharge was generated in the sound tube by passing a high-voltage DC pulse between a stainless steel needle electrode and copper plate ground electrode fixed 10 mm apart. The electrodes were installed at the node position of the sound pressure (125 mm distant from the closed end of the sound tube (**Fig. 1**)) where the vibration speed of the medium particles peaks under sound-wave irradiation.

2. 2. Measurements of Resonance Frequencies and Stationary Waveforms

Sound-wave irradiation and the associated reactions were carried out under atmospheric pressure. A sound wave distribution with a maximum pressure of 2 kPa was present in the sound tube. A measuring microphone (Sony Corp., Model ECM-155), connected to a stainless steel lead tube, was used for measurements of resonance frequencies and stationary waveforms, and sound pressures (P_s) were determined from the relationship of electromotive forces between the measuring microphone and a reference microphone (Brül & Kjaer, Model 4138). The irradiated sound wave was frequency-controlled with an oscillator (Kenwood Corp., Model AG204), and the input to the speaker was adjusted with an amplifier (Nihon Denon Co., Ltd., Model 1654). The resonance frequencies were measured from the sound pressures for various oscillation frequencies with the measuring microphone placed at the closed end of the sound tube. The stationary waveforms were measured from the relationship between the sound pressures and the insert lengths (L) of the measuring microphone from the closed end of the sound tube at various resonance frequencies. The states of the stationary waves were evaluated by the stationary wave ratio, as represented by the ratio of sound pressure at an anti-node to that at a node. Additionally, the discharge field was also evaluated through measurements of resonance frequencies for each type of supplied gas, so that stationary waveforms did not depend on the type of gas and only the sound pressure or the vibration speed was varied by the magnitude of the sound.

2. 3. Decomposition of Carbon Dioxide

Reactions were carried out under CO_2–Ar mixed gas (molar fraction of carbon dioxide (MF_{CO_2}) = 0.1) with the mixing ratio controlled by a mass flow controller (Kojima Instruments Inc., Model 3650) at a total molar flow rate of 2.1 mmol·min^{-1}. A voltage of 15 kV was applied to generate the discharge, and sound pressure at the closed end of sound tube (P_{s1}) was varied as the operational factor. A gas chromatograph (column: Molecular sieve 5A and Shincarbon ST; detector: TCD) was employed for qualitative and quantitative analyses of products. Energy efficiencies were evaluated from the relationships between formation rates of carbon monoxide and oxygen, and energy consumption.

3. Results and Discussion

3. 1. Effects of Sound-wave Irradiation on Discharge under Ar

Figure 2(a) shows the resonance frequencies measured for Ar flow. Resonance states were observed with sound-wave irradiation of 265, 450, and 685 Hz. Therefore, stationary waveforms were measured at three resonance frequencies. Collapse of the stationary waveform was observed in the region close to the speaker at 450 Hz. **Figure 2(b)** shows the stationary waveforms formed in the sound tube at the resonance frequencies of 265 and 685 Hz were applied. The stationary waveforms observed corresponded to 1/2 and 1 wavelength, respectively. Consequently, the present study used sound-wave irradiation at 685 Hz, which imposed fewer constraints in terms of the setting position of the electrodes.

Figure 3 shows the change in the discharge state when the sound-wave with 685 Hz was applied to DC pulse discharge from the vertical direction in Ar gas flow. A streamer clearly expanded into a fan shape with P_{s1} of 1.8 kPa. The degree of this expansion

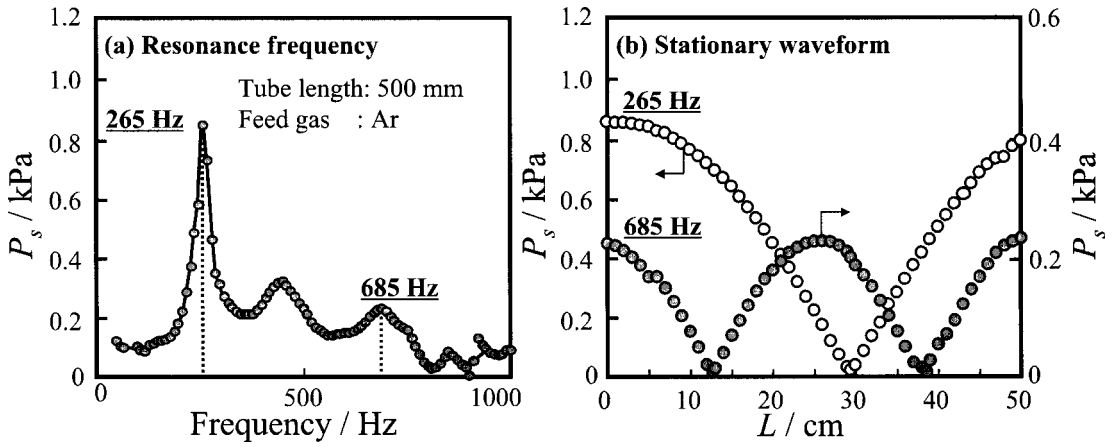

Fig. 2 Resonance Frequencies and Stationary Waveforms Formed in the Sound Tube

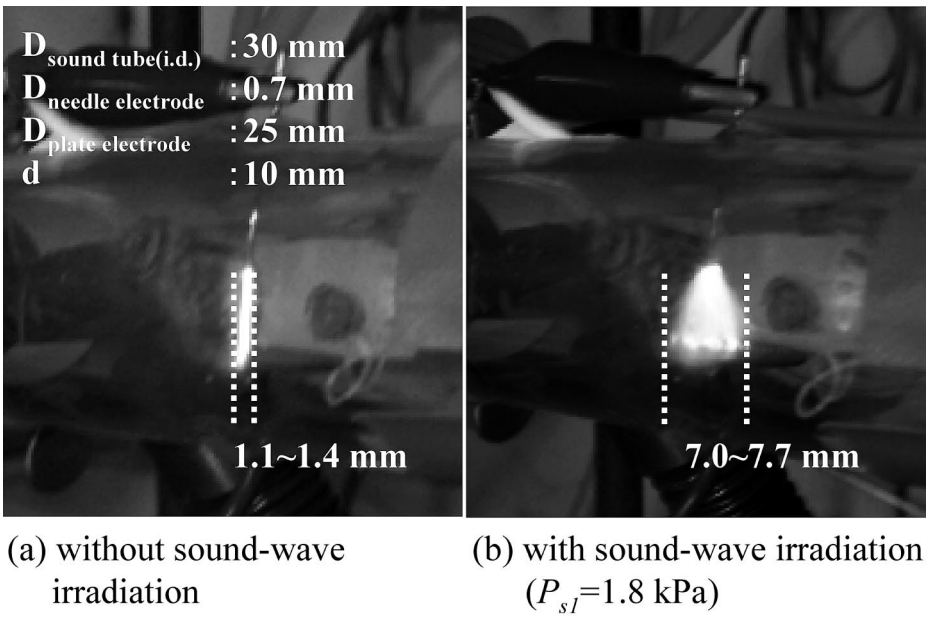

Fig. 3 Comparison of Discharge States

tended to be proportional to the increase in P_{s1}. With a P_{s1} of 1.8 kPa, approximately seven-fold expansion was observed above the plate electrode. Therefore, sound-wave irradiation increases the vibration of medium molecules in the sound tube. Theoretically, in a stationary-wave sound field, the node position of the sound pressure at the electrodes has the highest vibration speed, which relatively to P_{s1}. Therefore, the expansion of the streamer was probably caused by a cyclic change in the discharge field due to the violent vibration of medium particles in the neighborhood of the needle electrode.

3. 2. Effect of Sound-wave Irradiation on Efficiency of CO_2 Decomposition Reaction

Figure 4 shows the effects of sound-wave irradiation on the decomposition rate of carbon dioxide (r_{CO_2}), and formation rates of carbon monoxide (r_{CO}) and oxygen (r_{O_2}). The r_{CO_2} increased with P_{s1}, and r_{CO_2} at 1.8 kPa increased to approximately twice that for no sound-wave irradiation. The increase in the r_{CO_2} was probably attributable to increased probability of collisions between excited species of Ar and CO_2 due to higher vibration speed by sound-wave irradiation. Additionally, the individual measurements of r_{CO_2}, r_{CO} and r_{O_2} under the present experimental conditions showed that r_{CO_2} is close to r_{CO}, and that r_{CO}/r_{O_2} is approximately 2. Therefore, the direct decomposition of carbon dioxide progresses stoichiometrically. No precipitation of carbon was observed on the electrode surfaces. Therefore, to investigate the acceleration mechanism of carbon dioxide decomposition with sound-wave irradiation in CO_2–Ar mixed gas, measurements of emission spectra and V-I curves were performed.

Measurement of the emission spectra showed a peak

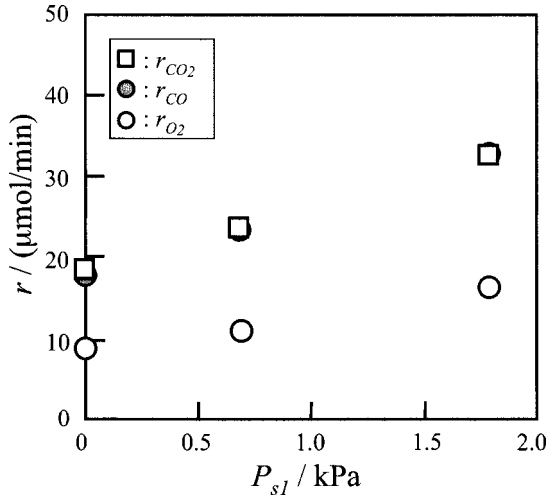

Fig. 4 Effects of Sound Pressure on Rates of Carbon Dioxide Conversion, and Rates of Formation of Carbon Monoxide and Oxygen

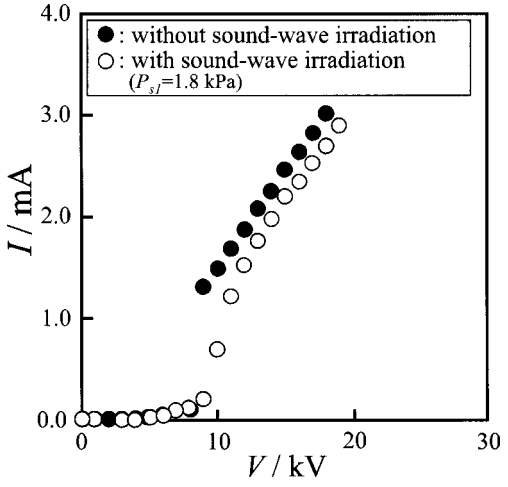

Fig. 5 V-I Curves Measured with and without Sound-wave Irradiation under CO_2–Ar (MF_{CO_2} = 0.1)

at 811 nm caused by Ar transition between 4s and 4p orbits. Additionally, the emission intensity slightly decreased and plasma distributions (densities) changed in association with expansion of the plasma space. However, no significant differences in the peaks were observed, suggesting that sound-wave irradiation has little effect on the active species formed in the system.

Figure 5 shows the V-I curves measured with and without sound-wave irradiation at 1.8 kPa under CO_2–Ar mixed gas. The V-I curve clearly shifted to the higher-voltage side with sound-wave irradiation. The degree of shift also increased with the P_{s1}. Therefore, sound-wave irradiation suppressed the discharge.

The effect of MF_{CO_2} on discharge is shown in **Fig. 6**. This figure shows the discharge current at an applied voltage of 15 kV, as read from the V-I curves. The current values (●) without sound-wave irradiation are

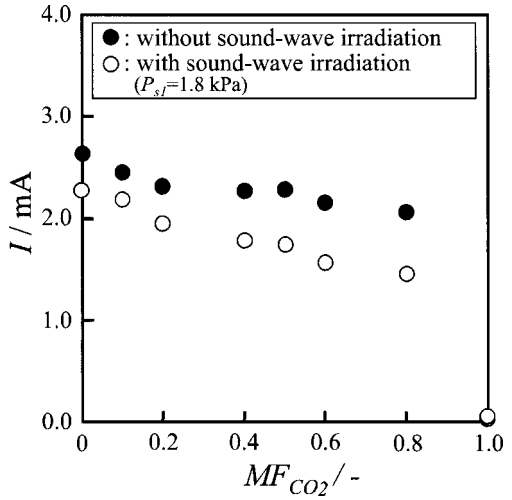

Fig. 6 Effects of MF_{CO_2} on Discharge Current at 15 kV with and without Sound-wave Irradiation

higher than those (○) with sound-wave irradiation, irrespective of MF_{CO_2} value. The shift to the higher-voltage side increased with higher MF_{CO_2}, suggesting that carbon dioxide resists discharge to a greater degree than argon, and that sound-wave irradiation increases the difference in the discharge properties between the two gases. Furthermore, when only carbon dioxide was supplied, at an applied voltage of 15 kV, only dark-current level discharge occurred, and no significant decomposition of carbon dioxide was detected. Investigation of the direct decomposition of carbon dioxide in a dilute Ar gas system without sound-wave irradiation indicated the presence of an energy transfer route via Ar gas from changes in emission spectra[7]. The energy level of Ar in a metastable state is 11.5 eV, which is higher than the dissociation energy (5.5 eV) of the OC=O bond. Therefore, a similar energy transfer route is likely for the present system, and the sound-wave irradiation is assumed to contribute either to activation of Ar gas (Ar to Ar*) or to an increase in the frequency of energy transfer from Ar* to molecular CO_2 due to the vibratory motion of particles in the neighborhood of the needle electrode.

Evaluation of photographs of the expansion of the discharge space in the sound tube cross-section with and without sound-wave irradiation showed that the discharge space with P_{s1} of 1.8 kPa sound-wave irradiation was approximately three times that without sound-wave irradiation. This expansion is equivalent to a 3.4% increase in the cross-sectional area of the discharge space. The factors governing the reaction rate in plasma (k: reaction rate constant) can be described by Eq. (1), as simplified to proportional to the product of the volume (V_d) of the space where discharge takes place, the density (N_n) of the gas in the space, the density (N_e) of discharged electrons, and the formation frequency (ϕ) of active species based on the dissociation cross-section

of CO_2.

$$r = k\, V_d\, N_e\, N_n\, \phi \quad (1)$$

Comparison of the discharge currents observed when the same voltage is applied with and without sound-wave irradiation indicates that sound-wave irradiation of 1.8 kPa (15 kV applied) decreases the current by 15-20%, which implies decreased N_e. In contrast, sound-wave irradiation presumably increases the molecular collision frequency, leading eventually to increased ϕ. Therefore, the increase in the reaction rate due to sound-wave irradiation can be attributed to the positive effect of the increases in ϕ and V_d, and the negative effect of the decrease in N_e.

3. 3. Consideration of Energy Efficiency

Calculation of the sound wave energy shows that the P_{s1} of 1.8 kPa is equivalent to approximately 159 db (= 8.2 kW·m^{-2}) and supplies 5.7 W of energy to the cross-section of the sound tube (7.06×10^{-4} m^2). Electrical energy for application of 15 kV supplies 30 W to the needle cross-section (3.85×10^{-7} m^2) for an assumed average discharge current of 2 mA; and the average value per unit area is estimated to be approximately 97.1 MW·m^{-2}. Therefore, the energy supplied by sound-wave irradiation was only around 1/10000th of the discharge energy. This large difference in the energy levels is unlikely to lead to distinct differences in the emission spectrum measurement results obtained under different conditions.

The evaluation of energy efficiencies associated with sound-wave irradiation was conducted based on DC pulse discharge at 15 kV under CO_2–Ar mixed gas with MF_{CO_2} adjusted to 0.1 at a total molar flow rate of 2.1 mmol·min^{-1}. Carbon dioxide conversion of 7% without sound-wave irradiation increased to 15% with sound-wave irradiation. The sound-wave energy supplied to the sound tube cross-section was approximately 5.7 J·s^{-1} under this condition. The energy consumption of the reaction estimated based on the increment in the carbon dioxide conversion was approximately 0.77 J·s^{-1}. Therefore, 13% of the sound energy is assumed to be used in the energy conversion of carbon dioxide. Consequently, the energy efficiency (4%) with sound-wave irradiation is twice that without irradiation (2%) in terms of the overall system, including the electrical discharge energy. Evaluation of discharge fields is generally based on electric power per unit volume, whereas sound energy is represented by energy per unit cross-sectional area. Therefore, the supply of energy per unit time was used as the criterion of comparison. The increase of energy efficiency observed may be applicable to larger scales, because this plasma-sound wave combined reaction is suitable for a small-scale reactor.

4. Conclusion

Sound-wave irradiation of a plasma field formed by electrical discharge accelerates the decomposition of carbon dioxide due to expansion of the discharge space. Confirmation of a significant increase in energy efficiency due to application of sound energy of around 1/10000th of the discharge energy suggests that sound-wave irradiation is an effective control method for plasma reactions.

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要　　旨

直流パルス放電場での二酸化炭素の分解反応に対する音波の照射効果

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放電プラズマ中での化学反応に対する音波の複合化効果を検討した。放電プラズマは局所的に高エネルギーを付与できることから，熱力学支配を受けない非定常反応場を容易に構築することができる。一方，放電空間は極めて限定的であり，反応は量的に制限される。本研究では，媒質粒子の荷電粒子化であるプラズマと媒質粒子の振動運動である音波を複合化することを考えた。音波未照射時に帯状であったストリーマ放電は音波の照射により扇型に拡張され，その拡張の程度は照射した音の強さに比例することが明らかとなった。そこで，音波の照射効果を二酸化炭素の直接分解反応により評価した。二酸化炭素の分解反応速度は音響管端における音圧とともに増加する傾向を示し，1.8 kPa の音波を照射した際の分解速度は未照射の約2倍に達した。この分解速度の増加は放電空間の拡張や荷電粒子の振動に起因した反応効率の向上によると推測される。この非接触での制御技術は新たなプラズマ反応場の構築につながると考えられる。

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