Decomposition of Carbon Dioxide by the Dielectric Barrier Discharge (DBD) Plasma Using $Ca_{0.7}Sr_{0.3}TiO_3$ Barrier

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$Ca_{0.7}Sr_{0.3}TiO_3$ was sintered adding $Li_2Si_2O_5$, and used as a dielectric barrier of DBD to decompose CO_2 for the first time. DBD plasma was successively generated using $Ca_{0.7}Sr_{0.3}TiO_3$. CO_2 was converted to CO and O_2 by DBD plasma without catalyst and reducing substance. The CO_2 conversion using $Ca_{0.7}Sr_{0.3}TiO_3$ barrier was much higher than that using conventional barrier material such as SiO_2 and Al_2O_3.

The remediation of CO_2 has received increasing attention.[1–6] Recently, many nonthermal plasma technologies have been developed and used to break CO_2.[7–10] In these studies metal catalysts or low-carbon compounds such as CH_4 etc. were usually used.

The DBD plasma which is generated by applying high voltage between the electrodes, one of which is at least covered with dielectric barrier material, has been applied to produce ozone[11,12] and has received attention for the application to the decomposition of CO_2,[10] pollution control, etc.[13–15] Its inherent advantage is that "hot" electrons produced in the microdischarges induce the plasma chemistry, while the temperature of the heavier particles (molecules, atoms, and ions) remains near the average gas temperature in the filaments. The efficiency of DBD plasma chemical reaction is expected to increase by increasing the permittibity of the barrier material, since the transported charge which leads to excitation, dissociation, or ionization of plasma reaction is proportional to the permittivity of the dielectric material.[16] However, a high permittivity ceramic tends to be broken by supplying a high voltage because of its modest dielectric strength. Consequently, the low permittivity material such as SiO_2 has generally been used as a dielectric barrier.

$MTiO_3$ (M = Ca, Sr, Ba) ceramics are typical dielectric materials possessing variety of dielectric properties.[17–22] We found that $Ca_{0.7}Sr_{0.3}TiO_3$ sintered using $Li_2Si_2O_5$ as a sintering aid could be used as a dielectric barrier to generate a high energy DBD plasma. In the present study the sinterability, mechanical, and dielectric properties of $Ca_{0.7}Sr_{0.3}TiO_3$ were investigated using $Li_2Si_2O_5$ as a sintering additive at first. And then this ceramic was applied as a dielectric barrier for the decomposition of CO_2 by the DBD plasma without any catalyst and reducing substance. For comparison, commercial alumina and silica glass were also used as the barrier materials.[7–10]

Appropriate quantities of $CaTiO_3$, $SrTiO_3$, and $Li_2Si_2O_5$ were wet-mixed in a polyethylene bottle with ZrO_2 balls and ethanol for 16 h. The dried powder was compacted and sintered at 1200 °C for 2 h in air. The crystallographic phase was characterized by X-ray diffraction (XRD) analysis. The density of the sintered ceramics was measured using the Archimedes method. The permittivity and dielectric strength were determined by an impedance analyzer (Agilent Tech., 4299A) and a withstanding voltage tester (Kikusui, TOS5101), respectively.

The experimental setup is shown in Figure 1. The planar DBD plasma reactor, which outside shell was made of Teflon, was used in this work. The reactant mixed gas (CO_2:N_2 = 10:90) was fed into the discharge gap at the space velocity of 20800 h^{-1}. Two parallel-plate electrodes ($24 \times 12 \times 3$ mm) were made of stainless steel. The ground electrode was covered with a 1-mm thick of dielectric layer (30×15 mm) of alumina, silica glass or $Ca_{0.7}Sr_{0.3}TiO_3$ ceramics. The gap space between the dielectric barrier and counter electrode was 1 mm. A sinusoidal voltage was applied to the reactor by an ac high-voltage amplifier with a function generator (Trek 12193). During the operation, the electric parameters such as the ac wave shape, input voltage, current and frequency were continuously monitored by a multichannel digital oscilloscope (Iwasaki DS-8812). The CO_2 concentration was quantitatively analyzed by a CO_2 meter (Shimadzu URA107).

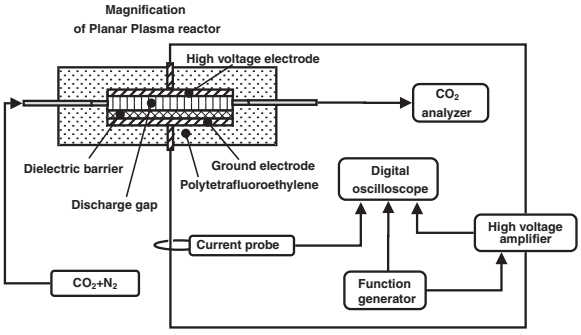

Figure 1. Schematic diagram of experimental apparatus.

Both $Ca_{0.7}Sr_{0.3}TiO_3$ samples sintered at 1200 °C for 2 h with 0.5 wt % and without $Li_2Si_2O_5$ consisted of a single phase, i.e. $Ca_{0.7}Sr_{0.3}TiO_3$ solid solution according to the XRD analysis. This is in good agreement with the previous results.[17,18] The characteristics of the sintered bodies are summarized in Table 1. The relative densities of the samples with 0.5 wt % and without $Li_2Si_2O_5$ were 95.6 and 78.1%, respectively. The dramatic increase in the density by adding the sintering additive may be probably due to the liquid phase sintering since the melting temperature of $Li_2Si_2O_5$ is ca. 1030 °C. Their permittivities were 207 and 119 at the temperature of 100 °C and frequency of 10 MHz, while the dielectric strengths were 11.6 and 10.9 kV/mm, respectively. The increase of dielectric properties was attributed to the higher relative density after adding $Li_2Si_2O_5$. This $Ca_{0.7}Sr_{0.3}TiO_3$ with 0.5 wt % $Li_2Si_2O_5$ was successfully used as a DBD barrier to generate a plasma. On the other hand, the specimen without additive was fractured before generating a DBD plasma because of its modest dielectric strength and mechanical

Table 1. Relative densities, three point bending strengths, permittivities and dielectric strengths of $Ca_{0.7}Sr_{0.3}TiO_3$ sintered at 1200 °C for 2 h with and without $Li_2Si_2O_5$

$Li_2Si_2O_5$ Content / wt %	Relative Density / %	3-point Bending Strength / MPa	ε / 100 °C, 10 MHz	Dielectric Strength / kV/mm
0.5	95.6	306.8	207	11.6
0	78.1	98.5	119	10.9

strength.

The degrees of CO_2 conversion with different input frequencies using this $Ca_{0.7}Sr_{0.3}TiO_3$ with 0.5 wt % $Li_2Si_2O_5$, commercial alumina or silica glass dielectric barriers are shown in Figure 2. The permittivities of three kinds of ceramics at 100 °C and 10 MHz were in the order of $Ca_{0.7}Sr_{0.3}TiO_3$ (207) ≫ alumina (10.4) > silica glass (4.6). It is seen that the conversion of CO_2 slightly increased with increasing input frequency and greatly changed depending on the barrier materials, in the order of $Ca_{0.7}Sr_{0.3}TiO_3$ ≫ alumina > silica glass, i.e., the same order as the permittivity at each input frequency.

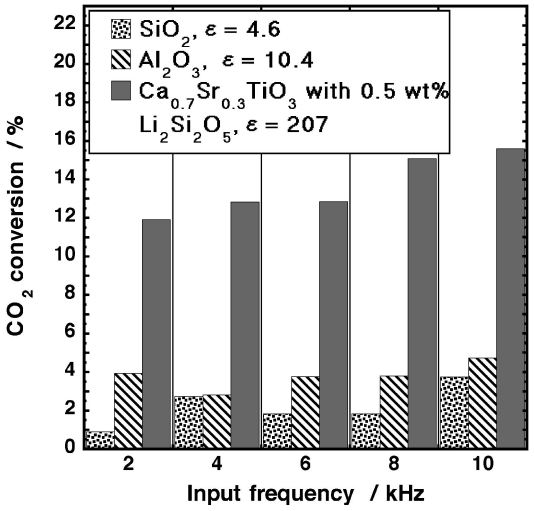

Figure 2. Input frequency dependence of CO_2 conversion using different dielectric barriers (their permittivities are shown in the legend).

The improved CO_2 reduction activity is interpreted by the principle of discharge physics. The capacitive energy stores connected in parallel electrodes could be expressed as below:

$$C = \varepsilon s/d \quad (1)$$

where C is the electric capacity, ε is the permittivity, s is the area of electrode, d is the distance between parallel-plate electrodes or the top electrode and dielectric barrier.

According to Eq 1, the electric capacity is proportional to the permittivity. That means if the permittivity is higher, the polarization in the dielectric barrier will be strong, i.e., much more charges generate on the dielectric surface. The acceleration a of an electron in an electric field E can be written as

$$a = eE/m \quad (2)$$

m is the mass of the electron with charge e.[11] The fast electrons created by the discharge mainly initiate the chemical reactions in the plasma. They collide with the gas molecules and excite them to a higher energy level, thereby losing part of their energy. The excited molecule can now, because of its high internal energy, either dissociate or initiate other reactions. In other words, high permittivity of the barrier corresponds to more "hot" electrons to take part in the chemical reaction.

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