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Author(s)	Matsuura, Fumiya; Wakamatsu, Takafumi; Natsui, Shungo et al.
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CO Gas Production by Molten Salt Electrolysis from CO₂ Gas

Fumiya MATSUURA, Takafumi WAKAMATSU, Shungo NATSUI, Tatsuya KIKUCHI and Ryosuke O. SUZUKI*

Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Kita-13 Jou, Nishi-8 Chome, Kita-ku, Sapporo, Hokkaido, 060-8628 Japan.

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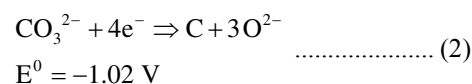
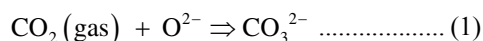
CO₂ gas is decomposed to CO and C by the molten salt electrolysis using CaCl₂–CaO and solid state electrolyte, zirconia, as the anode. Partially CO₂ gas dissolves to form CO₃²⁻ and it is electrochemically decomposed to carbon. The other portion of CO₂ gas bubbles reacts with metallic Ca electrochemically deposited near the cathode, and forms C or CO gas. By increasing the flow rate of CO₂ gas to the reactor, a high concentration of CO gas is generated. By increasing the concentration of CO₂ gas in the initial gas, a large amount of CO gas was produced in the exhaust gas, and its rate approached to 3.32×10⁻⁸ m³/s in our experimental setup. These experimental evidences reflect the electrochemical decomposition of CO₃²⁻ in the molten salt.

KEY WORDS: carbon dioxide; carbon monoxide; molten salt electrolysis; zirconia.

1. Introduction

Many attempts to reduce CO₂ gas are widely examined to promote the countermeasures of global warming. In Japan, a large amount of CO₂ gas is emitted from the steel making industries, and the exhaust gas from blast furnaces and converters particularly affects the emission of CO₂ gas.¹⁾ If the emitted CO₂ gas can be efficiently decomposed to carbon and oxygen, or to CO gas and oxygen, these products such as carbon can be used as the reducing agent of iron ore. Oxygen will be also used as blowing gas into the converters. CO gas has been used as the effective fuel in the steel making plants. This means that all the products after CO₂ decomposition can be consumed in the steel plants as a precious raw material or energy resources, as shown in Fig. 1. The authors have applied the molten salt electrolysis that has been developed as the method of reduction of metallic oxides,^{2,3)} and tried to decompose CO₂ gas as one of gaseous oxides.⁴⁻⁶⁾ This method is interesting because it can decompose CO₂ gas directly to carbon and oxygen at high temperatures, which are also available as the exhaust heat in the steel plant.⁴⁻⁶⁾

The molten salt was also used as the media to dissolve CO₂ gas and to electrolyze CO₃²⁻ to carbon precipitates. For example, Yin *et al.* successfully converted CO₂ gas in molten Li₂CO₃–Na₂CO₃–K₂CO₃ to carbon deposition on the cathode.⁷⁾ Novoselova *et al.* electrochemically synthesized carbon nanotubes from CO₂ in molten salts.⁸⁾ The dissolution of CO₂ gas into the molten salt and the electrolysis of CO₃²⁻ anion were basically accepted as the reasonable mechanism.⁷⁻¹³⁾



This reaction looks strange because the CO₃²⁻ anion reacts with electron at the cathode, not at the anode. CO gas formation can not be explained in two reactions, and the additional thermochemical reaction such as Boudouard reaction among C, CO and CO₂, should occur if CO gas coexists.

In the previous studies from the authors' group,⁴⁻⁶⁾ CaCl₂–CaO and LiCl–Li₂O are used as molten salt for the decomposition of CO₂ gas and the production of carbon. Because these salts can dissolve both the reductants, Ca^{14,15)} and Li,¹⁶⁾ and the by-products, CaO¹⁷⁻¹⁹⁾ and Li₂O,²⁰⁾ many oxides could be reduced to metallic state at the cathode.^{2,3)} Their reactions were analyzed as the thermo-chemical reduction by calcium and lithium deposited electrochemi-

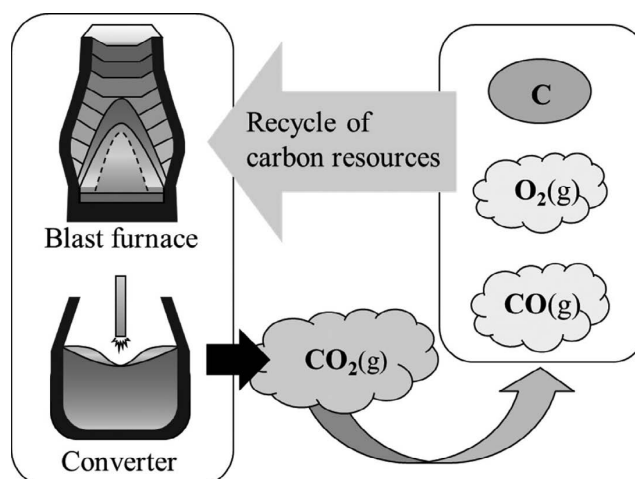
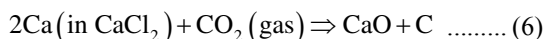
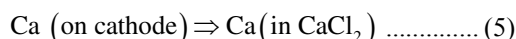
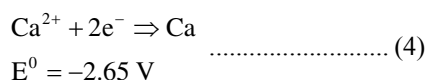
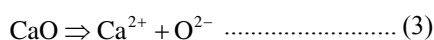


Fig. 1. Image of CO₂ gas decomposition for steel industry.

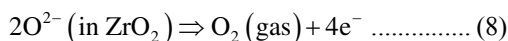
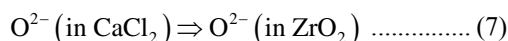
* Corresponding author: E-mail: rsuzuki@eng.hokudai.ac.jp
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cally by the electro-deposition from CaO and Li₂O, respectively.⁴⁻⁶⁾ This mechanism is a little different from the previous reports⁷⁻¹³⁾ at the point that the electrolysis of CO₃²⁻ was not considered, but that metallic reductant works as the agent for thermochemical reaction.⁴⁻⁶⁾

Their reported reaction mechanisms can be briefly summarized as follows, by taking the example in the CaCl₂–CaO bath. CaO dissolves firstly in the melt,¹⁷⁻¹⁹⁾ and it ionizes in the molten CaCl₂ above its melting point, 1115 K. When an electrical voltage is applied between two electrodes in the molten salt, metallic Ca is produced on the cathode as in Eq. (4). This Ca precipitate dissolves near the cathode due to solubility of Ca in CaCl₂ melt,^{14,15)} and reacts as the reductant with CO₂ gas as in Eq. (6). At this time, the by-product CaO is simultaneously produced as well as carbon, and CaO is again ionized in the melt in Eq. (3). Therefore, these reactions can be circulated. In short, CO₂ gas is decomposed continuously without any new addition of CaO.



Conventionally a carbon anode has been often used in the molten salt electrolysis, however, it is consumed and oxidized to CO₂ gas due to the anodic reaction with O²⁻ anion. In order to resolve this problem, the ZrO₂ solid electrolyte that is a good oxygen ion conductor^{21,22)} is applied as the anode instead of carbon electrode.^{4-6,23)}



This new electrode is the anode which can remove oxygen from molten salt. This idea enables to prevent the produced carbon from reoxidizing because oxygen is emitted out of the reaction system. Both reactions at the cathode and anode worked efficiently in the CaO–CaCl₂ bath.

However, as mentioned above, another mechanism was reported that CO₂ gas once dissolves in the molten salt as carbonate ion and that it is decomposed on the cathode.⁷⁻¹³⁾ Because the both mechanisms are possible depending on the applied potential, the authors infer that carbon production by CO₂ gas decomposition can be caused by combining these two mechanisms. The preferable mechanism may be selected by the applied electrochemical and thermodynamical conditions.

Carbon production was the major concern in previous studies. For example, Otake *et al.*⁴⁻⁶⁾ reported the carbon production from CO₂ gas with CaO–CaCl₂ and Li₂O–LiCl at 1173 K and 923 K, respectively. They showed the existence of carbon nano-fibre as well as spherical particles of amorphous carbon. The formation of carbon fibre in the molten salt was interesting. The precious carbon fibre could be formed in the liquid, not in open environment such as gaseous atmosphere. The two morphologies of carbon implied, however, that at least two mechanisms were work-

ing in CO₂ decomposition. The contamination of iron in the carbon fibre may suggest the electro-deposition of CO₃²⁻ on the steel cathode. Gupta *et al.*²⁴⁾ reported that Sn-filled multi-walled carbon nanotubes and carbon nanoparticles were synthesized by molten salt electrolysis, when SnCl₂ was used as a part of electrolyte.

Only a few examples were reported that CO gas was formed as by-product in those electrolysis, however, it has not been studied systematically about the conditions where CO gas was dominantly formed. If the mechanism of CO gas formation is revealed, it will be possible to produce selectively CO gas starting from CO₂ gas.

A strong reducing atmosphere is thermodynamically needed to remove oxygen from CO₂ gas, and a specially careful handling is required to produce carbon powder from CO₂ gas because the produced carbon is ultrafine powder frangible even in open air. On the other hand, such a strong reducibility for carbon precipitation may be not required for CO gas production. Additionally CO gas can be continuously taken out from the reaction vessel because it is gaseous. A high concentration of CO mixed with the unreacted CO₂ gas can be used as fuel in the steel industries.

The purpose of this study is to investigate the conditions of CO gas production and to produce high concentration of CO gas by CO₂ gas decomposition by using the electrolysis in molten CaCl₂–CaO.

2. Experimental

The experimental procedures are referred to briefly here because the previous papers reported the details.⁴⁻⁶⁾

Figure 2 shows the schematic appearance of the furnace and reactor used in this study. A MgO crucible (99.5% in purity, 90 mm in diameter, 200 mm in height) was set with CaCl₂–CaO mixed powder (approximately 600 g) which

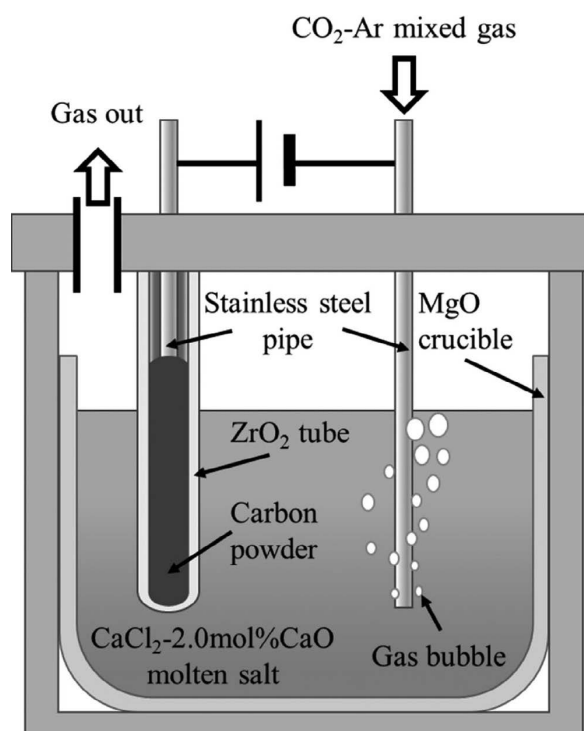


Fig. 2. Schematic illustration of the reactor used in this study.

had been precisely weighed so that the concentration of CaO is 2.0 mol%. The salt was dehydrated at 873 K in vacuum. After one night, it was continuously heated to 1173 K in an argon gas atmosphere, and CO₂-Ar mixed gas was then blown through the cathodic stainless steel pipe (6 mm in outer diameter) into the molten salt at a desired gas flow rate and a desired gas concentration. A constant voltage of 3.10 V was applied between two electrodes at 1173 K. The concentration of CO₂ gas and CO gas emitted out of the system during electrolysis was measured with an infrared spectrophotometry. Because the response of spectrophotometry was varied by the gas flow rate, it was calibrated before and after each measurement using the standard gas.

3. Results and Discussion

3.1. Current and Gas Analysis during Electrolysis

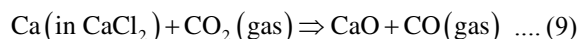
Figure 3 shows the time dependency of CO₂ and CO gas concentrations in the exhaust gas and that of current density during the electrolysis. The measured current in the circuit was divided by the anodic surface area and shown as current density in Fig. 3.

Just after the voltage was applied, the electrolysis time was started to count. It is common that the large current density was measured at the initial stage of the electrolysis, but that it decreased as the electrolysis time proceeds. The current approached to a stable at the later stage. The decrease of CO₂ concentration in the exhaust gas was confirmed at the initial stage of the electrolysis. However CO₂ gas concentration gradually increased at the later stage. On the other hand, CO gas concentration increased at the initial stage, and it decreased at the later. Due to the dead volume in the reacting vessel, the analyzed concentration is delayed from the real reaction time at the molten salt, but the slow increase and decrease of CO₂ and CO gas, respectively, at the later stage show the change of reaction mechanism during the electrolysis.

The amounts of the decomposed CO₂ gas and the produced CO gas were calculated from the area hatched in Fig. 3. Resultantly from Fig. 3(c), CO₂ gas was decomposed at 3.32×10^{-8} m³ per second, and about half of them were served for the conversion to CO gas. And current efficiency was calculated. It was defined as the ratio of the electric charge consumed for the CO gas production to the all of electric charge consumed for this electrolysis. In this condition, current efficiency was 36.9%. It was low because electric charge was consumed to produce carbon as well as CO gas. Therefore, suppressing the carbon production increased the current efficiency.

3.2. Feeding Rate of CO₂ Gas during Electrolysis

CO₂ gas can be decomposed partially by calciothermic reduction and partially by the decomposition of carbonate ions, as shown in Eqs. (6) and (2), respectively. If the larger amount of CO₂ gas is supplied, namely if CO₂ gas is blown at the higher rate, CO₂ gas will be converted to CO gas preferentially.



Because the limited amount of Ca is produced per time by electrolysis, CO gas is more dominant if the larger amount

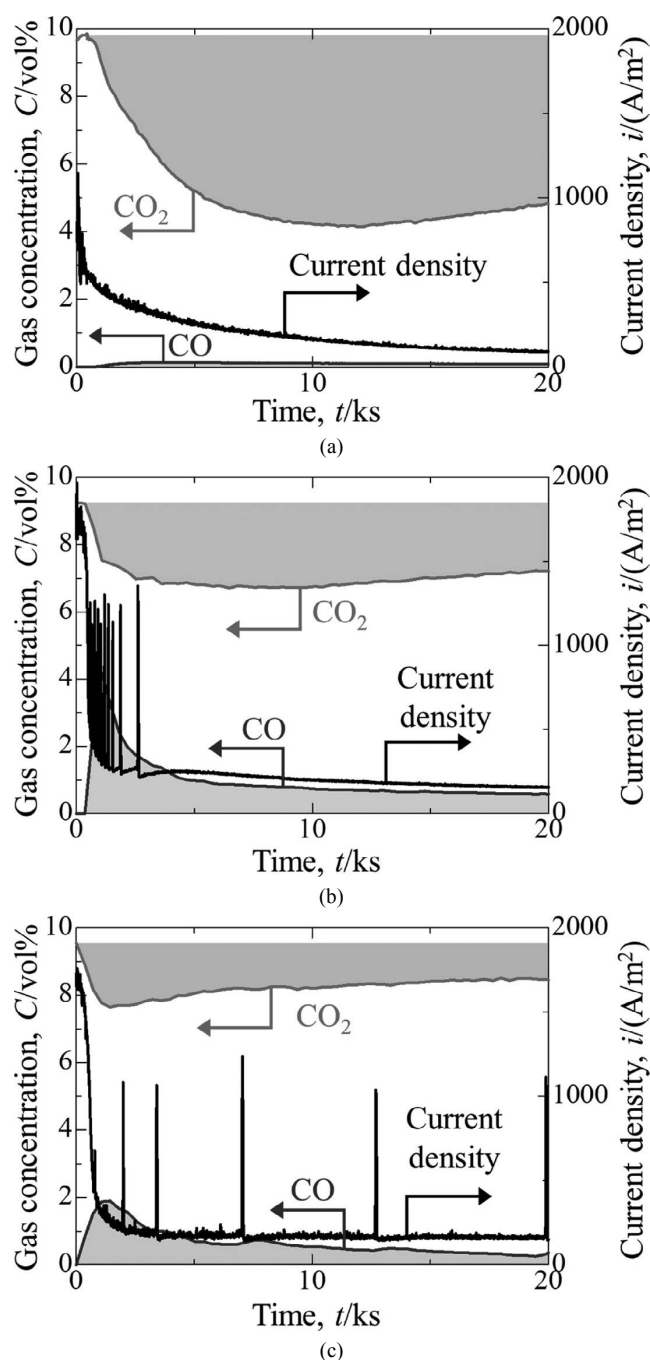
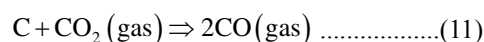
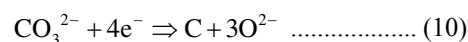


Fig. 3. Time dependences of exhaust gas compositions and current density, where the gas flow rate from the cathodic nozzle was 0.517×10^{-6} , 1.67×10^{-6} and 2.58×10^{-6} m³/s at (a), (b) and (c), respectively.

of CO₂ gas is supplied in a limited period. In the case of electrochemical decomposition of carbonate ion, it is not easy to consider CO gas formation directly. The possible mechanism of CO gas generation may come from Boudouard reaction between carbon deposit and the unreacted CO₂ gas.



Therefore, in order to examine the reaction mechanism, the supplied CO₂ gas concentration and the gas flow rate were varied.

Figure 3 shows the results that the gas mixture of 9.67

vol%CO₂-Ar was used. The gas flow rate from the cathodic nozzle was 0.517×10^{-6} , 1.67×10^{-6} and 2.58×10^{-6} m³/s at Figs. 3(a), 3(b) and 3(c), respectively. The rates at (b) and (c) were greater than that at (a) by about 3 times and 5 times, respectively. Little CO gas was produced when the gas flow rate was small, but by increasing the flow rate, significantly large amount of CO gas was produced.

The amount of decomposed CO₂ gas and the amount of produced CO gas, v , were also calculated from the concentration $C(t)$ as a function of time, t , and a constant gas flow rate, Q .

$$v = Q \frac{\int_0^t C(t) dt}{t} \quad (12)$$

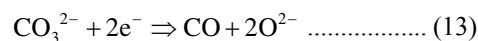
Figure 4 shows the relationship of the amounts of decomposed CO₂ gas and produced CO gas as a function of the gas flow rate. The amount of decomposed CO₂ gas reached the maximum when the gas flow rate was 1.67×10^{-6} m³/s. The amount of produced CO gas reached the maximum when the gas flow rate was 2.58×10^{-6} m³/s. This indicates that CO gas favorably generates when the gas flow rate becomes larger. The amount of produced CO gas drastically increased in the range of gas flow rate of 0.5×10^{-6} and 1.7×10^{-6} m³/s.

Several reasons will be discussed: The first reason is as follows. As the gas flow rate is larger, the stirring of the molten salt becomes more intense due to gas bubbles, and the electrochemically produced calcium at the cathode disperses out easily. The thermochemical activity then becomes lower, and CO gas is preferentially produced.

The second reason is as below; Because the amount of CO₂ gas blown per unit time increases, the CO₂ gas can not sufficiently contact with calcium, and the perfect reduction from CO₂ gas to carbon does not complete, but the conversion to CO gas became favorable.

Thirdly, the contribution of carbonate ions can be considered apart from calcium. As the gas flow rate increases, the amount of carbonate ions also increases. This is because the dissolution of CO₂ gas to the molten salt becomes more significant, as the larger amount of unreacted CO₂ gas remains. In cathodic reactions with carbonate ion, 4 electrons are used for carbon production, but only 2 electrons are used for

CO gas formation.



Therefore, CO gas production occurs more easily, when the larger amount of carbonate ions are decomposed with the constant electric charge.

3.3. Effects of Gas Concentration

Figures 5(a) and **5(b)** show the results when the gas mixture of 6 vol%CO₂ and 16 vol%CO₂ are used, respectively. CO₂ gas was decomposed in both cases, and the CO gas evolution was detected in Fig. 5(b), while the formation of CO gas was not seen in Fig. 5(a).

Figure 6 shows the ratio of the amount of produced CO to that of decomposed CO₂. When the initial CO₂ gas concentration was higher, the ratio increased. This means that the rate of CO gas production increased with increasing in the CO₂ gas concentration. Larger portion than 90% of the supplied CO₂ gas was converted to CO gas in the high concentration range between 14 and 20%. This shows that CO gas was more favorably produced as the concentration of CO₂ gas was higher.

As CO₂ gas concentration is higher, the molar fraction of carbonate ion may increase in molten salt, and it affects the production rate of CO gas. This correlation may be explained easily by the carbonate route in reaction mechanism as shown in Eqs. (1) and (2). However, as the high carbonate ion concentration is an evidence that the supplied CO₂ is not converted to carbon but to CO gas and carbonate,

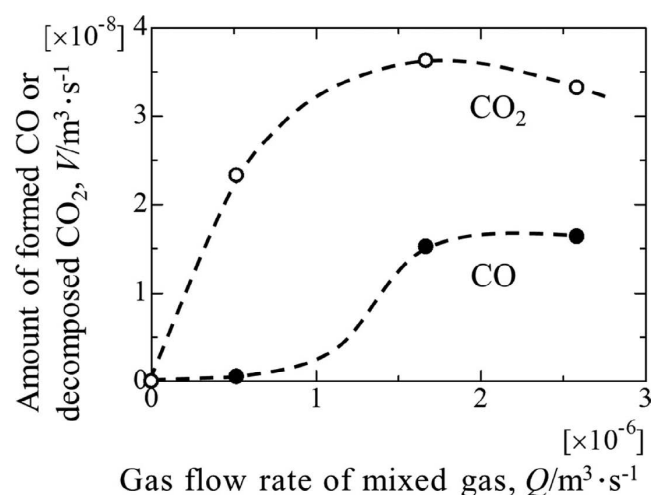


Fig. 4. Amounts of decomposed CO₂ gas and produced CO gas as a function of gas flow rate.

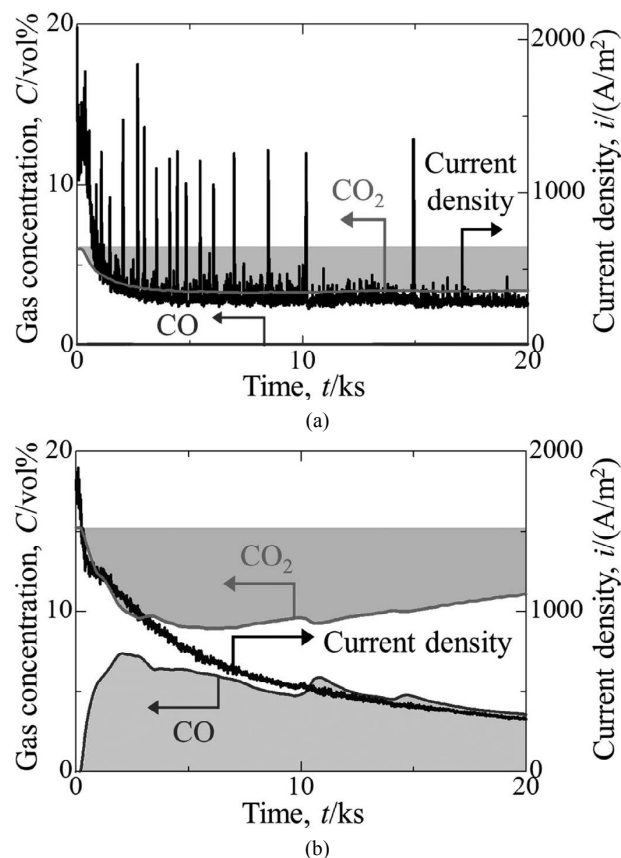


Fig. 5. Time dependences of exhaust gas compositions and current density. (a) initial gas mixture of 6 vol%CO₂, and (b) 16 vol%CO₂ are used.

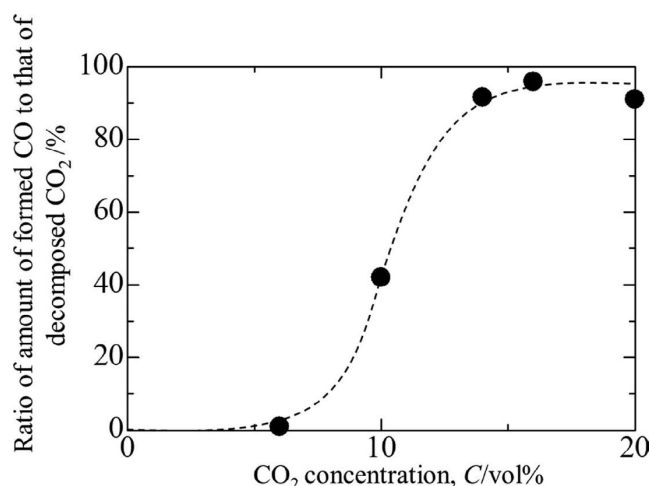


Fig. 6. Ratio of amount of formed CO gas to that of decomposed CO₂ gas as function of initial gas concentration of CO₂.

the effective conversion to CO gas may be explained by calciothermic reaction, too. This means that too much CO₂ gas bubbles existed per the electrodeposited Ca, and a large portion of CO₂ gas dissolved as carbonate ions. However, the reacted portion was converted to CO gas due to dean Ca concentration.

4. Conclusion

As a result of the constant-voltage electrolysis using molten salts consisting of CaCl₂–CaO and solid state electrolyte, zirconia, as the anode, the production of CO gas was enhanced by increasing the gas flow rate. The higher conversion to CO gas from CO₂ gas was obtained at the higher concentration of CO₂ in the initial gas mixture. 3.32×10^{-8} m³/s of CO gas was produced in our experimental conditions.

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