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Conversion of CO₂ to CO gas using molten CaCl₂ and ZrO₂ anode

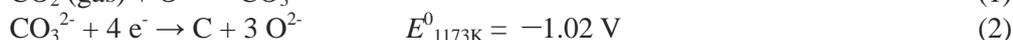
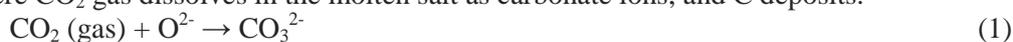
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Abstract: Preferential decomposition of CO₂ gas to CO gas was examined by using a combination of CaCl₂-CaO melt as a reaction media and ZrO₂-8mol% Y₂O₃ solid-state electrolyte as anode. The conversion ratio of CO₂ to CO became larger at the higher temperature, and approached the maximum (88.2%) at 1273 K. The highest CO concentration was generated at cell voltage of 2.55 V, which is close to theoretical decomposition voltage of CaO. Therefore, in addition to calciothermic reaction between precipitated Ca and CO₂ gas bubbles, CO₂ decomposes preferentially via the decomposition reaction of carbonate ions. Namely CO₂ gas dissolves to form CO₃²⁻ under coexistence of CaO in the melt, CO₃²⁻ precipitates carbon or CO gas bubbles on the cathode, and a part of carbon reacts with the blown CO₂ gas to form CO. CO gas is used as an effective fuel with easy handling in steel plants.

1. INTRODUCTION

This study attempts CO₂ gas decomposition into CO and O₂ gases, without forming solid C. If CO₂ gas can be efficiently decomposed to CO gas, it can be used as an effective fuel in steel plants and as important raw material of chemical engineering. O₂ is used as the blowing gas into the steel converters. Thus, two products arising from CO₂ decomposition can become raw material and energy resource, respectively, in steel plants. Because the industrial utilization of gaseous CO is favorable due to easy transportation and handy use as fuel, the determination of the optimal conditions to form CO gas becomes practically important. Carbon also precipitates from CO₂ and it exhibits a wide variety in morphology. For example, carbon nanofibers and nano-powder were electrochemically produced from CO₂ using molten salts [1-3]. A mechanism for CO₂ decomposition in the molten carbonates has been reported [4], where CO₂ gas dissolves in the molten salt as carbonate ions, and C deposits.



The authors have proposed calciothermic reduction coupled with molten salt electrolysis, which is called as the OS process, and developed as a new method to reduce metallic oxides such as titanium oxide in CaCl₂ melt [5]. Either CaCl₂-CaO or LiCl-Li₂O can decompose CO₂ gas to C [3,6-10], because Ca and Li hold a strong reducing potential after electrodeposition of dissolved CaO and Li₂O, respectively. By considering CaCl₂-CaO as an example, OS mechanisms are briefly summarized as follows. Firstly, CaO dissolves and ionizes in molten CaCl₂ as described by CaO → Ca²⁺ + O²⁻ [5-8]. When a suitable electrical voltage is applied between two electrodes, metallic Ca is deposited on the cathode, as indicated by Ca²⁺ + 2 e⁻ → Ca. This Ca precipitate dissolves near the cathode due to its solubility in liquid CaCl₂, and reacts as the reductant with CO₂.



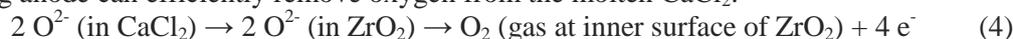
CaO is simultaneously produced with C, but CaO is again ionized in the melt. Therefore, these reactions can be continuously circulated, and CO₂ gas disappears without any addition of CaO or Ca.

Therefore, the analysis in [3,6-10] were slightly different from the other reports of the CO₃²⁻ decomposition mechanism [1,2]. Because both mechanisms are feasible depending on the applied potential, we think that CO production by CO₂ gas decomposition may occur via combination of these two mechanisms. The preferred mechanism would be selected by the applied electrochemical and thermodynamic conditions. Only a few examples of CO gas production were reported. Kaplan *et al.* converted CO₂ to CO by electrolysis of molten Li₂CO₃ [11]. Our previous study [3,6-10] reported the CO gas formation accompanied by the decomposition of CO₂ gas. The gas flow rate and the concentration of mixed gas affected the production rate of CO gas [10]; larger amounts of CO₂ blown

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into the bath lead to higher concentrations of CO gas production.

Carbon anode has been often applied in molten salt electrolysis because of its electrochemical and thermal stabilities. However, C is oxidized to CO₂ due to strong anodic reaction with O²⁻ anions. The consumption of carbon anode is non sense from the view point of CO₂ removal. Therefore, a good oxygen-ion conductive ZrO₂ solid electrolyte has been applied as the anode [6-10]. The use of this oxygen absorbing anode can efficiently remove oxygen from the molten CaCl₂.



C is not good electronic conductor, and its precipitation on cathode (Eq.2) may interrupt continuous electrolysis. It is difficult to continuously remove fine C powder from the reaction vessel, because C deposited on the cathode and adhered to it strongly. CO gas can be continuously removed from the reactor as exhaust gas. A high concentration of CO gas can be used as fuel in the steel industry even if it is mixed with unconverted CO₂ gas. Obviously the combustion efficiency as the fuel increases as the CO gas concentration increases. In actual operation of the current steel plants, the gas mixing ratio ($C_{\text{CO}}/C_{\text{CO}_2}$) is in the range of 0.8–1.2 as fuel. The purpose of this paper is to produce a high concentration of CO gas from CO₂. Particularly, the effects of the electrolysis temperature and voltage on the production of CO gas are examined.

2. EXPERIMENTAL PROCEDURES

The reactor used in this study is illustrated in Fig.1. A ZrO₂-8 mol% Y₂O₃ tube with one end closed (OD: 16.5 mm, 2 mm thick, 500 mm long) was used as the anode [6-10,12]. Platinum thin wires (0.07 and 0.5 mm in diameter) were fixed with the inner surface of ZrO₂ tube by Pt paste, and connected to a stainless steel pipe (electric lead). Anhydrous CaCl₂ (600g) was mixed with 2.0 mol% CaO, and filled in a MgO crucible. It was dehydrated at 873 K in vacuum, and melted at the desired temperature in Ar gas. Subsequently, gas mixture (20 vol%CO₂, 80 vol%Ar) was blown through the cathodic stainless steel pipe (OD: 6 mm) into the melt. The exhaust gas was carried from the gas outlet to a gas analyser. A voltage was applied between the two electrodes after the exhaust gas concentration became equal to that of the initial gas, and the current was recorded.

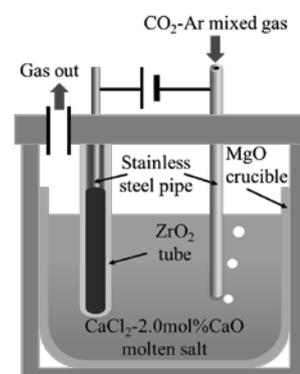


Fig.1 Experimental setup.

3. RESULTS AND DISCUSSION

3.1. Time dependence of CO formation

Fig.2 shows the CO₂ and CO gas concentrations in the exhaust gas during electrolysis. The measured current in the circuit was divided by the anodic surface area to yield the current density. A large anodic current density and increment of CO concentration were observed during the electrolysis. The CO₂ and CO gas concentrations reached steady-state values in the later stage of the electrolysis. Due to the dead volume in the reaction vessel and slow feeding rate of CO₂ ($1.67 \times 10^{-6} \text{ m}^3/\text{s}$), there is a discrepancy between the analyzed concentration and the actual concentration in the molten salt.

The amounts of the CO₂ decomposition and CO production are evaluated from the hatched area in Fig. 2. The conversion ratio of decomposed CO₂ converted to CO gas was evaluated as 75%, and the current efficiency (the ratio of the electric charge consumed for CO gas production to the total supplied electric charge) was 42.9%. Because the measurement of exhaust gas was interrupted due to the removal of electrodes before cooling, the residual amount of CO gas in the reaction vessel was not considered. Therefore, both the conversion ratio and current efficiency were slightly underestimated. The low conversion ratio and current efficiency indicate that the supplied electric charge was partially consumed to produce carbon as well as CO gas. In fact, a large amount of black and fine carbon powder precipitated on the surface of the solidified salt and on the cathode pipe after electrolysis.

3.2. Temperature dependency

CO gas can be steadily produced at high temperatures by the Boudouard reaction.

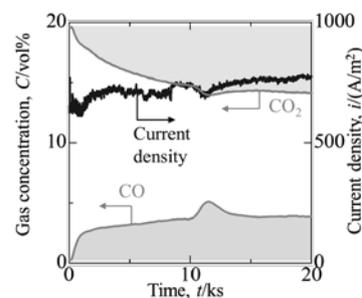
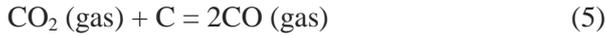
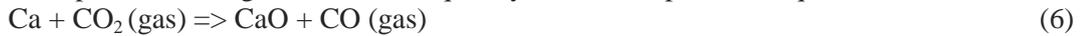


Fig.2 Time dependence of exhaust gas compositions and current density [9].



The amounts of both the decomposed CO_2 gas and produced CO gas increase at higher temperatures. At 1273 K (the highest temperature in this work), the CO_2 decomposition rate and CO production rate were the maximum, 6.87×10^{-5} m/s and 6.06×10^{-5} m/s, respectively, by normalized by the anodic surface area. These values are the largest reported in our studies [3,6-10]. With increasing reaction temperature, the conversion ratio correspondingly increased and approached the maximum value of 88.2% at 1273 K, as shown in Fig. 3. It is to be noted that the electrical conductivity of Y_2O_3 -stabilized ZrO_2 increases with temperature increase. This suggests that both decomposed CO_2 and produced CO depend on the mobility of oxygen anions in ZrO_2 anode.

The mechanism for CO gas formation may be described by Eq.6, and the produced CO gas can be subsequently reduced stepwise in Eq. 7.



Because the Gibbs free-energy changes of these reactions are negative, the reactions can proceed forward strongly. In the operating temperature range (1123-1273 K), the Gibbs free-energy change corresponding to Eq.6 is lower than that to Eq.7, which indicates that the driving force for Eq. 6 is greater than that for Eq. 7 and that reaction 6 preferentially occurs in this experiment. At lower temperatures, the Gibbs free-energy change of reaction 5 becomes positive, and it is reasonable that the conversion ratio at lower temperatures is correspondingly lower, as shown in Fig. 3.

3.3. Feeding rate of CO_2 gas during electrolysis

As shown in Fig.4, CO gas favorably generates when the gas flow rate becomes larger. Several reasons are considered: firstly, the stirring of the molten salt becomes more intense due to gas bubbling, and the electrochemically produced Ca at the cathode disperses out easily. The thermochemical activity then becomes lower, and CO gas is preferentially produced.

The second reason is mass balance; because the amount of CO_2 gas blown per unit time increases, the CO_2 gas can not sufficiently contact with Ca, and the perfect reduction from CO_2 gas to C does not complete, but the conversion to CO gas becomes favorable.

Thirdly, when the larger amount of unreacted CO_2 gas remains, the CO_2 gas dissolution to the melt becomes more significant, and the concentration of CO_3^{2-} increases. CO gas production (2 electrons-reaction) occurs more easily at cathodic reactions.



3.4. Effects of applied voltage

In order to identify the reactions contributing to produce CO gas, electrolysis in molten salt was conducted at various voltages. The theoretical decomposition voltage of CaCl_2 , $E_{\text{CaCl}_2}^0$, is 3.21 V, and that of CaO , E_{CaO}^0 , is 2.65 V at 1173 K [13]. Therefore, pure Ca is not produced when the cell voltage is below 2.65 V, assuming that the voltage drops at the electrodes can be neglected. In the voltage range lower than 2.65 V, CO_2 gas decomposes preferentially by the decomposition reaction of CO_3^{2-} . In this study, the effect of the applied voltage on the conversion ratio was examined to identify the working mechanisms in molten salt, because the formation of CO gas proceeded simultaneously with the reactions of CO_3^{2-} .

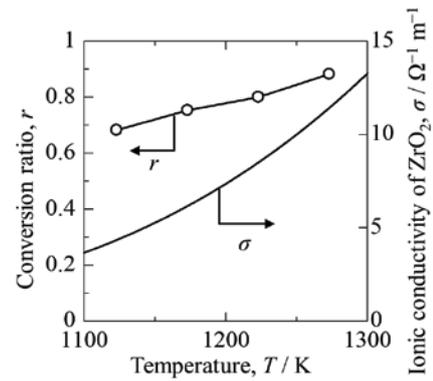


Fig.3 Conversion ratio to CO gas and electric conductivity of $\text{ZrO}_2\text{-Y}_2\text{O}_3$ as a function of temperature [10].

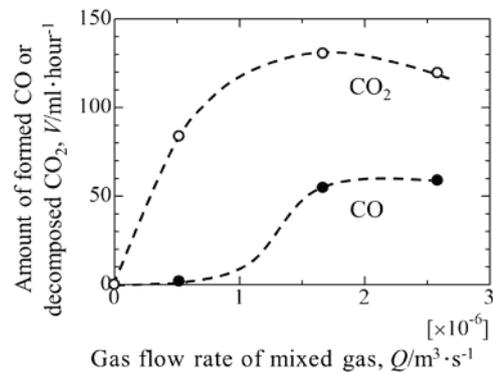


Fig.4 Amounts of decomposed CO_2 gas and produced CO gas at 1173 K [9].

Fig.5 shows the relationship between the applied voltage and the conversion ratio. CO₂ gas did not decompose at voltages lower than 1.0 V, for example, no decomposition was found at 0.90 V. The theoretical decomposition voltage for CaCO₃, $E^0_{\text{CaCO}_3}$, is evaluated as 1.02 V [13], which is the voltage when assuming that CO₃²⁻ is decomposed by Eq.2. In the voltage range from 1.25 V to 2.00 V, CO₃²⁻ can be decomposed, and in our study, the conversion ratio over this range was nearly constant. The conversion ratio was the maximum value at 2.55 V. It is to be noted that the conversion ratio at 2.55 V was larger than that at 3.10 V, which voltage was greater than E^0_{CaO} (2.65 V at 1173 K [13]). At the voltage of 3.10 V, Ca metal can be generated from CaO. Because pure Ca has a high reducing ability, it can reduce CO₂ to C, the most stable compound in the C–O binary system. It is reasonable that the conversion ratio of CO gas at 3.10 V was lower than that at 2.55 V. This is consistent with that a significant amount of C was produced on the cathode at 3.10 V, while very little carbon powder was collected after electrolysis for applied voltages lower than 2.55 V. At 3.10 V, the CO gas production was also significant. Because Ca is hardly produced at 2.55 V and only the decomposition reaction of CO₃²⁻ occurs, this decomposition contributed to produce a relatively larger amount of CO gas than due to thermochemical reduction by Ca. This suggests that the concentration of CO gas can be increased by controlling CO₃²⁻ concentration, for example, by adding CaCO₃ in molten salt.

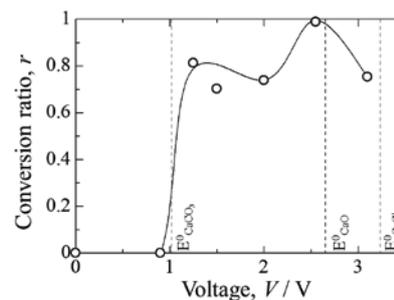


Fig.5 Conversion ratio as a function of cell voltage at 1173 K [10].

4. CONCLUSION

CO gas was converted from CO₂ gas during constant-voltage electrolysis with the use of a combination of molten CaCl₂-CaO and ZrO₂ solid-state electrolyte as the anode. The conversion to CO gas from CO₂ gas was more significant at higher temperatures and the higher flow rate. The decomposition of carbonate ions was more adequate in comparison with CO gas production via thermochemical reduction by Ca. This is because pure Ca decomposes CO₂ to the most stable substance, C. An extremely strong reducing environment precipitates C powder and suppresses the formation of CO gas. In future studies, the faster ionic conduction in the ZrO₂ anode is planned to apply this CO gas formation in industry.

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