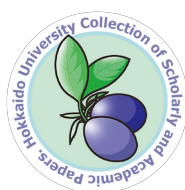




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CO₂ decomposition using electrochemical process in molten salts

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Abstract. The electrochemical decomposition of CO₂ gas to carbon and oxygen gas in LiCl-Li₂O and CaCl₂-CaO molten salts was studied. This process consists of electrochemical reduction of Li₂O and CaO, as well as the thermal reduction of CO₂ gas by the respective metallic Li and Ca. Two kinds of ZrO₂ solid electrolytes were tested as an oxygen ion conductor, and the electrolytes removed oxygen ions from the molten salts to the outside of the reactor. After electrolysis in both salts, the aggregations of nanometer-scale amorphous carbon and rod-like graphite crystals were observed by transmission electron microscopy. When 9.7 %CO₂-Ar mixed gas was blown into LiCl-Li₂O and CaCl₂-CaO molten salts, the current efficiency was evaluated to be 89.7 % and 78.5 %, respectively, by the exhaust gas analysis and the supplied charge. When a solid electrolyte with higher ionic conductivity was used, the current and carbon production became larger. It was found that the rate determining step is the diffusion of oxygen ions into the ZrO₂ solid electrolyte.

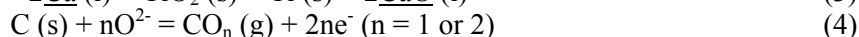
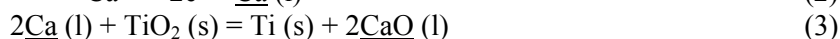
1. Introduction

Global environmental issues are currently regarded as one of the most urgent problems in the world, and the industrial sector accounts for a large fraction of CO₂ gas emissions [1]. The steel making industry emits a large amount of CO₂ gas, although it has been making great efforts to decrease the gas emission. Because the iron ore, Fe₂O₃, is reduced by coke, emission of a large amount of CO₂ gas from blast furnaces and converters is essential in the iron and steel making processes. The development of an innovative method is also required to decrease CO₂ gas emissions. However, there is only a few studies on the decomposition of CO₂ gas emitted from these furnaces. If all emitted CO₂ gas is efficiently decomposed, the amount of CO₂ gas emissions will decrease drastically.

As a new method to reduce metallic oxides such as titanium, vanadium, tantalum and nickel to their metallic state, a OS process consisting of electro-reduction of CaO and calciothermic reduction in a CaCl₂ bath has been studied [2-7]. In the present paper, a new method is proposed to decompose CO₂ gas to carbon and oxygen gas by applying the OS process to the reduction of gaseous oxides.

The reduction mechanism of the OS process for the case of titanium dioxide reduction was reported in previous papers [8-10]. At 1173 K, CaCl₂ can dissolve 20 mol% CaO and 2-4 mol% metallic Ca at equilibrium. CaO is ionized in the molten salt as presented in Equation (1). When an electrical voltage is applied between two electrodes, metallic Ca is produced near the cathode as shown in Equation (2).

The metallic Ca rapidly dissolves in CaCl_2 and the dissolved Ca then thermodynamically reacts with titanium dioxide near the cathode to produce metallic titanium and CaO as shown in Equation (3). Because CaO (by-product) is ionized again, the chemical reactions (Equations 1-3) are cycled in the furnace. Meanwhile, oxygen anions in the molten salt are removed as CO or CO_2 gas when a carbon anode is used as shown in Equation (4).



When we apply this OS process to CO_2 decomposition, the solid TiO_2 can not be simply converted to CO_2 gas. The decomposition of CO_2 gas occurs at the surface of CO_2 gas bubbles, and it is important that the reductant Ca exists near the surface of the CO_2 gas bubbles. In the case of electrolysis, the reductant does not precipitate on the bubble, but on the cathodic surface. Therefore, it is essential that the reductant dissolves in the molten salt and reacts with the gas bubbles to decompose CO_2 gas. If this process can be realized, the exhaust CO_2 gas can be converted to useful substances. For example, carbon and oxygen gas produced from CO_2 gas can be used as raw materials in the iron and steel making industry.

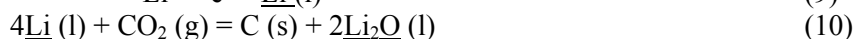
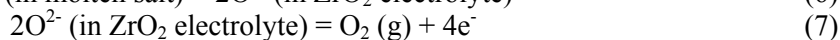
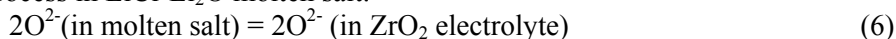
In this study, two new proposals were introduced to the original OS process to decompose CO_2 gas to carbon and oxygen gas. The first proposal involves using $\text{LiCl-Li}_2\text{O}$ molten salt as the solvent to prevent the occurrence of the Boudouard reaction, in which CO_2 gas preferentially reacts with carbon to form CO gas at high temperatures, as shown in Equation (5).



$$(\Delta G^0_{923\text{K}} = 8.802 \text{ kJmol}^{-1} [11], \Delta G^0_{1173\text{K}} = -34.917 \text{ kJmol}^{-1} [11])$$

This reaction is undesirable since carbon, the desired product is consumed. When $\text{LiCl-Li}_2\text{O}$ molten salt is used as the solvent, the operating electrolysis temperature can be decreased by about 250 K compared to the operating electrolysis temperature range 923-1173 K for $\text{CaCl}_2\text{-CaO}$ molten salt. The latter salt has a wider solubility range of Ca and CaO, while LiCl can dissolve up to 4.2 mol% Li_2O at 923 K [12], and thus metallic Li has enough ability to decompose CO_2 gas to carbon and oxygen gas thermodynamically.

The second proposal is to use a ZrO_2 solid electrolyte. In the conventional OS process, carbon anode is used to remove oxygen ions from the molten salt to the outside of reactor. In this case, however, oxygen anions are removed as CO or CO_2 gas after the reaction with carbon. This is undesirable since we want the decomposition of CO_2 gas to carbon, not to CO and CO_2 gas. Therefore, the ZrO_2 solid electrolyte which is an oxygen ion conductor is applied as the anode. The oxygen anions in the molten salt diffuse through the ZrO_2 solid state electrolyte as shown in Equation (6) and the oxygen anions are removed as oxygen gas at the opposite side of the ZrO_2 anode as shown in Equation (7). When considering the diffusion rate of oxygen anions in a ZrO_2 solid electrolyte, a higher electrolysis temperature is desired. The decomposition mechanism of CO_2 gas is shown in Equations (6)–(10) when we apply the OS process in $\text{LiCl-Li}_2\text{O}$ molten salt.



Another mechanism for carbon production in molten salt was reported [13-14], where the CO_2 gas dissolves as carbonate ions (Equation 11) and the electrochemical decomposition of carbonate ions occurs on the cathode as shown in Equation (12).



In the present study, a large amount of oxygen ions exists in the molten salt due to the dissolution of Li_2O or CaO, and CO_2 gas is blown into the molten salt. Therefore, carbonate ions can be produced in

the molten salt prior to electrolysis (Equation 11). The carbonate ions can receive electrons on the cathode, and carbon and oxygen ions are produced (Equation 12).

The purpose of this study is to decompose CO_2 gas to carbon and oxygen gas electrochemically in the molten salts using a ZrO_2 solid electrolyte. Another purpose is to investigate the rate determining step of this proposal in order to determine the key factor for an effective and faster CO_2 decomposition.

2. Experimental

CaCl_2 (>95 %, Wako Chemical Co.) was mixed with CaO (99.9 %, Kanto Chemical). The mixture was then calcined in air. The concentration of CaO was found to be 0.5 mol%. A magnesia crucible was filled with this mixture as the electrolyte (Figure 1). In a similar manner, LiCl (>99.0 %, Wako Chemical Co.) was mixed with 4.2 mol% Li_2O (>95 %, Wako Chemical Co.). A stainless steel pipe (6 mm in internal diameter) was used as the inlet of CO_2 -Ar mixed gas and as the cathode. Two kinds of tubes made of the ZrO_2 solid electrolyte were used to remove oxygen ions in molten salts. These two tubes were produced by Nikkato Co. under the commercial name of ZR-8Y and YSZ-8. The electrical conductivity of YSZ-8 is 2.39 times larger than that of ZR-8Y at 923 K ($\sigma_{\text{YSZ-8}} = 0.79 [\Omega^{-1}\text{m}^{-1}]$, $\sigma_{\text{ZR-8Y}} = 0.33 [\Omega^{-1}\text{m}^{-1}]$) as shown in Figure 2 [15]. These electrodes were attached to the cover of the stainless steel vessel using a silicone stopper. It was preferable that the inside of the ZrO_2 tube was applied with a platinum paste to provide electrical conductivity, but this was difficult to accomplish since the ZrO_2 tube was 500 mm long and its internal diameter was only 13 mm. As a result, carbon powder was used instead of a platinum paste. Since the outlet of the ZrO_2 tube was inside the reactor, oxygen gas which was produced at the internal surface of the ZrO_2 tube reacted with carbon produced in the molten salt, that is, the recombination of carbon with oxygen gas occurred. Therefore, it was important to make sure that the oxygen gas emitted did not make chemical contact with the molten salts.

After the salt was dehydrated, the CaCl_2 - CaO and LiCl - Li_2O mixtures were slowly heated to 1173 K and 923 K, respectively, in an Ar atmosphere. LiCl - Li_2O molten salt has a higher vapor pressure in comparison with that of CaCl_2 - CaO molten salt. Therefore, when LiCl - Li_2O molten salt was used, the electrolysis temperature was set at 923 K to prevent vaporization of the salt as much as possible. Next, 9.7 % CO_2 -Ar mixed gas (CO_2 gas and Ar gas were blown at $5.0 \times 10^{-8} \text{ m}^3/\text{s}$ and $4.7 \times 10^{-7} \text{ m}^3/\text{s}$, respectively) or 90 % CO_2 -Ar mixed gas (CO_2 gas and Ar gas were blown at $6.0 \times 10^{-8} \text{ m}^3/\text{s}$ and $6.7 \times 10^{-8} \text{ m}^3/\text{s}$, respectively) was blown through the cathodic pipe into the molten salts. The mixed gas

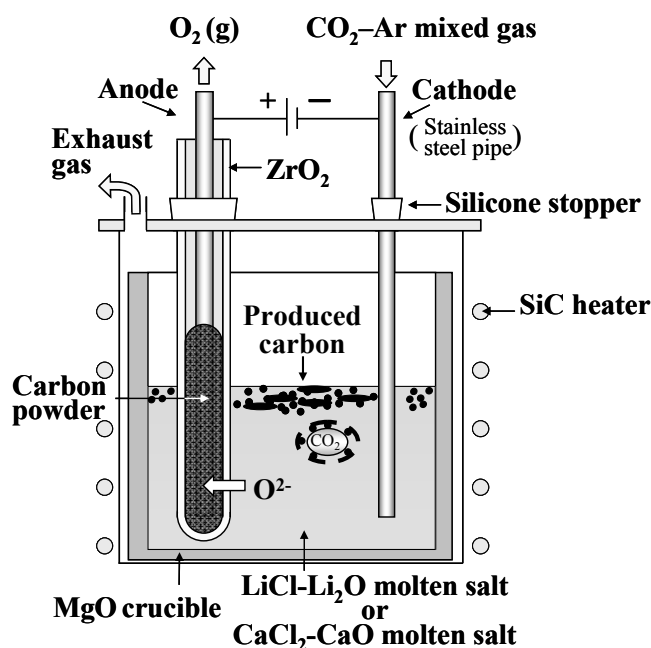


Figure 1. Experimental setup.

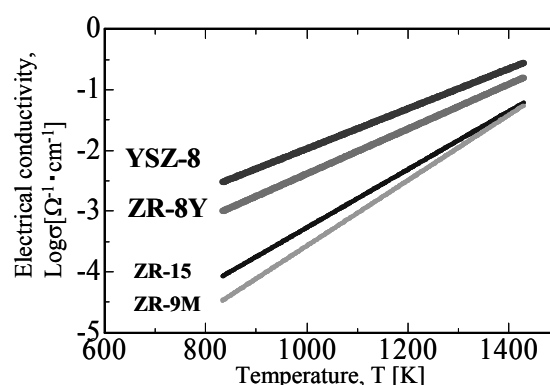


Figure 2. Temperature dependency of the electrical conductivity of each ZrO_2 electrolyte [15].

passed through the molten salts and the exhausted gas was introduced to the gas analyzers from the outlet. In the case when $\text{CaCl}_2\text{-CaO}$ molten salt was used, electrolysis was initiated at 3.1 V after the salt was saturated with CO_2 gas, while in the case when $\text{LiCl-Li}_2\text{O}$ molten salt was used, electrolysis was initiated at 3.2 V. The measured electrolysis voltage was larger than the theoretical decomposition voltage of the corresponding oxide, CaO or Li_2O , but smaller than that of the corresponding chloride, CaCl_2 or LiCl . During electrolysis of 9.7 % CO_2 -Ar mixed gas, the concentration of CO_2 and CO gases in exhaust gas was measured at the outlet to investigate the decomposition behaviour of CO_2 gas using an infrared gas analyzer (YOKOGAWA Co.) which can measure gas concentrations up to 10 %. The gas chromatograph (GC-2014, SHIMADZU Co.) was used when 90 % CO_2 -Ar mixed gas was blown. When the infrared gas analyzer was used, the concentrations of CO_2 and CO gases were able to be measured continuously, but the measurement by the gas chromatography was conducted about every 3.6×10^2 s interval. After electrolysis with a constant cell voltage, the furnace was cooled down to room temperature in an Ar atmosphere after the cathodic pipe was raised to the upper part of the vessel. The black reduction products existed at the surface part of the solidified salt and around the cathode, and they were collected and washed with solvents in the following order, distilled water, acetic acid, distilled water, ethanol and acetone to completely remove the solidified salt residue from the reduction products. The products were observed using a transmission electron microscope (TEM, JEOL JEM-2000FX, acceleration voltage of 200 kV) and identified by X-ray diffraction (XRD, Philips Co.) using $\text{Cu-K}\alpha$ radiation.

3. Results and discussion

3.1. Decomposition of 9.7 % CO_2 -Ar mixed gas.

Table 1 lists the experimental conditions.

Figure 3(a) shows the time dependency of CO_2 and CO gas concentrations in the exhaust gas and the time dependency of current density during the electrolysis of 9.7 % CO_2 -Ar mixed gas when $\text{LiCl-Li}_2\text{O}$ molten salt and ZR-8Y were used, while Figure 3(b) shows those when $\text{CaCl}_2\text{-CaO}$ molten salt and ZR-8Y were used. The current between the two electrodes were recorded every 10 s. The current density was determined by measuring the surface area of the electrode from the height of the solidified molten salt after cooling. The depth of the molten salt relates to the area where oxygen ions are transferred from the molten salt to the internal surface of the ZrO_2 tube. The effective surface area of the anode in the electrolysis of $\text{LiCl-Li}_2\text{O}$ and $\text{CaCl}_2\text{-CaO}$ molten salt was calculated as $2.45 \times 10^{-3} \text{ m}^2$ and $1.63 \times 10^{-3} \text{ m}^2$, respectively. The anodic current density was deduced from these surface areas.

To determine the optimal solvent, current density was measured when a constant voltage was applied to between the two electrodes. After the electrolysis was initiated, the concentration of CO_2 gas decreased, while the concentration of CO gas increased slightly, therefore, suggesting that the decomposition of CO_2 gas to carbon and oxygen gas occurred in the molten salts and the ZrO_2 solid electrolyte worked as an oxygen ionic conductor (as shown in Equations (6) and (7)).

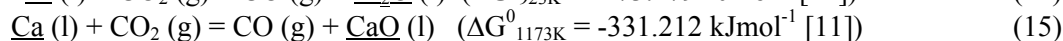
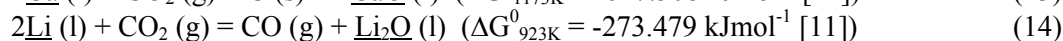
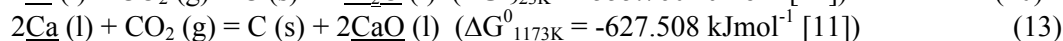
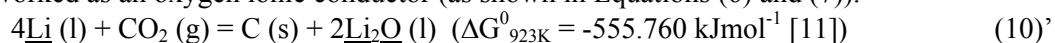


Table 1. Experimental conditions, current efficiency, yield and average current during electrolysis.

Run	Molten salt	Temperature [K]	Gas concentration	ZrO_2 electrolyte	Current efficiency[%]	Yield[%]	Averaged current[mA]
1	$\text{LiCl-Li}_2\text{O}$	923	9.7% CO_2 -Ar	ZR-8Y	89.7	29	75
2	$\text{CaCl}_2\text{-CaO}$	1173	9.7% CO_2 -Ar	ZR-8Y	78.5	36	506
3	$\text{LiCl-Li}_2\text{O}$	923	90% CO_2 -Ar	YSZ-8	26.7	24	178

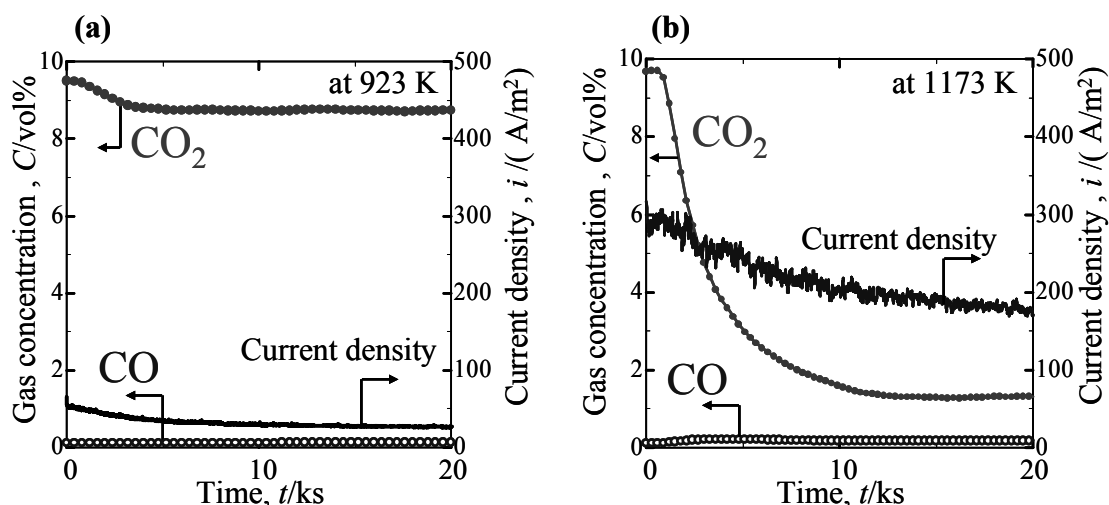
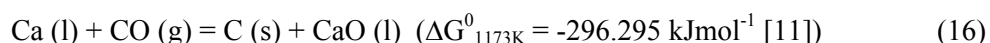


Figure 3. Changes in concentration of CO₂ and CO and current density (a) when LiCl-Li₂O and ZR-8Y were used and (b) when CaCl₂-CaO and ZR-8Y were used.

The decrease in CO₂ gas concentration for the case when CaCl₂-CaO molten salt was used is larger than that for the case when LiCl-Li₂O molten salt was used. This is because the reduction ability of metallic Ca is higher than that of metallic Li thermodynamically, although the difference in the free energy change is not significant as shown in Equations (10) and (13). Thus, the reason why the decrease of CO₂ gas concentration differs significantly would be due to the difference in electrolysis temperature, i.e., the decrease in CO₂ gas concentration depends on the diffusion rate of oxygen ions especially in the ZrO₂ solid electrolyte.

The Gibbs free energy change of the reaction between CO₂ gas and metallic Ca to produce carbon is lower than that of the reaction to produce CO gas. Similar relationship can be observed when metallic Li is used as a reductant as shown in Equations (10, 13-15). In particular, in the case when CaCl₂-CaO molten salt is used, CO gas tends to be produced by the Boudouard reaction as shown in Equation (5). However, even at a high electrolysis temperature, CO gas was not produced in both experiments (run 1 and 2) as shown in Figure 3. Therefore, in the case of CaCl₂-CaO molten salt, the fact that not only CO₂ gas, but also CO gas was decomposed can be explained by calciothermic reduction as shown in Equation (16).



Current density gradually decreases as the electrolysis duration becomes longer. This behaviour is due to two reasons. The first reason is the decrease in the concentration of oxygen ions in the molten salts. When CO₂ gas as a source of oxygen ions is supplied to the molten salts, oxygen ions in the molten salts are continuously removed as oxygen gas from the internal surface of the ZrO₂ solid electrolyte by electrolysis. Therefore, the concentration of oxygen ions can be reduced to maintain a constant current during electrolysis. If the metallic oxide, Li₂O or CaO, is promptly supplied to the molten salt during electrolysis, a constant current would be maintained, i.e., the decrease in CO₂ gas concentration could be much more significant. Another reason is the decrease in effective surface area at the ZrO₂ solid electrolyte. Oxygen ions transfer from the molten salt to the ZrO₂ solid electrolyte, and then to the internal surface of the ZrO₂ tube, where oxygen gas is produced. However, as mentioned above, carbon powder was inserted inside the ZrO₂ tube instead of a platinum paste to provide good electrical conductivity due to experimental difficulties. However, the oxygen ions react with the carbon powder at the interface of the carbon and the internal surface of the ZrO₂ solid electrolyte, and produce CO and CO₂, which is similar to the anodic reaction in the original OS process as presented in Equation (4). Because the carbon is consumed, the effective surface area inside the ZrO₂ tube decreases during electrolysis. We plan to resolve these problems in the future and believe that it is possible to maintain a constant high current density.

In the present paper, two kinds of efficiencies are defined: current efficiency and yield. The former is the ratio of carbon production, which can be estimated from the decrease in CO_2 gas concentration and the increase in CO gas concentration, to carbon production, which can be calculated from the electric charge supplied during electrolysis. The yield is defined as the ratio of the amount of collected carbon from the furnace after electrolysis, to that of the amount of calculated carbon from the electric charge supplied during electrolysis. In these estimations, it was assumed that all the electric charge was consumed for the production of metallic Li or Ca, and that all the formed metallic Li or Ca were stoichiometrically used as a reductant of CO_2 gas.

When $\text{LiCl-Li}_2\text{O}$ and $\text{CaCl}_2\text{-CaO}$ molten salts were used with ZR-8Y electrolyte as the anode, the current efficiency were calculated to be 89.7 % and 78.5 %, respectively, as shown in Table 1.

In run 1, the decrease in CO_2 gas concentration is small as shown in Figure 3. However, the calculated value showed that the electric charge was used efficiently for the decomposition of CO_2 gas as listed in Table 1. Meanwhile, the yields remained at a low percentage of 29 % and 36 % in run 1 and 2, respectively. The yield of collected product could not be evaluated precisely because the particle size of produced carbon was very small, and not all the product could not be collected from the molten salt. A special technique to recover these fine particles is needed to apply this product as a reductant of iron ore in the iron and steel making processes, where the fine carbon can be effectively used as a pulverized coal in the blast furnace process.

3.2. Decomposition of 90 % CO_2 -Ar mixed gas

The decomposition of 90 % CO_2 -Ar mixed gas by electro-reduction at 923 K was performed at 3.2 V using $\text{LiCl-Li}_2\text{O}$ molten salt and YSZ-8 (run 3). The electrical conductivity of YSZ-8 is 2.39 times larger than that of ZR-8Y at 923 K as shown in Figure 2 [15]. The concentrations of CO_2 and CO gases in the exhaust gas during electrolysis were determined from the gas chromatograph in Figure 4.

During the initial stage of the electrolysis, the concentration of CO_2 gas gradually decreased after application of the voltage between the two electrodes. In run 3, CO gas was produced even at the initial stage of the electrolysis and its concentration increased slightly during electrolysis.

The average current of run 3 is 2.37 times larger than that of run 1, although the other operating parameters were the same. In addition, the amount of collected carbon was 1.99 times larger and the concentration and flow rate of CO_2 gas increased from 9.7 % to 90 % and from $5.0 \times 10^{-8} \text{ m}^3/\text{s}$ to $6.0 \times 10^{-8} \text{ m}^3/\text{s}$, respectively. The increase in average current and amount of collected carbon does not depend on the variation in CO_2 gas concentration and flow rate, but on the difference in electrical conductivity of the ZrO_2 solid electrolyte used in this study. Therefore, it is considered that the rate determining step of this proposal is the oxygen ionic transfer in the solid electrolyte used as the anode. If the surface area of the ZrO_2 solid electrolyte becomes larger or the thickness of the ZrO_2 tube

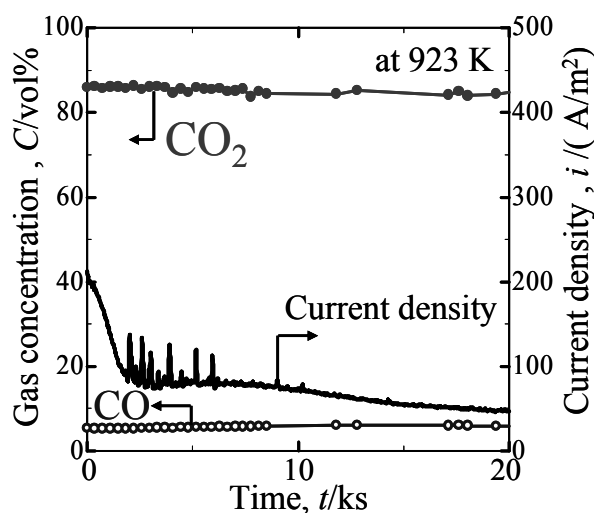


Figure 4. Changes in gas concentration and current density when $\text{LiCl-Li}_2\text{O}$ and YSZ-8 was used and 90 % CO_2 -Ar mixed gas was blown.

becomes thinner, the decomposition rate of CO_2 gas would increase and the carbon production rate would become much larger.

Although the average current increased when using YSZ-8 which has better electrical conductivity than ZR-8Y, the current efficiency decreased in run 3 compared with run 1 and 2. It is noted that the average current is proportional to the amount of metallic Li because it is produced by electrochemical reaction on the cathodic electrode (Equation (9)). It is desired that all the metallic Li reacts with CO_2 gas in the molten salt. When the flow rate of CO_2 gas exceeds the ability of metallic Li to decompose CO_2 gas, some CO_2 gas blown into the molten salt will be exhausted from the outlet without reacting. Therefore, it is reasonable that the current efficiency was lower in run 3 than those of run 1 and 2. In summary, it is important that CO_2 gas bubble remains in the molten salt for a longer time to react with the precipitated Li for obtaining higher current efficiency and larger carbon production.

3.3. The morphology of the produced carbon

After electrolysis, the reduction product adhered to the cathode, and some black powder was recovered from the solidified salt. They were washed to remove the solidified salt and then observed by TEM. The images of the carbon produced in the molten salts are shown in Figure 5.

Despite the types of salts used, two kinds of carbon materials were observed. One is the aggregations of fine particles of amorphous carbon (Figures 5 (a)-(c)). Their particle size was as large as 1 nm. The halo-pattern which is derived from the existence of an amorphous phase was observed as shown in Figure 5 (c). The d-spacing of these halo rings corresponded to the amorphous carbon.

Another is the rod-like graphite crystals (Figures 5 (d)-(f)). This material consists of aggregations of cubic-like graphite which are connected in a specific direction as shown in Figures 5 (d)-(f). The four diffraction rings derived from the diffractions of crystalline phases was also observed in Figure 5 (f).

Figures 6 (a) and (b) show the XRD pattern of the sample precipitated on the cathode. Most samples were recovered from the upper surface of the salt. XRD pattern of carbon was identified in both samples. In particular, the sample collected from the solidified salt contained graphite with a better crystalline symmetry. The diffraction peak at $2\theta = 26.6^\circ$ can be assigned to the characteristic (002) diffraction line of graphitized carbon. The other peaks at about 42.5° , 44.5° , and 58.8° correspond to the (100), (101) and (004) reflections, respectively. Significant broadening of the diffraction peak at

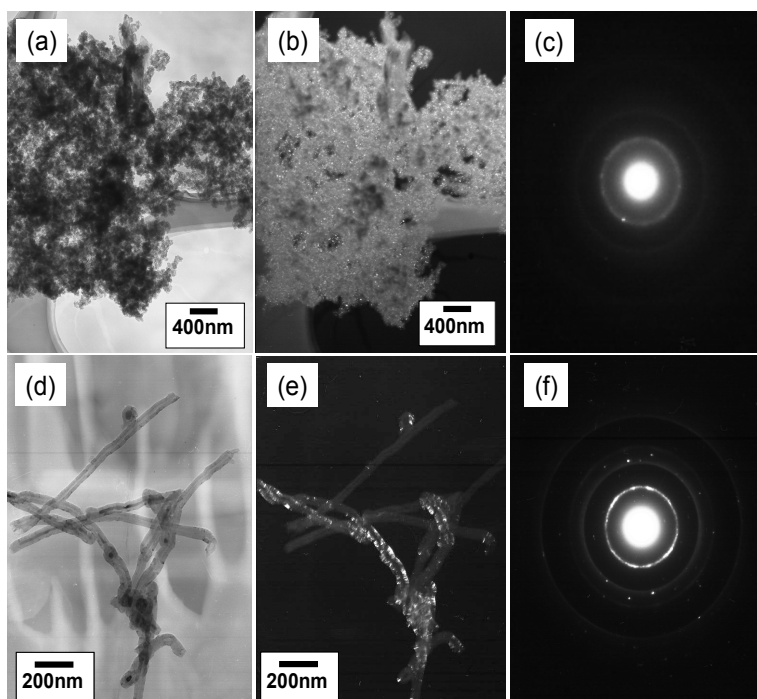


Figure 5. TEM images of carbon obtained from the molten salts: (a) and (d) bright field, (b) and (e) dark field, and (c) and (f) electron diffraction.

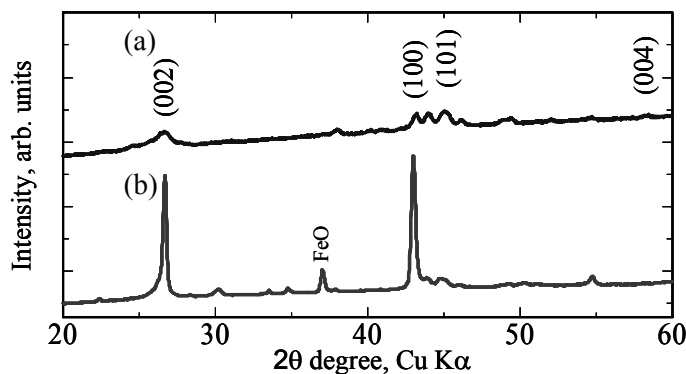


Figure 6. XRD pattern of products (a) precipitated on the cathode and (b) collected from the molten salts.

$2\theta = 26.6^\circ$ was observed as shown in Figure 6 (a). This result shows that most part of the sample was amorphous. The XRD measurement results are in good agreement with the TEM observations.

4. Conclusions

CO_2 gas was decomposed electrochemically either in $\text{LiCl-Li}_2\text{O}$ or $\text{CaCl}_2\text{-CaO}$ molten salt. The OS process for the refractory oxide reduction was applied to CO_2 gas decomposition. The ZrO_2 solid electrolyte could remove oxygen ions from the molten salts when it was used as the anode. Gaseous oxides such as CO_2 and CO gases were electrochemically reduced in the molten salts. When $\text{CaCl}_2\text{-CaO}$ molten salt was used at 1173 K, the decrease in CO_2 gas concentration was larger than that when $\text{LiCl-Li}_2\text{O}$ molten salt was used at 923 K. The average current for the carbon production did not depend on either the concentration or the flow rate of CO_2 gas, but on the electrical conductivity of the ZrO_2 solid electrolyte. Therefore, we conclude that oxygen ionic transfer in the ZrO_2 solid electrolyte is the rate determining step. Despite the types of salts used, the aggregations of nanometre-scale amorphous carbon particles and rod-like graphite crystals were observed by TEM.

Acknowledgements

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