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CO₂ gas decomposition to carbon by electro-reduction in molten salts

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Abstract

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

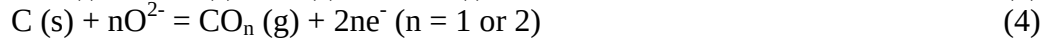
1. Introduction

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]. Steel making industry has emitted a large amount of CO₂ gas although it has made great efforts to decrease the gas emissions. Because the iron ore, Fe₂O₃, is reduced by the coke, it is essential that a large amount of CO₂ gas is exhausted from the blast furnace and converter in steel making process, and the development of innovative method is expected to decrease CO₂ gas emissions. However, the decomposition of CO₂ gas which is emitted from these furnaces has not been studied so much. If all the emitted CO₂ gas is efficiently decomposed, the amount of CO₂ gas emissions decreases drastically.

In the present paper, a new method is proposed to thermochemically reduce CO₂ gas to carbon using molten salt. As a method to decompose CO₂ gas, OS process proposed by Ono and Suzuki is applied in this research [2,3]. The original of OS process is known as the method to reduce metallic oxides such as titanium, vanadium, tantalum and nickel to their metallic state. It consists of the electro-reduction of CaO and the calciothermic reduction in the CaCl₂ bath [2-7].

The reduction mechanism was reported in the previous papers [2-7], and it is briefly written as below in case of reduction of titanium dioxide. CaCl₂ can dissolve 20mol% CaO and 2-4mol% metallic Ca at 1173K in equilibrium [8-10]. CaO is ionized in the

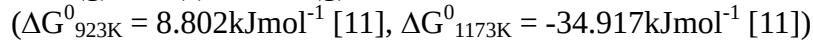
molten salt as presented in Eq. (1). When an electrical voltage is applied between the two electrodes, metallic Ca is produced near the cathode as shown in Eq. (2). This metallic Ca rapidly dissolves into CaCl_2 and then the dissolved Ca thermodynamically reacts with titanium dioxide near the cathodic electrode to produce metallic titanium and CaO as presented in Eq. (3). Because this by-product CaO is ionized again, these chemical reactions (Eqs. 1-3) are cycled in the furnace. On the other hand, oxygen anions in the molten salt are removed as CO gas or CO_2 gas when the carbon anodic electrode is used as shown in Eq. (4).



where the underline in this paper denotes that the substance is dissolved in CaCl_2 melt.

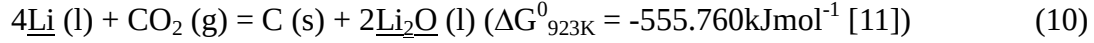
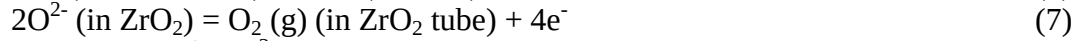
When we apply this OS process to CO_2 decomposition, the solid TiO_2 can not replace to CO_2 gas simply. The decomposition of CO_2 gas occurs at the surface of CO_2 gas bubbles, and it is important that the reductant Ca exists near the surface of CO_2 gas bubble. In the case of electrolysis, the reductant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

In this study, two new ideas were added to the original OS process to decompose CO_2 gas to carbon and oxygen gas. The first ingenuity is that the $\text{LiCl-Li}_2\text{O}$ molten salt is used as solvent to avoid occurrence of Boudouard reaction. Boudouard reaction is shown in Eq. (5).



In case of higher temperature, CO_2 gas preferentially reacts with carbon to form CO gas. Because the carbon should be product, this is undesirable for this proposal. When the molten $\text{LiCl-Li}_2\text{O}$ is used as solvent, the operating electrolysis temperature can decrease by about 250K compared to the temperature range (923-1173K) where the molten $\text{CaCl}_2\text{-CaO}$ is effective. The latter salt has the wide solubility of Ca and CaO, while LiCl can dissolve Li_2O up to 4.2mol% at 923K [12], and metallic Li has enough ability to decompose CO_2 gas to carbon and oxygen gas thermodynamically.

The second ingenuity is that the ZrO_2 solid electrolyte is used. In OS process, carbon anode is commonly used to remove oxygen ions from the molten salt to the outside of reactor. In this case, however, oxygen anions are removed as CO gas or CO_2 gas after the reaction with carbon. This is undesirable because we aim at the decomposition of CO_2 gas to carbon not to CO gas. Therefore, the ZrO_2 solid electrolyte which is oxygen ions conductor is applied as the anode. The oxygen anions in the molten salt diffuse through the ZrO_2 solid state electrolyte and they are removed as oxygen gas at the opposite side of the ZrO_2 anode as shown in Eq. (6). When we consider the diffusion rate of oxygen anions in ZrO_2 solid electrolyte, the higher electrolysis temperature is desired. The decomposition mechanism of CO_2 gas is expected in Eqs. (6)–(10) when we apply the OS process in the molten $\text{LiCl-Li}_2\text{O}$.



As explained later, the oxygen gas evolution (Eq.(7)) was experimentally difficult to realize here because of technical issue of anode construction. The complete decomposition of CO_2 gas to carbon and oxygen is desired but could not. This experimental paper will report the validity of these reactions except for Eq.(7).

Another mechanism is carbonate formation in molten salt [13-19]. CO_2 gas dissolves as the carbonate ions (Eq. 11) and the electrochemical decomposition of carbonate ions occurs on the cathodic electrode as shown in Eq. (12).



The electrochemical analysis was often conducted with TEM analysis. However, all of the previous works considered the mechanism of decomposition of CO_3^{2-} and precipitation of carbon, and the precipitation of Li or Ca was never considered.

In the presented study, a large amount of oxygen ions exists in the molten salt due to dissolution of oxide, 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 the electrolysis (Eq. 11). The carbonate ions can receive electrons on the cathodic electrode, and carbon and oxygen ions are produced (Eq. 12).

The carbonate formation in CaCl_2 was previously studied by Hashizume et al. [8]. Atmospheric pressure of CO_2 gas could be in equilibrium with CaCl_2 liquid within 15 min. at 1123 K. Its saturation concentration of CO_2 gas showed the complete mixing of CaCl_2 - CaCO_3 by 15 mol% CaO . At the higher temperature by 50 K, the saturation concentration of CO_2 decreases reflecting the instability of CaCO_3 at the higher temperature. The solubility of CO_2 gas in LiCl - Li_2O is not studied yet, but it is expected from the strong thermodynamic stability of Li_2CO_3 that most of O^{2-} in LiCl can react with CO_2 gas to form CO_3^{2-} if the equilibrium is established. However, a slow reaction rate at the lower temperature should be noted to achieve the equilibrium. In addition, CO_2 gas bubbles in gas injection exist only for a few second at longest.

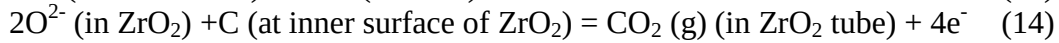
Laboratoire et al.[20] reported the electrochemical reduction of liquid carbonates mixture to obtain amorphous carbon. They proposed various mechanisms available to explain the data measured by cyclic voltammetry, and the formation of a hypothetical compound CO_2Li_2 was expected. Considering the slow kinetics of CO_2 dissolution as carbonates both in CaCl_2 and LiCl , the multiple mechanisms should be considered.

The purpose of this research is to decompose CO_2 gas to carbon in the molten salts by using ZrO_2 solid electrolyte, and to investigate the carbon morphology and the rate determining step of this proposal in order to know the key for the effectiveness and speeding up of the CO_2 decomposition.

2. Experimental

CaCl_2 (>95%, Wako Chemical Co.) was mixed with CaO (99.9%, Kanto Chemical) which was calcined in air in advance. CaO was weighed to be 0.5mol%. This mixture was used as electrolyte by filling inside a magnesia crucible (Fig. 1). In a similar way,

LiCl (>99.0%, Wako Chemical Co.) was mixed with Li₂O (>95%, Wako Chemical Co.) weighed to be 4.2mol%. A Stainless steel pipe (6mm in internal diameter) was used as the inlet of CO₂-Ar mixed gas and as the cathodic electrode. Two kinds of one-end-closed tube made of ZrO₂ solid electrolyte were used to remove oxygen ions in molten salts. These two kinds of tube (17 mm in outer diameter, 2 mm in thickness) were produced by Nikkato Co. as the commercial name as ZR-8Y and YSZ-8. The former was more popular as hard ceramic material and suitable as structural element such as anode. The latter is also yttria stabilized zirconia but it is more brittle. ZR-8Y was taken as the standard tube. The electrical conductivity of YSZ-8 is 2.39 times larger than that of ZR-8Y at 923K ($\sigma_{\text{YSZ-8}} = 0.79[\Omega^{-1}\text{m}^{-1}]$, $\sigma_{\text{ZR-8Y}} = 0.33[\Omega^{-1}\text{m}^{-1}]$) as shown in Fig. 2 [21]. These electrodes were attached to the cover of stainless steel vessel using silicone stopper. It was desired that platinum paste was applied inside ZrO₂ tube to give an electrical conductivity, but it was technically difficult to paste, because the ZrO₂ tube was 500 mm long and the inner diameter was only 13 mm. Therefore, carbon powder was alternatively inserted inside the ZrO₂ tube to give an electrical conductivity instead of platinum paste. Then, the anodic reaction Eq.(7) should be modified as,



The reaction (14) occurs inside the ZrO₂ tube and it is not desired from the viewpoint of complete CO₂ decomposition to carbon and oxygen gas. This technical problem should be clarified in future. This paper studies the fundamental base of combined electrolyte of the molten salt and the solid oxygen conductor in order to complete the full decomposition of CO₂.

If this outlet of the ZrO₂ tube was inside the reactor, oxygen gas which was produced at the internal surface of the ZrO₂ tube reacted with carbon produced in the molten salt. Namely, recombination of carbon with oxygen gas occurred. Therefore, it was important that oxygen gas was emitted without making a chemical contact with molten salts by using the long tube.

The mixture CaCl₂-CaO or LiCl-Li₂O was heated up slowly to 1173K or 923K, respectively in Ar atmosphere after the salt was dehydrated. Then, 9.7%CO₂-Ar mixed gas (CO₂ 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%CO₂-Ar mixed gas (CO₂ 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 passed through the molten salts and the exhausted gas was introduced to the gas analyzers from the outlet. After the salt was saturated with CO₂ gas, electrolysis was started at 3.1V when the molten CaCl₂-CaO was used, and in case when the molten LiCl-Li₂O was used, electrolysis was conducted at 3.2V. Each electrolysis voltage was larger than the theoretical decomposition voltage of the corresponding oxide, CaO or Li₂O, and smaller than that of chloride, CaCl₂ or LiCl, respectively. During electrolysis, the concentration of CO₂ gas and CO gas in exhaust gas was measured at outlet to investigate the decomposition behavior of CO₂ gas by using infrared gas analyzer (Yokogawa Co.), when 9.7%CO₂-Ar mixed gas was blown. The gas chromatograph (GC-2014, Shimadzu Co.) was used when 90%CO₂-Ar mixed gas was blown. When infrared gas analyzer was used, the concentration of CO₂ gas and CO gas was able to be measured continuously, although the maximum concentration was 10vol%. The gas chromatograph can measure to 99 vol% but the measurement was conducted in about $3.6 \times 10^2\text{s}$ interval. Both analyzers were often calibrated by the standard gas. After

electrolysis with a constant cell voltage, the furnace was cooled down to room temperature in Ar atmosphere after the cathodic pipe was raised to upper part of the vessel. The black reduction products existed at the surface part of solidified salt and around the cathodic electrode, and they were collected and washed to remove the solidified salt residue from the reduction products completely by distilled water, acetic acid, distilled water, ethanol and acetone in exact order. The products were observed by transmission electro microscope (TEM, JEOL JEM-2000FX, acceleration voltage was 200kV) and identified by powder X-ray diffraction (XRD, X'pert Pro, Philips Co.) measurement using Cu-K α radiation.

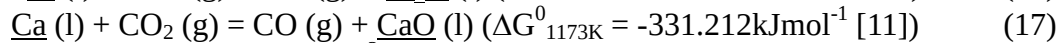
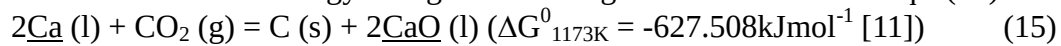
3. Results and discussion

3.1 Decomposition of 9.7%-Ar mixed gas

Table 1 listed the experimental conditions such as the choice of molten salt, gas concentration, kinds of ZrO₂ tube used for electrolysis, current efficiency, collected yield and the current averaged during electrolysis. 9.7% CO₂ was taken as the artificial gas similar with the exhaust gas from the blast furnace in steel industry.

Fig. 3(a) shows the time dependency of CO₂ and CO gas concentrations in exhaust gas and of current density during electrolysis of 9.7%CO₂-Ar mixed gas when molten LiCl-Li₂O and ZR-8Y were used (Run 1). Fig. 3(b) shows those of the case the molten CaCl₂-CaO and ZR-8Y were used (Run 2). Current between the two electrodes were recorded in every 10s. The surface area of electrode for evaluation of current density was measured from the height of solidified molten salt after cooling. The depth of molten salt relates to the area where oxygen ions are transferred from molten salt to the internal surface of ZrO₂ tube. The surface area 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.

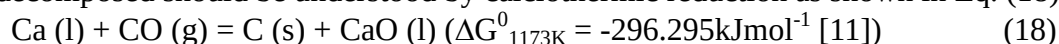
For the better choice of solvent, current density was measured when a constant voltage was applied to between the two electrodes. After the electrolysis was started, the concentration of CO₂ gas decreased. On the other hand, the concentration of CO gas did not increase so much. Therefore, CO₂ gas was decomposed to carbon and O²⁻ in the molten salts as shown in Eq. (8)-(10) or Eq. (11)-(12). This means that the ZrO₂ solid electrolyte worked as oxygen ionic conductor (as shown in Eq. (6)-(7) or Eq. (13)-(14)). The decrease of CO₂ gas concentration in case the molten CaCl₂-CaO was used is larger than that of the case the molten LiCl-Li₂O was used. This is because the reduction ability of metallic Ca is higher than that of metallic Li thermodynamically, although the difference of the free energy change is not so significant as shown in Eqs. (10) and (15).



LiCl-Li₂O melt forms CO₃²⁻ by CO₂ gas bubbling [13-16], while the formability of CO₃²⁻ depends on temperature; 15mol%CO₂ dissolves in the melt at 1123 K, but the solubility of CO₂ decreases at the higher temperature corresponding to thermodynamic instability of CaCO₃ [8]. Therefore, the reason why the decrease of CO₂ gas concentration differs significantly would be derived from the difference of electrolysis temperature, i.e., the decrease of CO₂ gas concentration depends on the diffusion rate of

oxygen ions especially in 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. This relation is the same when metallic Li is used as reductant as shown in Eqs. (10, 15-17). Especially in case that the molten CaCl₂-CaO is used, CO gas tends to be produced by Boudouard reaction as shown in Eq. (5). However, even at high electrolysis temperature, CO gas was not produced in both experiments (run 1 and 2) as shown in Fig. 3. Therefore, in case of molten CaCl₂-CaO, the fact that not only CO₂ gas but also CO gas was decomposed should be understood by calciothermic reduction as shown in Eq. (18).



Current density gradually decreases as electrolysis time is longer. Three reasons can be discussed for this behavior. One is the decrease of the concentration of oxygen ions in the molten salts. When CO₂ gas is supplied into the molten salts as oxygen ions resources, oxygen ions in the molten salts are continuously removed as oxygen gas from the internal surface of the ZrO₂ solid electrolyte forcedly by the electrolysis. Therefore, the concentration of oxygen ions can be short to keep constant current during electrolysis. If metallic oxide, Li₂O or CaO, is added timely to the molten salt during electrolysis, the constant current would be maintained, i.e., the decrease of CO₂ gas concentration could be much more significant.

Another interpretation is also available considering the contribution of CO₃²⁻: Assuming the reaction between CO₂ and Li₂O or CaO (Eq.11) is fast, a large amount of CO₃²⁻ may be generated before the electrolysis. This CO₃²⁻ decomposes to carbon and O²⁻ by the electrolysis as given in Eq.(12). O²⁻ is extracted from the anode. Therefore the O²⁻ concentration in the melt depends on the feeding speed of CO₂ and on the extraction speed of O²⁻. When too much CO₂ gas is supplied, most of gas remains unreacted, and the efficiency becomes worse. When CO₂ gas supply is too small, the CO₃²⁻ concentration becomes smaller and the current decreases. Assuming the reaction between CO₂ and Li₂O or CaO is slow, a small amount of CO₃²⁻ does not contribute the reaction mechanism. If too much O²⁻ is extracted in the early stage of electrolysis for example, the CO₃²⁻ concentration and the current becomes smaller at the later stage of electrolysis.

Third reason is the decrease of effective surface area at the ZrO₂ solid electrolyte. Oxygen ions transfer from the molten salt to ZrO₂ solid electrolyte, and then to the internal surface of ZrO₂ tube, where oxygen gas is produced. As mentioned above, however, carbon powder was inserted inside the ZrO₂ tube to give a good electrical conductivity because of the experimental reason in this work. The oxygen ions react with the carbon powder at the interface of the carbon and the internal surface of ZrO₂ solid electrolyte, and produce CO and CO₂, which are the same as anodic reaction in the original OS process as presented in Eq. (4). Because the carbon particles are consumed and disappear, the effective surface area inside ZrO₂ tube decreases as electrolysis time passes. Even though some ingenuity is needed for experimental equipment, we plan to improve these difficulties and believe that it becomes possible to keep current density constantly high.

In the presented paper, two kinds of efficiencies are defined as current efficiency and yield. The former is the ratio of carbon production which can be estimated from the decrease of CO₂ gas concentration and the increase of 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 carbon which is experimentally collected from the furnace after electrolysis, to that of carbon which is calculated 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 reductant of CO₂ gas.

When the molten LiCl-Li₂O and molten CaCl₂-CaO were used with ZR-8Y electrolyte as the anode, the current efficiency were evaluated as 89.7% and 78.5%, respectively, as shown in Table 1.

In case of run 1, the decrease of CO₂ gas concentration looks small as shown in Fig. 3. However, the exact calculation showed that the electric charge was used efficiently for decomposition of CO₂ gas as listed in Table 1. On the other hand, the yields remained at a low level as 29% and 36% in run 1 and 2, respectively. The collection could not be evaluated precisely because the produced carbon was very fine, and it was difficult to collect the entire product from the molten salt. A special technique to recover these fine particles is needed to apply this product as reductant of iron ore in steel making process, where this fine carbon can be effectively used as the pulverized coal in blast furnace process.

3.2 Decomposition of 90%CO₂-Ar mixed gas

A high concentration of CO₂ was tested as the raw gas. This is because the concentrated gas is favorable to keep the reactor at the high temperature. In order to carry the exhaust gas to the detector outside of the reactor, we added 10%Ar. Therefore, a gas mixture of 90%CO₂-Ar was supplied. For analysis of concentrated gas, the gas chromatograph was introduced.

The decomposition of 90%CO₂-Ar mixed gas by electro-reduction at 923K was performed at 3.2V using molten LiCl-Li₂O and YSZ-8 (run 3). The electrical conductivity of YSZ-8 is 2.39 times larger than that of ZR-8Y at 923K as shown in Fig. 2 [21]. The gas concentration of CO₂ gas and CO gas in the exhaust gas during electrolysis was measured by gas chromatograph as shown in Fig. 4.

After the voltage is applied to between the two electrodes, the concentration of CO₂ gas slowly decreases at the initial stage of the electrolysis. In this run 3, CO gas was produced even at the initial stage of the electrolysis and its concentration increased by a small extent as electrolysis time passes.

The averaged current of run 3 is 2.37 times larger than that of run 1, although the other operating parameters were set as the same. The amount of collected carbon became 1.99 times larger. In run 3, the concentration and flow rate of CO₂ 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, comparing with those at run 1. The increase of the averaged current and the collected carbon do not depend on the variation of CO₂ gas concentration and flow rate but on the difference of electrical conductivity of ZrO₂ solid electrolyte used in this study. Therefore, it is considered that the rate determining step of this proposal is oxygen ionic transfer in the solid electrolyte used as the anode. If the surface area of ZrO₂ solid electrolyte become larger or the thickness of ZrO₂ tube could become thinner, the decomposition rate of CO₂ gas would increase and the carbon production rate would become much larger.

Although the averaged current increased by using YSZ-8 which has the better electrical conductivity than that of ZR-8Y, the current efficiency decreased in run 3

compared with run 1 and 2. It is noted that the averaged current is proportional to the amount of metallic Li because it is produced by electrochemical reaction on the cathodic electrode (Eq. 9). It is desired that the all the metallic Li reacts with CO₂ gas in the molten salt. When the flow rate of CO₂ gas exceeds the ability of metallic Li to decompose CO₂ gas, a part of CO₂ gas which is blown into the molten salt will be exhausted from the outlet without reacting. Therefore, it is reasonable that the current efficiency became lower in run 3 than that of run 1 and 2. In brief summary, it is important that CO₂ gas bubble remains in the molten salt for a longer time enough to react with the precipitated Li for obtaining the higher current efficiency and the larger carbon production.

3.3 The morphology of the produced carbon

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

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

Another is the rod-like graphite crystals (Fig. 5 (d)-(f)). By the precise observations indicated in Fig. 5 (d) - (f), this material consists of the aggregations of cubic-like graphite which are connected in a particular direction. The four diffraction rings derived from the diffractions of crystalline phases was observed as shown in Fig. 5 (f).

Fig. 6 (a) and (b) show the XRD pattern of the sample precipitated on the cathodic electrode. Most of sample was recovered from the upper surface of the salt. From the both samples, XRD pattern of carbon was identified. Especially, the sample collected from the solidified salt contained the graphite with the 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. Broadening of the diffraction peak at $2\theta = 26.6^\circ$ was significant as shown in Fig. 6 (a). This reflects that most part of the sample was amorphous. These results of XRD measurements are in good agreement with TEM observations.

4. Conclusions

CO₂ gas was decomposed electrochemically either in the molten LiCl-Li₂O or the molten CaCl₂-CaO. The OS process for the refractory oxide reduction was applied to CO₂ gas decomposition. The ZrO₂ solid electrolyte could remove oxygen ions from the molten salts when it was used as the anode. The gaseous oxides such as CO₂ and CO gas were electrochemically reduced in molten salts. When molten CaCl₂-CaO was used at 1173K, the decrease of CO₂ gas concentration was larger than that of when the molten LiCl-Li₂O was used at 923K. The averaged current for the carbon production did not depend on either the concentration or on the flow rate of CO₂ gas but on the

electrical conductivity of ZrO_2 solid electrolyte. Therefore, we conclude that oxygen ionic transfer in ZrO_2 solid electrolyte is rate determining step. Whichever the salts were used, the aggregations of nanometer-scale amorphous carbon and rod-like graphite crystals were observed by TEM.

Acknowledgements

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Figure caption

Fig.1 Cell design.

Fig.2 Relationship of temperature and electrical conductivity of ZrO_2 solid electrolyte.

Fig.3 Time dependency of gas concentration and current density (a) when molten $\text{LiCl-Li}_2\text{O}$ and ZR-8Y were used (Run1) and (b) when molten $\text{CaCl}_2\text{-CaO}$ and ZR-8Y were used (Run 2).

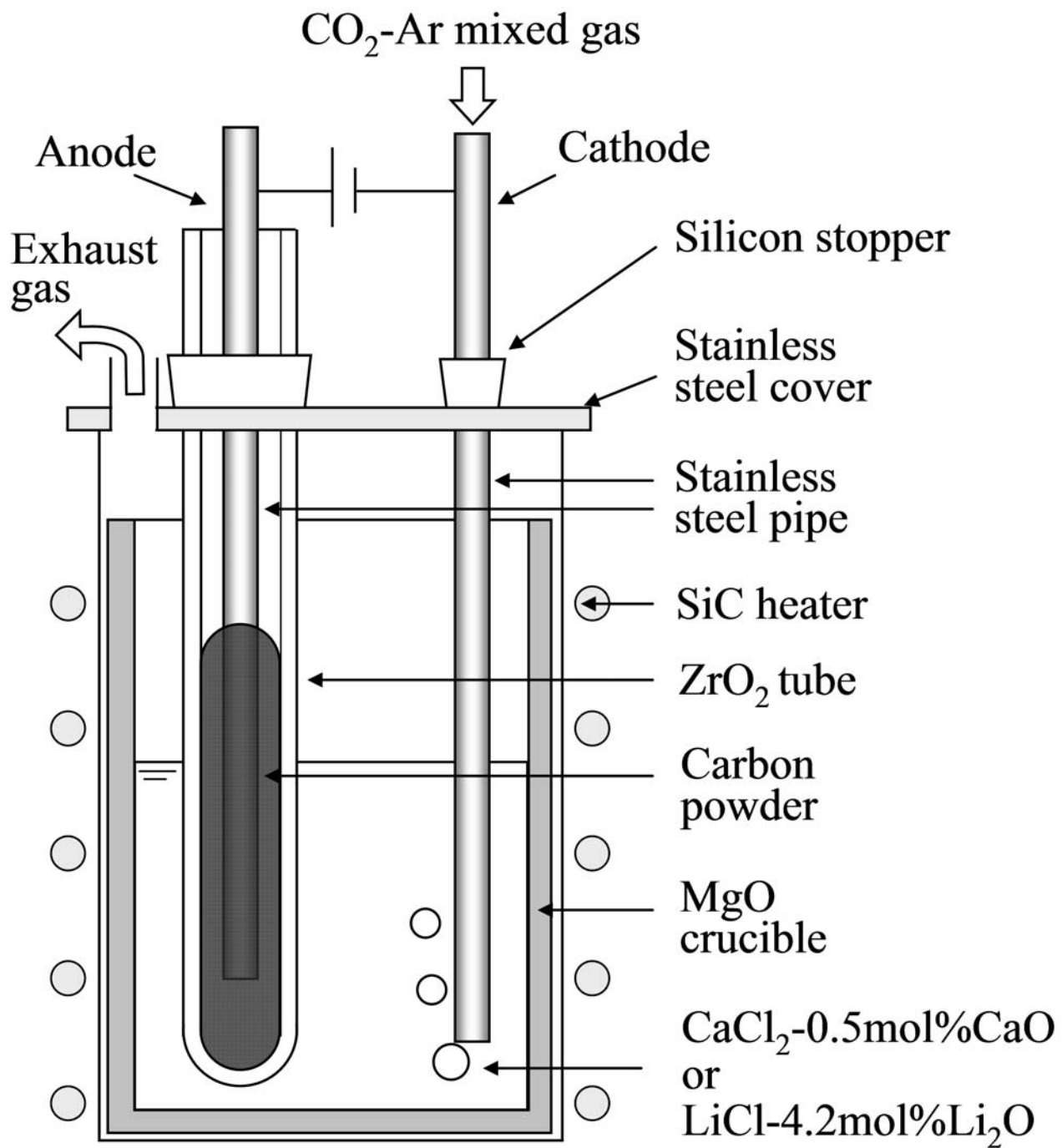
Fig.4 Time dependency of gas concentration and current density when molten $\text{LiCl-Li}_2\text{O}$ and YSZ-8 were used, and 90% $\text{CO}_2\text{-Ar}$ mixed gas was blown (Run 3).

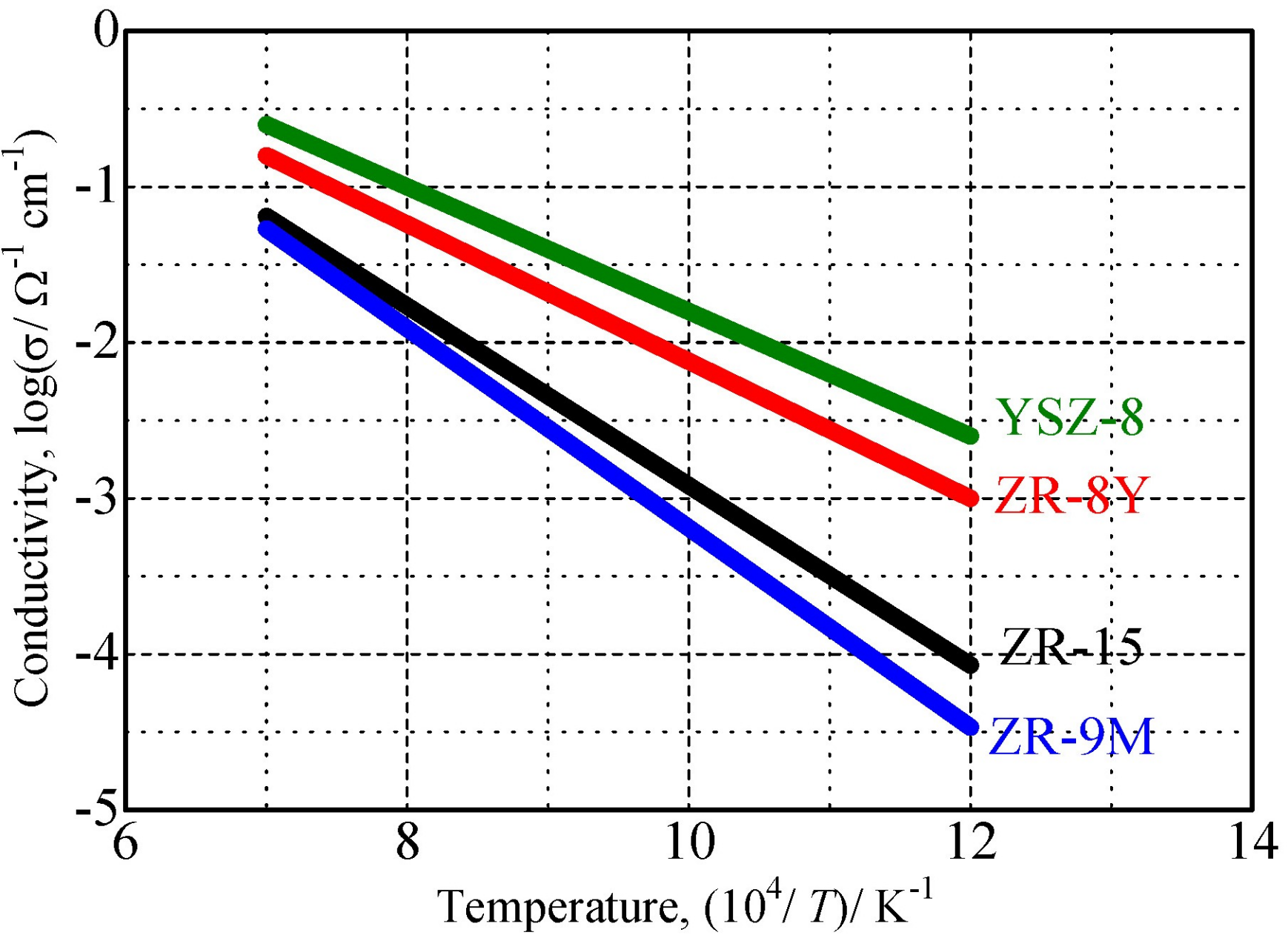
Fig.5 TEM images of the carbon produced in molten salts, (a) and (d) bright field; (b) and (e) dark field; (c) and (f) diffraction.

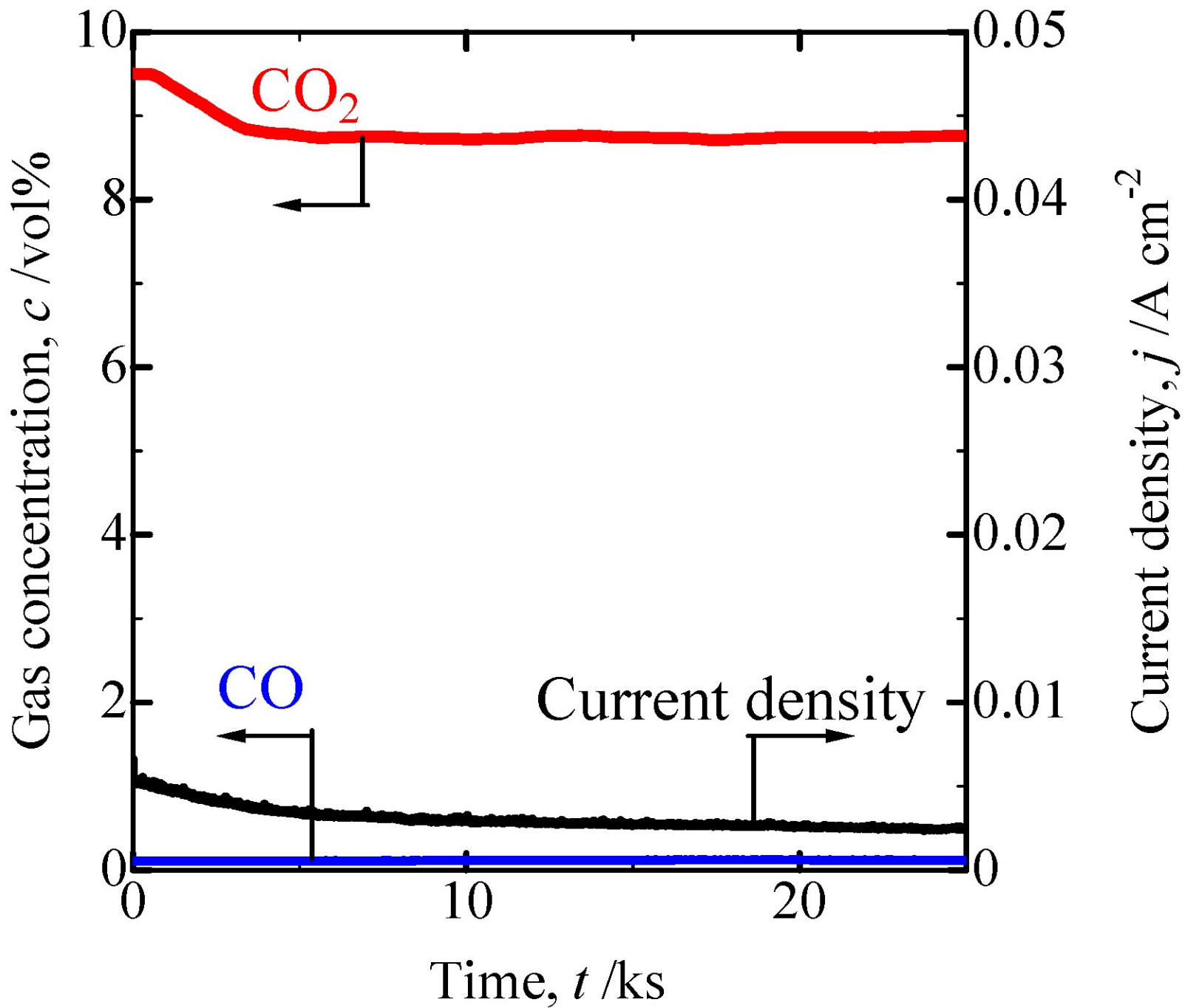
Fig.6 XRD pattern of reduction products (a) precipitated on the cathodic electrode and (b) collected from molten salt.

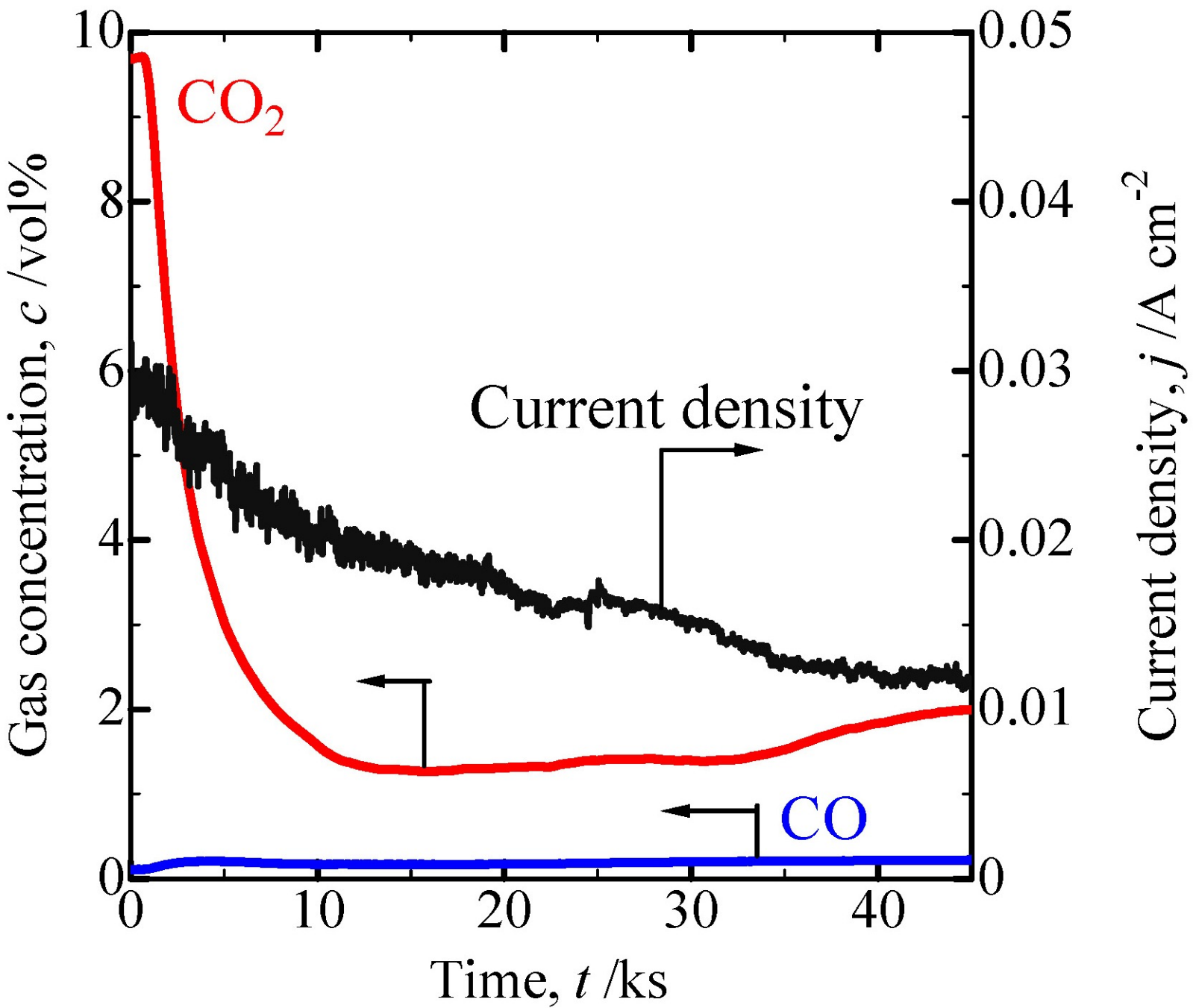
Table 1 Experimental conditions, current efficiency, yield and average current during electrolysis.

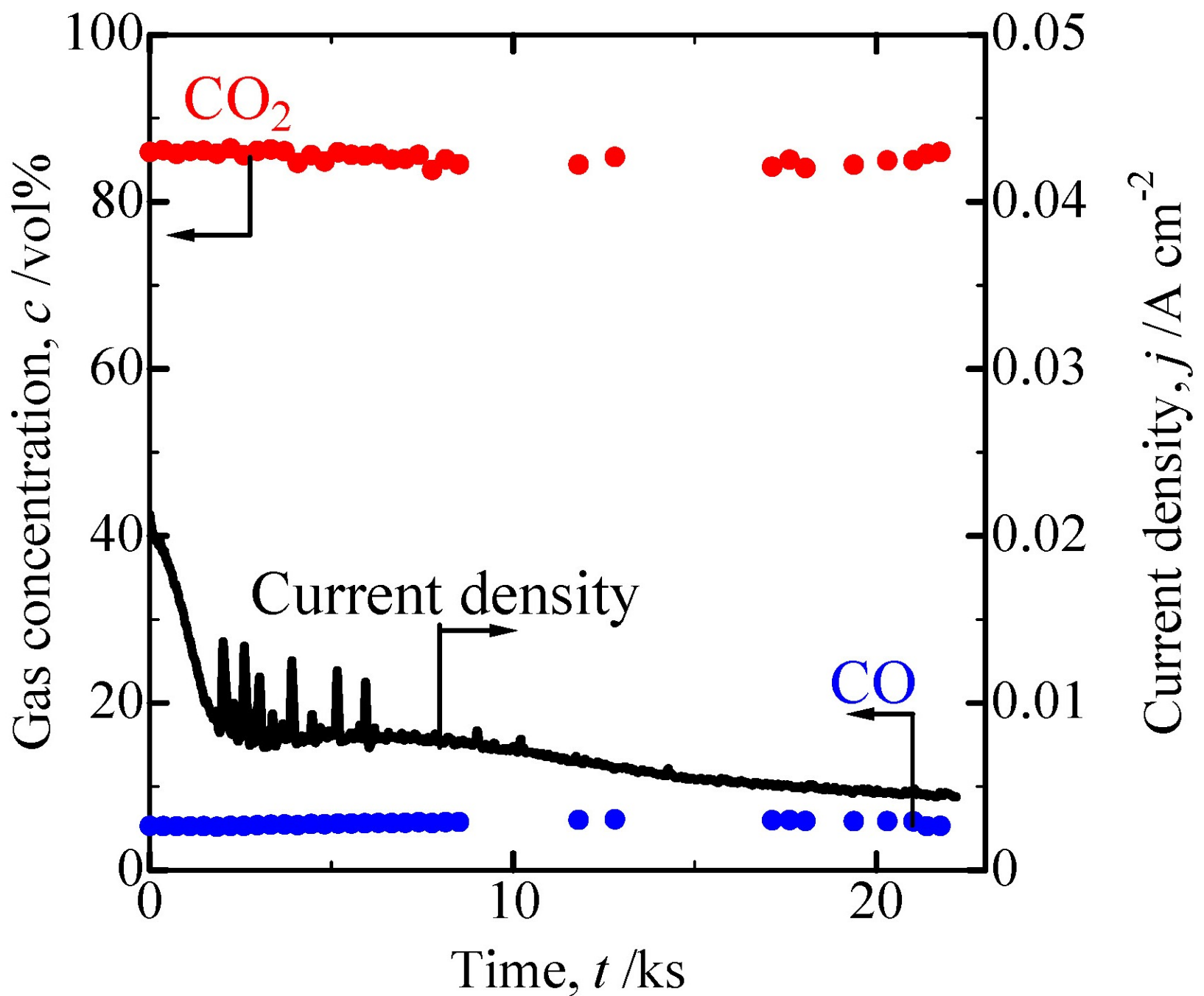
Run	Molten salt	Gas Concentration	Kinds of ZrO ₂	Current efficiency [%]	Yield [%]	Averaged current [mA]
1	LiCl-Li ₂ O	9.7%CO ₂ -Ar	ZR-8Y	89.7	29	75
2	CaCl ₂ -CaO	9.7%CO ₂ -Ar	ZR-8Y	78.5	36	506
3	LiCl-Li ₂ O	90%CO ₂ -Ar	YSZ-8	26.7	24	178

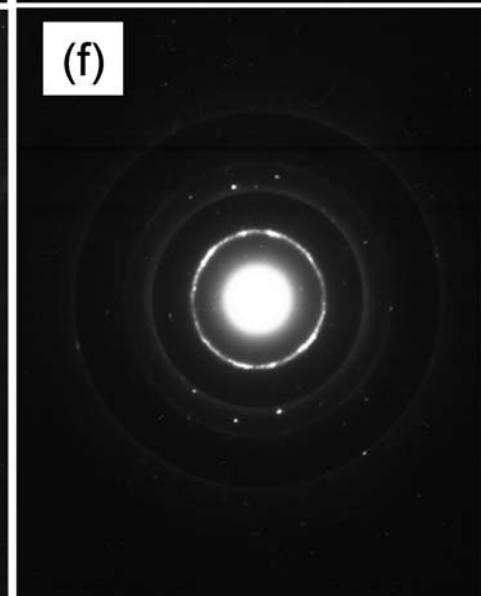
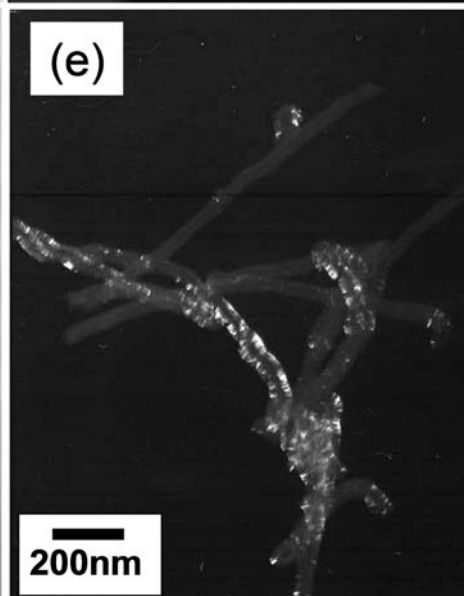
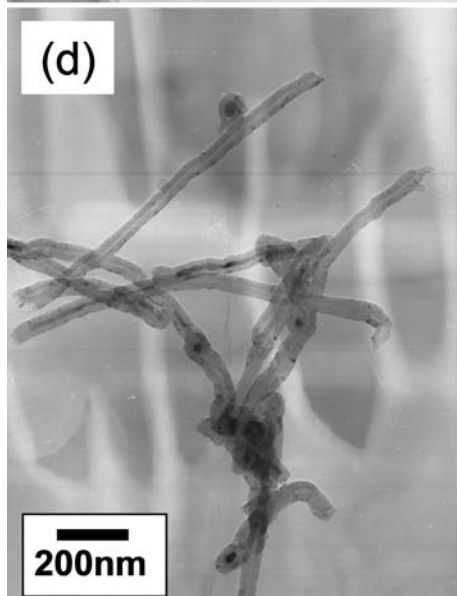
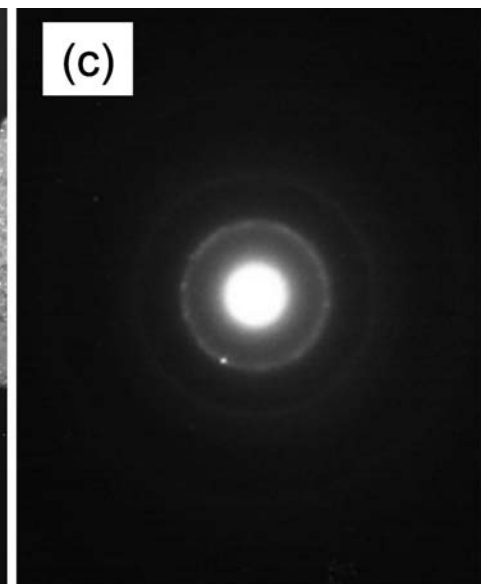
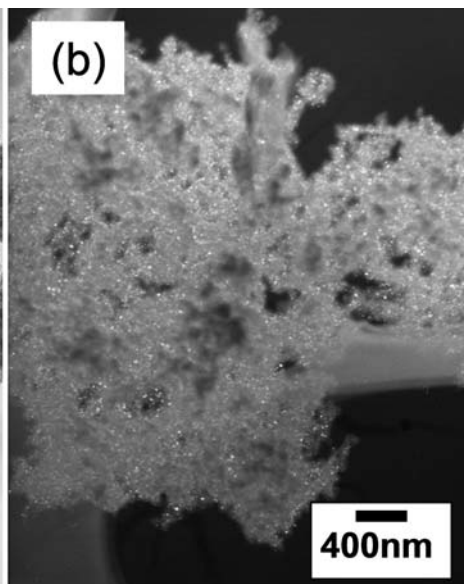
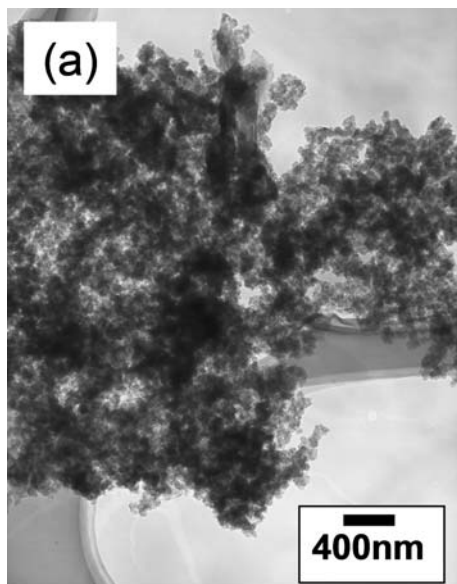












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