Condensation and reduction of CO_2 gas by electrochemical systems with molten salts and ionic liquids electrolyte

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Abstract

We constructed an electrochemical system that condenses dilute CO_2 gas by using molten salts and ionic liquids as electrites. During fabrication and testing, it was found that the wettability of the porous support ceramics with electrites is important to prevent the destructing gas leak. In particular, we found that the wettability between Si_3N_4 ceramics and the molten carbonate salt was extremely poor (the contact angle was more than 150^o). This result strongly suggests that Si_3N_4 is a potential candidate of protective coating of the electrochemical system using molten salts. Finally we succeeded to demostrate the condensation of dilute CO_2 gas by the electrochemical system.

1. Introduction

Reduction of CO_2 gas exaust is necessary to prevent and reverse the grobal warming process. The ultimate means for that is to equip pumps that condense and collect CO_2 gas in every chimney and chemically reduce the CO_2 to make fuels and chemicals. This type of technology consumes energies in the form of electricity, but it might become economically feasible in the near future in view of Carbon Offset, not to mension about the advance of solar energy conversion in the long term. This research project aimed at the assembling of electrochemical CO_2 gas condensation system by using molten carbonate salts and ionic liquids. We also made experimental attempts of reducing CO_2 by electrochemical processes (Fig.1).

The mebrain which we would like to fabricate in this research is something like "Maxwell's Daemon" reversing the entropy transport. How to perform this action with minimum energy is the key issue in the recovery of CO_2 from the exhaust gas, which will become important in the near future in relation to the carbon offset. We believe that the higher efficiency is obtained by thermomechanical way such as absorption and desorption controlled by pressure/temperature difference but by electrochemistry which is used in fuel cell. Since it is difficult to oxidize or reduce CO_2 electrochemically, the report on the electrochemical pump has rarely be found[1,2]. We focus on the molten carbonate salt-type fuel cell to make the CO_2 pump, in which the reduction of O_2 is coupled with the transport of CO_2. This kind of devices can be fabricated with a compact

size and easily attached to the existing chimneys in various facilities.

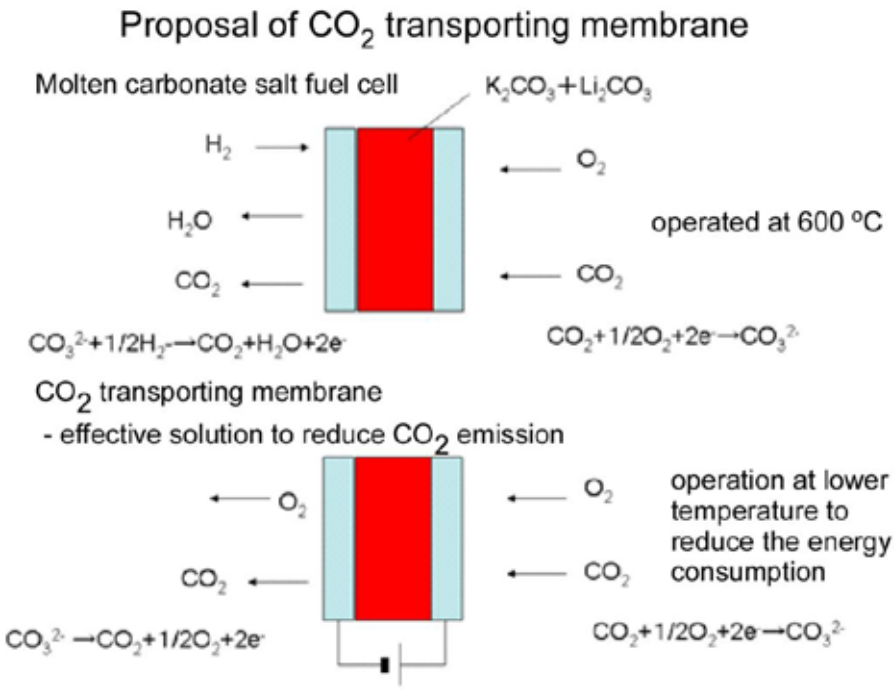

Fig.1 Proposal of CO_2 tansporting membrane

2. Experiment

A. Electrodes and electrolytes

We first used the carbonate molten salts as the electrolytes, since the possibility in the fuel cell is established. We chose the mixture of $NaCO_3$: $LiCO_3$ = 48: 52 (molar ratio, eutectic point 514℃) because of its low melting point. We used porous Ni as the electrodes. We successfully immersed the molten salt into the porous Ni as shown in the SEM images below (Fig.2).

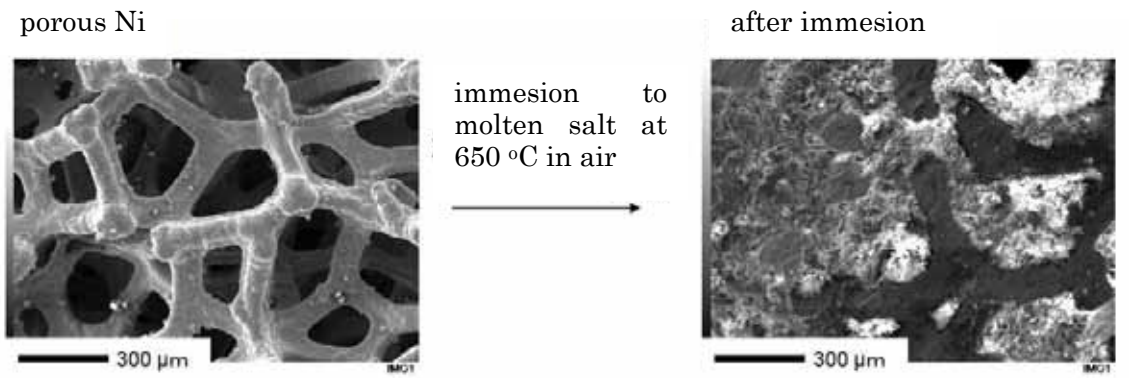

Fig.2 Porous electrode and immersion to molten salt

B. Electrolyte support

It is necessary to use an porous ceramic electrolyte support that is resistant to the

strongly corrosive molten carbonate salts. Since little is known about the corrosion of ceramics to carbonate salts, we examined the properties of Si_3N_4 and Al_2O_3 ceramics. Si_3N_4 is characteristic in its high mechanical strength and high resistance to thermal stress. Al_2O_3 ceramics has thecharacteristics of high mechanical strength and high corrosion reistance.

We synthesized porous Si_3N_4 ceramics. We mixed Si_3N_4 power, carbon fiber and added Al_2O_3 and Y_2O_3 as the sintering reagent. The mixture was thoroughly mixed with a ball mill (one day with ethanol), follwed by sintered in a hotpress at 1850 °C 24MPa. We used commetial Al_2O_3 porous ceramics. SEM images and X-ray diffraction pattern (XRD) are shown in Fig.3.

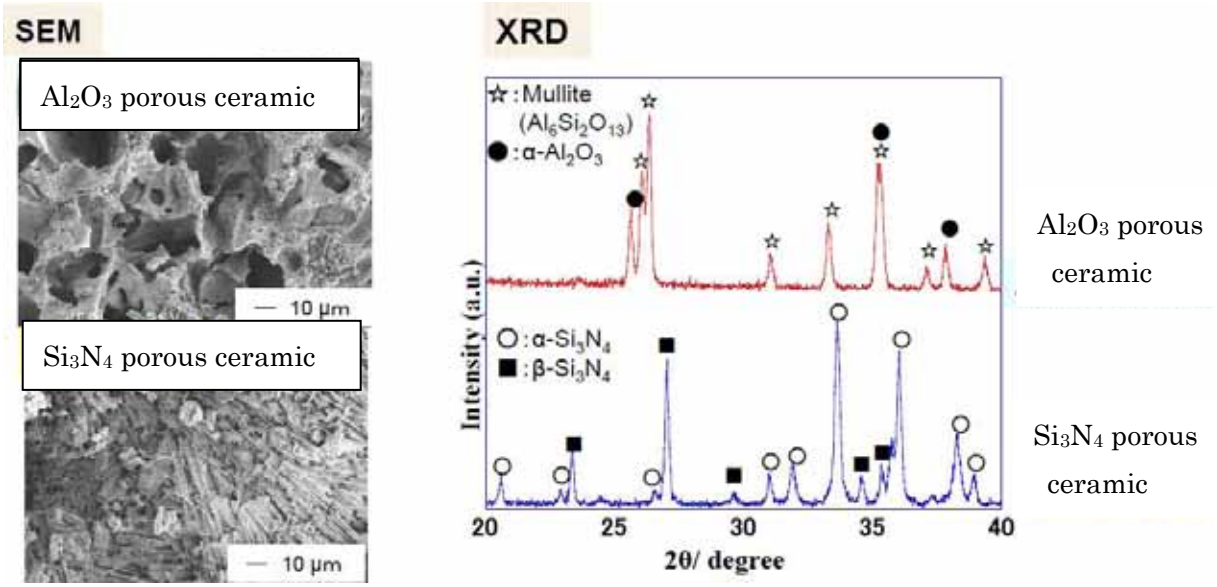

Fig.3 Characterization of electrolyte supporting porous ceramics

C. Assemble of electrochemical cell

We fabricated an electrochemical cell as shown in Fig.4. Porous ceramics and porous Ni electrodes were separately immersed in molten carbonate and they were put together and glued from outside by alumina adhesive which has excellent gas sealing properties (left figure). The electrode-electrolyte complex was further glued to one end of alumina tube and then covered by alumina tube with larger diameter. They were all heated in the electric furnace during the operation. In the outer tube (cathode tube) mixed gas of Ar, CO_2 and O_2 was flown, while in the inner tube He gas was flown in a constant rate and the gas flowing to outside was collected and analyzed by gas chromatography.

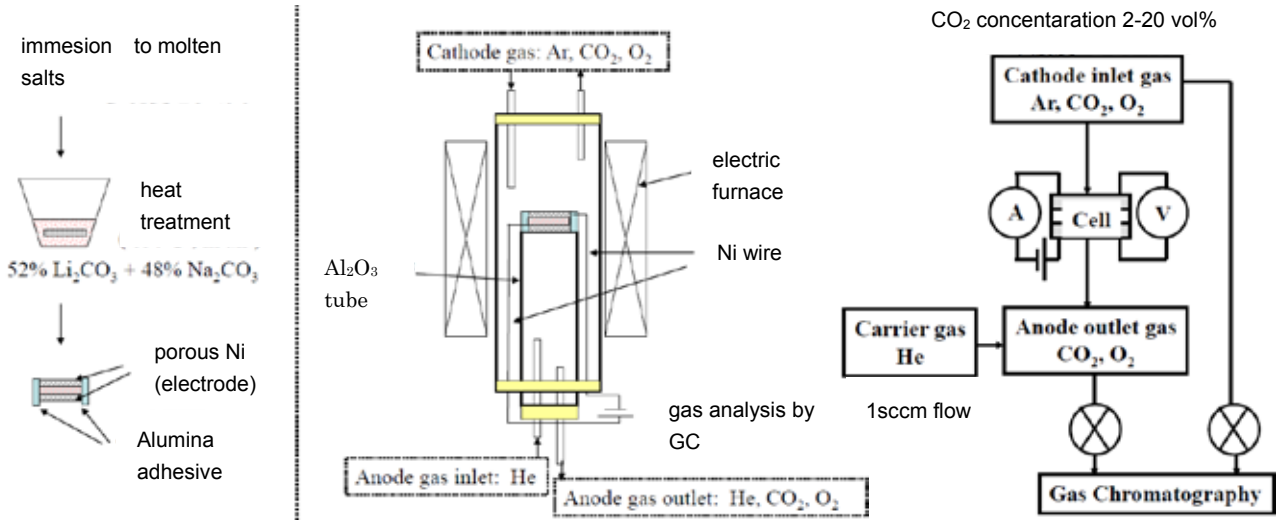

Fig. 4 Electrochemical CO_2 pump system

D. Experiment using ionic liquids and attempt to reduce CO_2 electrochemically

Molten carbonate salt electrochemical systems must be operated at relatively high temperature of 650 °C and it might deteriorate the energy efficiency. Therefore, we attempted to use ionic liquids with carbonate species to lower the temperature. We mixed Ag_2CO_3 to various imidazorium chloride derivative ionic liquids to make the ionic liquid with carbonate species by precipitating AgCl. We found a problem during this experiment that CO_2 is emitted from the liquid associated with silver salt preciptation and we wer not successful in the synthesis of new ionic liquids with CO_3^{2-} component. We attempted various other way but we have not obtained fully positive results until now. We are planning to make efforts to fabricate a room temperature electrochemical CO_2 pump by using ionic liquids.

3. Results

A. Discorvery of extremely low wettabilitty between Si_3N_4 and molten carbonate salts.

The figure below shows the GC analysis results of anode gas when Si_3N_4 was used as the electolyte support. It is noticed that cathode gas (mixture of Ar,O_2 and CO_2) is leaked to the anode side. On the other hand, there was no noticeable leak when Al_2O_3 ceramic was used as the support. Since it is impossible to condense CO_2 with such leaks in the system, we examined the cause of the leak in Si_3N_4 support.

We mirror-polished the surface of Si_3N_4 ceramics in the experiment. The same carbonate salt powder as in the electrochemical system was placed on the surface and heated. As shown in Fig. 6 (a), the molten salt became spherical and the contact angle was found to be more than 150°. It is reasonably explained that the gas leak occurred because the molten salt could not enter into the small holes of Si_3N_4 due to this low wettability. On the other hand, the wettability of Al_2O_3 was perfect with the contact

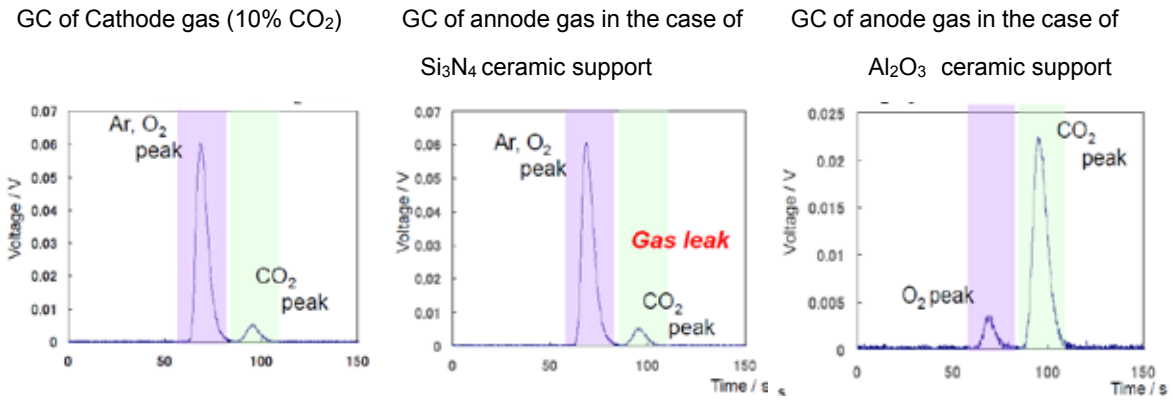

Fig.5　GC analysis

angle almost 0° as in Fig. 6 (b).　It leads to the good adhesion of the molten salt to the inside of porous Al_2O_3.

The present result about Si_3N_4 is negative in view of making the electrochemical CO_2 pumps, but this finding is extremely useful to develop a coating material for electrochemical system with corrosion resistance using the carbonate salts.　We are continuing the experiments about wettability and corrosion resitance of Si_3N_4 fabricated by plasma-assisted chemical vapor deposition (plasma CVD) with various molten salts including various carbonates and phosphates.

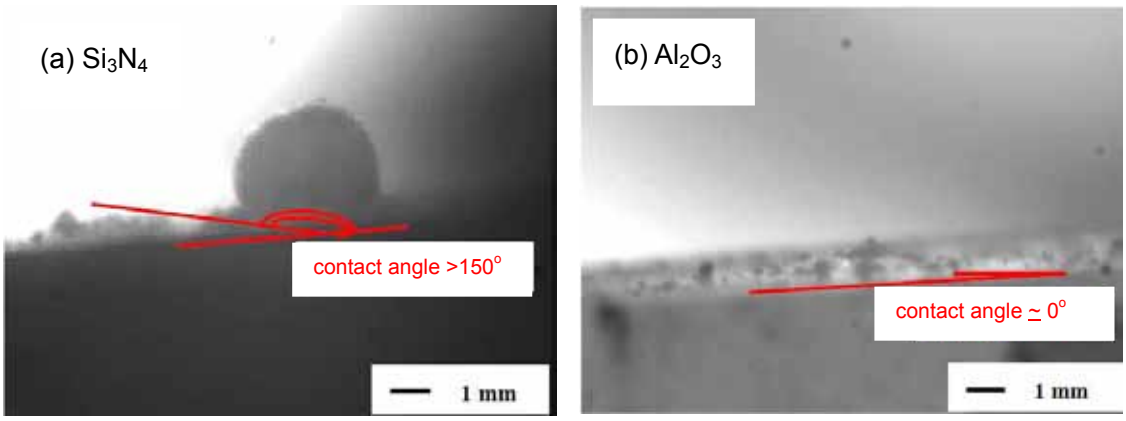

Fig. 6 Contact angles of moletn carbonate salt (a)Si_3N_4,(b) Al_2O_3

B. Performance of an electrochemical CO_2 pump using porous Al_2O_3 ceramic support

The results shown above indicate that electrochemical system without gas leak can be assembled by using Al_2O_3 ceramic electrolyte support.　Fig. 7 shows the performance of the electrochemical system operated as a CO_2 pump.

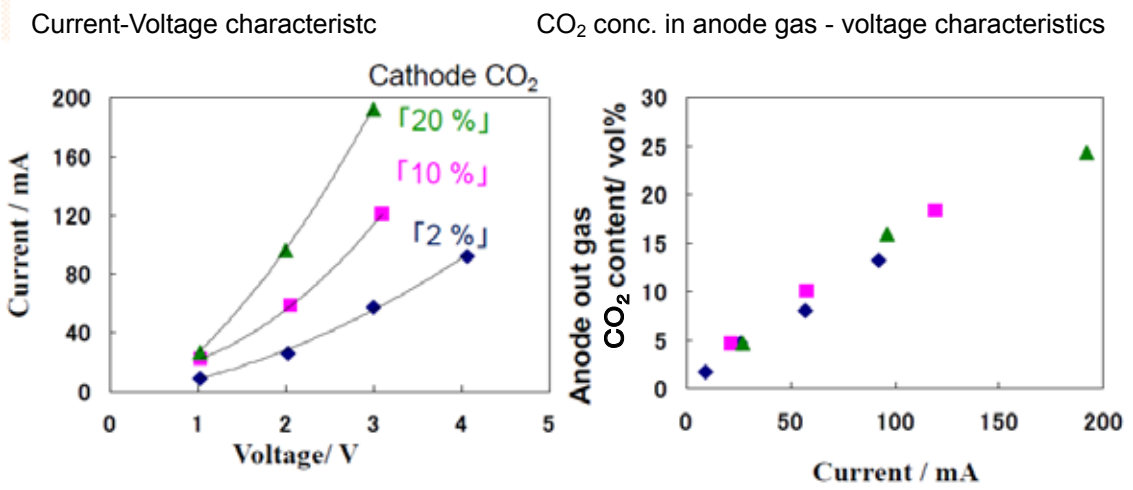

Fig.7　Performance of electrochemical CO_2 pump

The current-voltage curve in the left figure shows that current at the same voltage is increased when the concentration of CO_2 in the cathode gas is increased. It suggests that CO_3^{2-} derived from CO_2 gas carry the current. The CO_2 concentration in the right figure shows that the CO_2 concentration in the anode gas is proportinal only to the current, without strong dependence on the cathode gas concentration. These results clearly indicate that the CO_2 pump operation is realized by the present system. We have achieved the first objective of the proposed research.

4. Summary and future outlook

Systems for CO_2 condensation and recovery from the exhaust gas are actively studied right now, but main stream of the research is on the chemical adsorption and release of CO_2. This type of system is inevitably poorly efficient because it uses thermomechanical work. In the present research, we aimed at construction of electrochemical pump for the CO_2 condensation from dilute gas by using carbonate molten salts including ionic liquids. This approach is promising in terms of size-reduction and efficiency improvements. We attempted to find good catalysts for the CO_2 ionization.

As a result. we have succeeded in the assembling CO_2 pump system using molten carbonate salts. As a byproduct, we found that the wettability of Si_3N_4 and carbonate molten salts are extemely poor (contact angle > 150º). The latter results opens a new technique for corrosion protection to the molten salt devices such as fuel cells using Si_3N_4 coating.

The remaining works on this proposal are as follows. Using low temperature molten salts such as ionic liquids to reduce the operation temperature and improve the

power efficiency. Also we need to find a good catalyst to promote the reaction $CO_2 + 1/2\ O_2 + 2e^- \rightarrow CO_3^{2-}$ at low temperature. We will continue these researches after the period of JFE 21 Century Foundation funding because we have found promising findings.

The present work was supported by JFE 21 Century Foundation. In the end of this report, we would like to thank JFE 21 Century Foundation for supporting us about this project. We have made our idea of electrochemical CO_2 pump into reality and obtained various hints for future research.

References

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