High Temperature Electrochemical Separation of Carbon Dioxide Using Molten Carbonate

Hidekazu KASAI*, Takahiro MATSUO, Minoru HOSAKA, Naobumi MOTOHIRA,
Nobuyuki KAMIYA† and Ken-ichiro OTA†

Received December 26, 1997 ; Accepted March 24, 1998

The electrochemical separation and concentration of CO₂ at high temperature (923 K) were studied using molten carbonate as the electrolyte. An electrolysis system was examined in the present study since a molten carbonate fuel cell had already demonstrated the concentration of CO₂. Maximum concentration of CO₂ after electrolysis using molten carbonate was 67%, as determined by electrolysis using Li/K molten carbonate and lithiated NiO as the cathode and anode, respectively. The cell voltage was 220 mV at a current density of 100 mA/cm². These results show that the separation and concentration of CO₂ by electrolysis proceed smoothly and theoretically. This method is expected to be applicable to CO₂ and O₂ recovery processes.

1 INTRODUCTION

1.1 General

Recently, it had been pointed out that CO₂ gas contributes significantly to the green house effect. To recover or store CO₂ effectively, it should be separated from other gases and concentrated. Various methods are available for this. Absorption of CO₂ on a solvent ^{1,2)}, adsorption by solids, ³⁾ into separation through use of an membrane, ⁴⁾ and distillation at low temperature are methods presently in use. Most of such methods are

Department of Fuel Cell Development Ishikawajima Harima Heavy Industry Co., Ltd. (1-15, Toyosu, 3-chome, Koto-Ku, Tokyo 135-8732, Japan)

† Department of Energy Engineering, Yokohama National University (79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan)

Key Words: CO₂ separation, CO₂ concentration, Molten carbonate, Electrolysis

conducted at room temperature or low temperature. However, the high temperature separation seems to be more suitable for combustion exhaust gases than low temperature methods.

1.2 Separation of CO₂ using molten carbonate

Molten alkaline carbonates or their mixtures, stable above 770 K, are available to the electrolytes of high temperature electrochemical separation systems. In this system, the diffusion species in the electrolysis carbonate ion, so that CO₂ and O₂ move from the cathode to anode selectively. Molten carbonate fuel cells (MCFC) seem to be useful owing to high energy conversion efficiency and are applicable to CO₂ separation and concentration. Figure 1 shows the mechanism of CO₂ concentration in MCFC. Gas analyses at the inlet and outlet of MCFC showed that CO₂ in

the cathode inlet gas was concentrated at the site of the anode outlet.³⁾ The concentration of CO_2 has been studied by Weaver⁴⁾ using MCFC.

Fig.1 Schematic drawing of CO_2 separation using MCFC.

And the introduction of MCFC to power plants was also studied by Miyauchi⁵⁾. Separation is also possible in other process using molten carbonate as the electrolyte.

Fig.2 Schematic drawing of CO_2 separation using molten carbonate electrolytic cell.

In this case, electrical energy is required for electrolysis. This system is shown schematically in Fig. 2. Electrode reactions are as follows,

The reaction (2) is the reverse of (1). Raw gas is introduced into the cathode and carbonate ions are formed. Carbonate ions move from the cathode to the anode. CO_2 and O_2 are produced by the decomposition of carbonate ions at the anode with a ratio of 2:1. Therefore the concentration of CO_2 at the outlet is limited to 67 %. And 33 % O_2 is obtained theoretically, that means the concentration of O_2 is also increased in this process.

Fig.3 Theoretical voltage for the CO_2 separating in case of the same O_2 pressure between cathode and anode at 923K.

The theoretical potential difference U_r for reactions (1) and (2) is expressed as follows,

$$U_r = (RT/2F) \ln(P_{\text{CO}_2(\text{a})} P_{\text{O}_2(\text{a})}^{0.5} / P_{\text{CO}_2(\text{c})} P_{\text{O}_2(\text{c})}^{0.5}) \quad (3)$$

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where (a) and (c) indicate the anode and cathode, respectively. Figure 3 shows the theoretical potential difference necessary for CO₂ separation and concentration at 923 K when oxygen pressure is the same at the cathode and anode. Only 0.09 V is required for 10 times concentration of CO₂. In this process, the overpotential arising from electrode kinetics and resistance of the electrolytic cell are key factors for the practical application. Then we attempted to confirm the concentration of CO₂ in this study.

2 EXPERIMENTAL

All components of the electrolytic cell are shown in Fig. 4. SUS310S was used for exterior material and the current collector was SUS316L. The electrolytic matrix was LiAlO₂ and the electrolyte, a 70/30 carbonate mixture of Li₂CO₃ and K₂CO₃ near the eutectic point.

Fig.4 Electrolytic cell components.

The electrolyte plates and electrodes were formed by tapecasting. Both electrodes consist of porous NiO that oxidized and lithiated with carbonate. Assembled cell are shown in Fig. 5. These

components specifications are described in Table 1. The experimental system for CO₂ separation is presented in Fig. 6.

Fig.5 Electrolytic cell for CO₂ separation.

Fig. 6 CO₂ separation system.

The electrolytic cell was placed in an electric furnace for heating. Cell temperature was measured by chromel-

alumel thermocouples inserted into the cell housing. Gas supply tubes were used for parts of circuit for measurement of cell voltage and current during CO₂ separation.

Table 1 Cell component specifications.

	Thickness (mm)	Diameter (mm)	Prosity (%)	Marerial
Cathode	0.8	40	57	Ni
Anode				(in situ NiO)
Electrolyteplate	1.0	54	58	LiAlO ₂
				Li ₂ CO ₃ /K ₂ CO ₃ =70/30

Cell voltage was measured and recorded by a data-logger (ADVANTEST R7326B). The gas composition was determined by a gas chromatograph (SHIMAZU GC-8A) and cell resistance was measured by AC 4 probes provided with a milliohm-meter (HEWLETT PACKARD 4328A). The gas flow rate was measured by a film flow meter (STEC SF-1100).

Table 2 Electrolytic cell operating cndition.

Temperature	923 K
Pressure	1 atm
Cathode gas flow rate (inlet)	175 cm ³ /min
Anode gas flow rate (inlet)	0 cm ³ /min
Current density	0 ~ 150 mA/cm ²

Cell operating conditions are indicated in Table 2. Electrolysis was conducted at 150 mA/cm² for cathode inlet gas of 10.0 % CO₂ and O₂ of 19.0 %. This concentration of CO₂ is closed to the value of the exhaust gas from electric power station.

3 RESULTS AND DISCUSSION

During electrolysis, gas composition of anode outlet is shown in Table 3.

Table 3 Gas composition.

Sample position	(%)		
	O ₂	N ₂	CO ₂
Cathode inlet	19.0	71.0	10.0
Anode outlet	33.3	0.0	66.7

Anode outlet gas was always maintained at CO₂ 66.7 %, O₂ 33.3 %. This composition is equal to the theoretical value determined based on the stoichiometricratio of carbonate ion decomposition at the anode. Unexpected products were not detected in anode outlet gas. CO₂ concentrationin the anode outlet gas was 6.7 times higher than that of cathode inlet gas. Further more in this case, increase of O₂ concentration is also possible. The flow rate of anode outlet gas agreed with the theoretical flow rate calculated from the cell current. The results are shown in Table 4.

Table 4 The current dependence of the flow rate of anode outlet gas.

(A)	Anode flow rate(cm ³ /min)	
Cell current	Theoretical	Measured
1.24	13.0	13.0
1.57	16.4	16.4
1.88	19.6	19.6

Therefore it was found that the current efficiency for CO₂ separation was almost 100 %. At 150 mA/cm² of current density, approximately 1 cm³

CO₂ separates per 1cm² electrode area from the cathode to the anode and these values correspond to 72 % CO₂ in inlet supply gas. The cell voltage, which actually decided the efficiency, significantly depended on current density during electrolysis. This relation is shown in Fig.7.

Fig.7 I-V curve of CO₂ separation at 923K.

Theoretical potential difference for CO₂ concentration of the cathode inlet gas was 87 mV from equation (3). The cell voltage approached this value at the lower current density. At high current density and constant inlet gas flow rate, the potential difference becomes greater since the partial pressure of CO₂ in cathode gas decreases due to the consumption. The similar situation occurs in MCFC and the potential is designated as Nernst loss. With change in gaseous composition considered, theoretical potential difference can be fixed by average concentrations of cathode and anode gases. The cell voltage includes potential difference of both electrodes gases, overpotential of the electrodes reactions and internal resistance of the cell (IR loss). IR loss of the cell was obtained by internal resistance and current. Therefore overvoltage (U_p) of reactions may be determined by subtracting potential difference (U_r) and IR loss (U_{IR}) from total cell voltage (U) by the equation (4):

$$U_p = U - U_r - U_{IR} \quad (4)$$

Figure 8 shows the dependence of applied voltage on current density. At 150 mA/cm² potential difference was found to be 120 mV and the IR loss was 40 mV. From equation (4) the sum of overvoltage due to cathode and anode reactions was 200 mV, which is roughly twice the cathode overvoltage of MCFC[®] in which oxygen reduction occurs. It thus indicates that the overvoltage of oxygen evolution (reverse of oxygen reduction) and that of oxygen reduction should be basically equal.

Fig. 8 Constitution of cell voltage for electrolytic CO₂ separation at 923K

Because overvoltage is determined by the efficiency of electrode, it can be improved. In actual operation of CO₂ concentration, the most suitable condition should be established.

4 CONCLUSIONS

CO₂ separation and concentration were confirmed to occur in a high temperature electrolysis cell using molten carbonate and NiO electrodes. Current efficiency was almost 100 % and stoichiometric gas composition at the anode outlet was obtained. At low current density, cell voltage was essentially the same as potential

difference of gas composition in both electrodes. At high current density, increase in IR loss, overpotential and variation in potential were obtained.

The authors express their appreciation for the financial support of NEDO (New Energy and Industrial Technology Development Organization) of the Original Industrial Technology R&D Promotion Program.

References

- 1) Handbook of Green House Effect, (Ed., H.Komiyama), p.341, IPC Publ. Tokyo (1990).
- 2) A.S.Holmes, J.M.Ryan, B.C.Price, E.Styring, *Hydrocarbon Processing*, 61, 131(1982).
- 3) T.Watanabe, T.Abe, T.Shimizu, S.Sato and T.Matsuyama, CRIEP Yokosuka Research Laboratory Rep. No. W89046.
- 4) J.L.Weaver and J.Winnick, *J.Electrochem.Soc.*, **130**, 20(1983).
- 5) T.Miyauchi, H.Uematsu, H.Hirata, T.Watanabe, K.Tanimoto and Y.Miyazaki, *Energy and Resources*, **11**, 455 (1990).
- 6) Y.Mugikura, Y.Izaki, T.Watanabe, T.Abe, T.Shimizu, S.Sato and T.Matsuyama, CRIEP Yokosuka Research Laboratory Rep.No. W9302.