Short communication

Stability and solubility of electrolyte matrix support material for molten carbonate fuel cells

Seiji Terada [a,*], Kenjin Higaki [a], Ikuo Nagashima [a], Yasuhiko Ito [b]

[a] *Akashi Technical Institute, Kawasaki Heavy Industries, 1-1, Kawasaki-cho, Akashi, Hyogo 673-8666, Japan*
[b] *Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan*

Abstract

To maintain the amount of electrolyte in the matrix at an appropriate level for long-term operation is of great importance in prolonging the life of a molten carbonate fuel cell (MCFC). Lithium aluminate, the state-of-the art material for the matrix substrate, still requires improvement in terms of the stability of crystal phase and the particle growth. Phase transformation and particle growth proceed rapidly at high temperature, at low partial pressure of carbon dioxide, or in strong basic molten carbonate. Such phenomena are considered to occur through 'dissolution–precipitation processes'. In this research, a strong correlation is observed between the solubility and the stability of $LiAlO_2$. © 1999 Elsevier Science S.A. All rights reserved.

1. Introduction

The most important problem for the commercialization of molten carbonate fuel cells (MCFCs) is the development of long-life cell components. Because of the high temperature and the high corrosiveness of the carbonate melt, deterioration of cell components restricts the cell life. Lithium aluminate, the state-of-the-art matrix support material, plays a role of maintaining the amount of electrolyte in the matrix at an appropriate level. Pore coarsening of the electrolyte matrix is one of the major factors responsible for MCFC deterioration. It is caused by the growth and the phase transformation of lithium aluminate particles during prolonged operation.

In previous work [1], the particle growth and phase transformation of lithium aluminate were found to be influenced by the environmental conditions, i.e., the temperature, the gas atmosphere, and the composition of the molten salt. Moreover, the rates of particle growth and phase transformation of lithium aluminate are considered to be markedly dependent on the solubility.

In this research, the solubilities of α- and γ-lithium aluminates under various conditions have been measured. It has confirmed that the particle growth and the phase transformation of lithium aluminate is strongly related to the solubility of lithium aluminate.

2. Experimental

2.1. Surface area of lithium aluminate particles

Immersion tests were conducted to investigate the particle growth of lithium aluminate under humidity conditions. Gamma-lithium aluminate powder (manufactured by Cyprus Foote Mineral, HSA-10) was used to measure the particle growth. The carbonate mixture was $Li:NaCO_3 = 52:48$.

Immersion tests were conducted for 500 h at 923 K in a crucible made of 99.5% pure alumina. The carbonate (14.00 g) and the lithium aluminate (6.00 g) were mixed and contained in the crucible. Steam was introduced by bubbling gas through water at 343 K. The atmospheric gas was 100% air, a mixture of 70% air and 30% CO_2, or 100% CO_2. The lithium aluminate particles were washed with a 1:1:2 mixture of acetic acid, acetic anhydride and

* Corresponding author. Tel.: +81-78-921-1636; Fax: +81-78-921-1689; E-mail: terada@ati.khi.co.jp
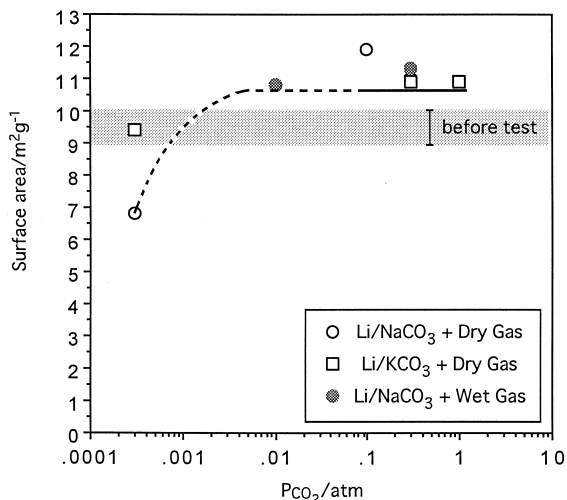
Fig. 1. Influence of steam on matrix surface area (Matrix HSA-10, 650°C, 500 h). ▨Wet Gas; CO_2 + air + 70°C-steam.

methanol. The particles were then dried. The surface area of the lithium aluminate was measured by means of the BET method.

2.2. Solubility of lithium aluminate in molten carbonates

2.2.1. Preparation of sample

The lithium aluminate sample used for the measurement of solubility was prepared as follows: (i) α-lithium aluminate powder was sintered at 1123 K for 4 h in an argon environment under 500 atm; (ii) γ-lithium aluminate powder was sintered at 1473 K for 2 h in an air environment; (iii) the tablets were pulverized; (iv) the plaques were sieved; (v) the sample was composed of particles between 1 and 2 mm in diameter.

After sintering, α-lithium aluminate particles were found, by X-ray diffraction (XRD) analysis, to contain 1 wt.% of γ-lithium aluminate phase. The α-lithium aluminate phase was not detected by XRD analysis in γ-lithium aluminate particles.

2.2.2. Solubility measurement

The carbonate mixture and the sample were put in a Au–Pd crucible. The mixture was heated and maintained at a given temperature. A portion of the molten carbonate was sampled periodically using a Au–Pd sampling cell while taking care not to include the solid lithium aluminate with the molten carbonate. Each sample was dissolved in hydrochloric acid. The solution was analyzed by means of inductively coupled plasma (ICP) analysis to determine the concentration of aluminum. The lithium aluminate solubility was obtained from the content of aluminum.

The atmospheric gas was 100% air, a mixture of 70% air and 30% CO_2, or 100% CO_2.

3. Results and discussion

3.1. Particle growth of lithium aluminate

The results of the study of particle growth of lithium aluminate reported previously [1] can be summarized as follows:
(i) particle growth occurs faster at higher temperature, in low CO_2 gas atmospheres;
(ii) particle growth occurs faster in the order: Li:NaCO₃ = 52:48 > Li:KCO₃ = 62:38 > Li:Na:KCO₃ = 43.5:31.5: 25.0;
(iii) particle growth is not affected by temperature and the melt composition in a 500-h immersion test under an atmosphere with > 10% CO_2.

In practical MCFCs, particle growth of lithium aluminate is considered to be accelerated by high humidity. The influence of steam on the particle growth of lithium aluminate has been investigated by out-of-cell tests. The influence of steam on the matrix surface area is shown in Fig. 1. In the 500-h immersion test, the particle growth of lithium aluminate is not observed with or without humidity at 923 K in an atmosphere with more than 1% CO_2.

3.2. Solubility of lithium aluminate

3.2.1. Influence of temperature, CO_2 partial pressure and carbonate composition

The effect of temperature on γ-LiAlO₂ solubility in Li:NaCO₃ is shown in Fig. 2. The solubility increases with temperature and the logarithm of solubility (log X) has a linear relation with the inverse of the absolute temperature (T^{-1}).

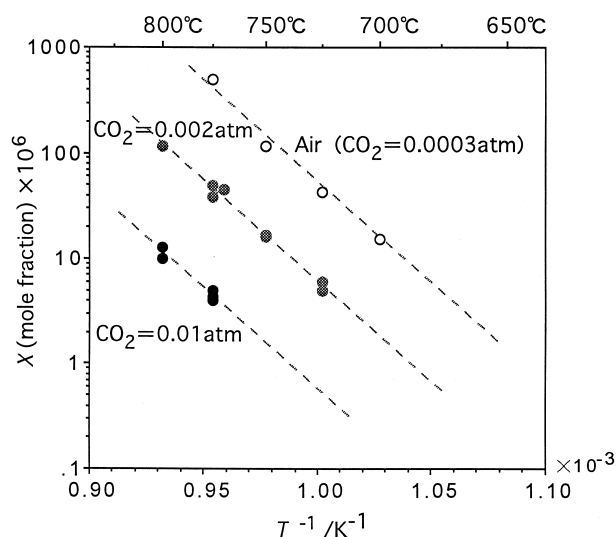The effect of CO_2 partial pressure (P_{CO_2}) on γ-LiAlO₂ solubility in Li:NaCO₃ is given in Fig. 3. The solubility

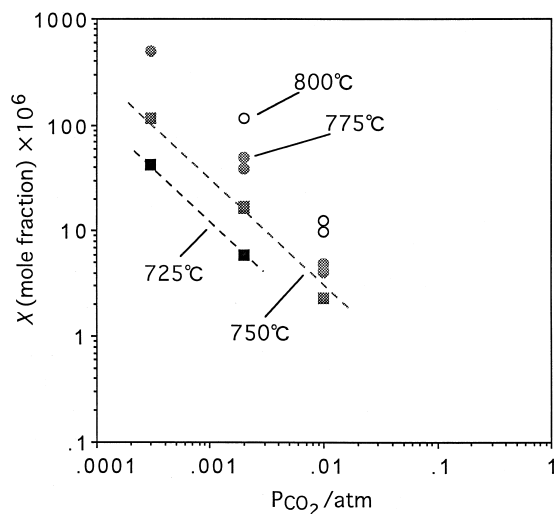Fig. 2. Effect of temperature on solubility of γ-LiAlO₂ in Li/NaCO₃.

Fig. 3. Effect of P_{CO_2} on solubility of γ-LiAlO$_2$ in Li/NaCO$_3$.

increases at lower P_{CO_2} and has an inverse relation with P_{CO_2}.

The solubilities X (mole fraction) are given by:

$$\log X = -18.4 \times 10^3/T - \log P_{CO_2} + 10.5 \qquad (1)$$

The effect of carbonate composition on γ-LiAlO$_2$ solubility is presented in Fig. 4. The solubility in Li:NaCO$_3$ is approximately three times as large as that in Li:KCO$_3$.

3.2.2. Influence of crystal phase

Changes in the amount of dissolved α- and γ-LiAlO$_2$ in Li:NaCO$_3$ with time are shown in Fig. 5. The amount of dissolved γ-LiAlO$_2$ does not change after 24 h, while that of α-LiAlO$_2$ changes with time and has a peak at about 32 to 48 h. This suggests that the phase transformation of α to γ has occurred and thus the apparent solubility of α-LiAlO$_2$ gradually decreases down to the level of γ-LiAlO$_2$ solubility.
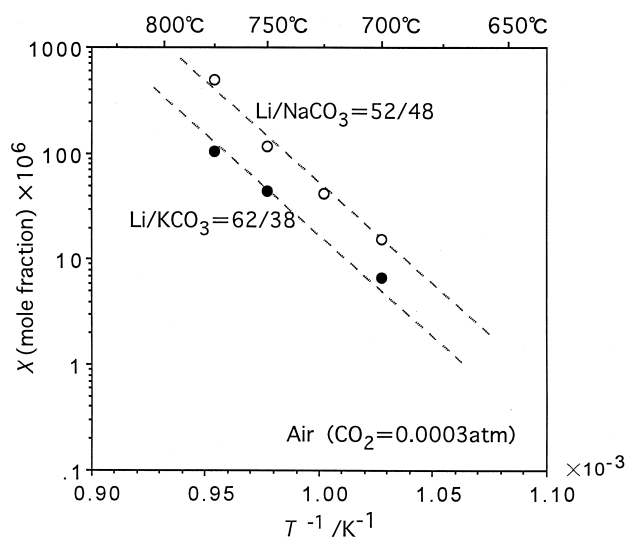

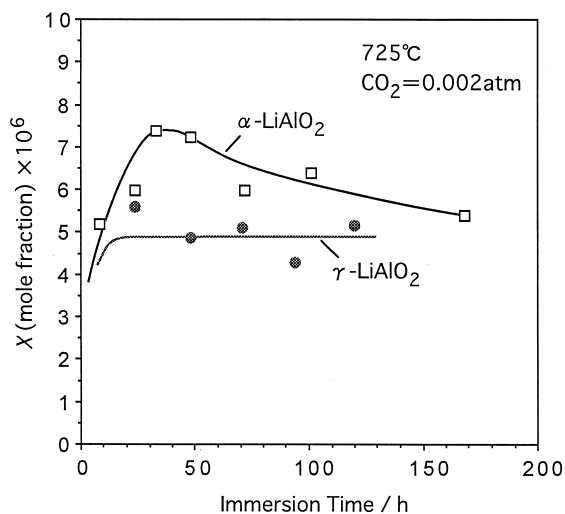
Fig. 4. Effect of carbonate composition on solubility of γ-LiAlO$_2$.

Fig. 5. Changes in amount of dissolved LiAlO$_2$ in Li:NaCO$_3$.

The amounts of dissolved α- and γ-LiAlO$_2$ in Li:NaCO$_3$ after 48 h immersion are shown in Fig. 6. The effect of temperature on the solubility of α- and γ-LiAlO$_2$ is qualitatively understood by the data in Fig. 6 although precise estimation is difficult, as mentioned above. At higher temperature (998 to 1048 K), the solubility of γ-LiAlO$_2$ is lower than that of α-LiAlO$_2$ while the solubility of α-LiAlO$_2$ is probably lower at lower temperature ($\sim$ 923 K). This is due to the difference of each dependency on temperature.

3.2.3. Relationship of particle growth and solubility

The surface area of LiAlO$_2$ particle after immersion for 500 h between 923 and 1073 K in Li:NaCO$_3$ under various conditions and the LiAlO$_2$ solubility under the same condition are summarized in Table 1. The particle growth is remarkable under such conditions where the solubility of
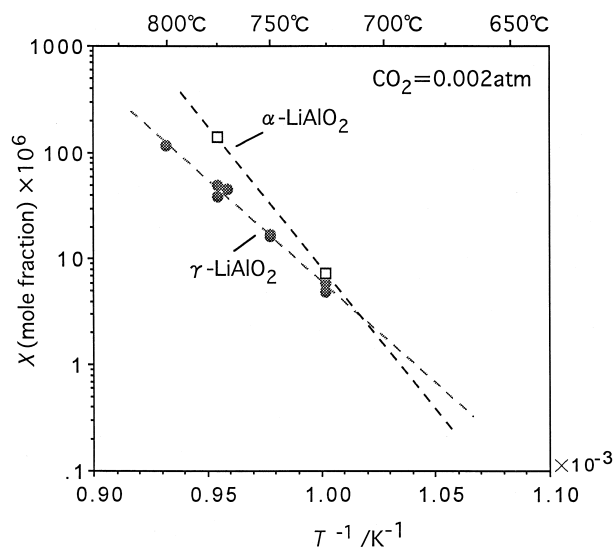

Fig. 6. Effect of temperature on amount of dissolved LiAlO$_2$ in Li:NaCO$_3$ after 48 h of immersion.

Table 1
Relationship between particle growth and solubility in Li:NaCO$_3$

P_{CO_2}	650°C	675°C	700°C	725°C	750°C	775°C	800°C
0.0003 atm	1.2	4.1	13	39	109	294	754
	6.8		< 1				
0.01 atm	0.04	0.12	0.39	1.2	3.3	8.8	23
						1.7	
0.1 atm	0.004	0.012	0.039	0.12	0.33	0.88	2.3
	11.9		11.0				
0.3 atm	0.001	0.004	0.013	0.039	0.11	0.29	0.75
	11.0		10.7				

▨Upper value: calculated solubility (mol-ppm) by experimental equation
($\log X = -18400/T - \log(P_{CO_2}) + 10.5$).
Lower value: surface area after 500 h of immersion.

LiAlO$_2$ is high. Through all series of immersion tests for 500 h, particle growth is observed when the solubility is 1 mol-ppm or more. In case of longer immersion, particle growth is supposed to occur even at lower solubility.

These results indicate that particle growth occurs via a 'dissolution–precipitation' mechanism.

3.2.4. Stability of α- and γ-LiAlO$_2$

At the cell operating temperature (923 K), α-LiAlO$_2$ is regarded to be more stable than γ-LiAlO$_2$ from both results of in-cell tests and out-of-cell tests, and is supposed to have lower solubility than γ-LiAlO$_2$, see Fig. 6. Thus, γ-LiAlO$_2$, which is relatively unstable and has higher solubility, is supposed to dissolve into the carbonate and to precipitate as α-LiAlO$_2$ during cell operation.

4. Conclusions

The results are summarized as follows.
(i) Particle growth of lithium aluminate occurs easily when its solubility is high.
(ii) Lithium aluminate transforms to a crystal phase whose solubility is lower.

These results suggest that the cell life can be predicted by measuring the solubility of the matrix support material, and that the stability of matrix support material can be improved by lowering its solubility.

References

[1] S. Terada, I. Nagashima, K. Higaki, Y. Ito, Journal of Power Sources 75 (1998) 223.