

Stability of LiAlO_2 as electrolyte matrix for molten carbonate fuel cells

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Abstract

In order to prolong the life of molten carbonate fuel cells, the amount of electrolyte in the matrix must be maintained at an appropriate level over long-term operation. Lithium aluminate, the state-of-the-art material for the matrix substrate, still presents some problems, such as crystal phase stability and particle growth. The mechanism of phase transformation and particle growth of lithium aluminate under various conditions (temperature, gas composition, carbonate composition) are investigated. Moreover, the effect of several additives for inhibiting particle growth are investigated. It is found that the allotropic phase transformation and particle growth occurs via a ‘dissolution–deposition’ mechanism. The results obtained suggest that lower temperature, higher partial pressure of CO_2 or lower basicity of carbonates are preferable to control the particle growth of lithium aluminate and that α -lithium aluminate appears more stable under typical MCFC operating conditions. Potassium tungstate inhibits the particle growth of the lithium aluminate containing β -phase. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Molten carbonate fuel cells; Electrolyte matrix; Particle growth; Phase transformation

1. Introduction

Fuel-cell power generation systems are expected to be commercialized early in the 21st century because of their high efficiency and pollution-free operation. The molten carbonate fuel cell (MCFC) in particular has the potential for much higher efficiency and can use not only natural gas but also coal gas as a fuel. Because of the high operation temperature (923 K) and the presence of corrosive molten alkaline carbonate, however, degradation of the components can easily occur.

The cell performance depends greatly on the amount of electrolyte in the cell. It is well known that one of the major causes of the deterioration of MCFCs is electrolyte depletion. Recently, it was pointed out [1] that the phase transformation and particle growth of lithium aluminate (LiAlO_2) particles, observed after a long period of cell operation, is a serious problem and must be overcome in order to attain more than 40 000 h of MCFC life. The effects cause pore coarsening of the porous matrix substrate and reduce the capillary force required to retain the

electrolyte in its pores. A number of recent studies have attempted to elucidate the mechanism of particle growth [2–4] and phase transformation [5] of lithium aluminate.

This paper presents several findings from studies of the mechanism of particle growth and phase transformation of lithium aluminate, as well as the effect of additives for inhibiting particle growth.

2. Experimental

Immersion tests were conducted to investigate the particle growth and phase transformation of lithium aluminates. Gamma-lithium aluminate powder (manufactured by Cyprus Foote Mineral Company, HSA-10) was used to measure the particle growth. A mixture of α -, β - and γ -lithium aluminate powder (Cyprus Foote Mineral Company, HSA-19), and a mixture of γ - and α -lithium aluminate powder (Cyprus Foote Mineral Company, specific surface area $\sim 10 \text{ m}^2 \text{ g}^{-1}$) were used to investigate the phase transformation. The carbonate mixtures used in this experiment were $\text{Li}/\text{NaCO}_3 = 52/48$, $\text{Li}/\text{KCO}_3 = 62/38$, and $\text{Li}/\text{Na}/\text{KCO}_3 = 43.5/31.5/25.0$.

Immersion tests were conducted for 500 h at 873, 923 and 973 K in a crucible made from 99.5% pure alumina.

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The carbonate (14.00 g) and the lithium aluminate (6.00 g) were mixed and contained in the crucible. The atmospheric gas used in the experiments was 100% air, a mixture of 70% air and 30% CO₂ or 100% CO₂. The lithium aluminate particles were washed with a 1:1:2 mixture of acetic acid, acetic anhydride and methanol and then dried. The surface area of the lithium aluminate was measured by means of the BET method and the phase was identified by X-ray diffraction (XRD) analysis.

3. Results and discussion

3.1. Influence of environmental conditions on particle growth of γ -LiAlO₂ (HSA-10)

3.1.1. Influence of temperature

The surface area of lithium aluminate was adopted as the indicator of the rate of particle growth. The surface area after immersion between 873 and 973 K and under various conditions is presented in Fig. 1. The surface area decreased with increasing temperature for a given environment and carbonate composition. It is found that the particle growth increases rapidly with increase in temperature, especially in an air atmosphere. In Air/CO₂ and CO₂ atmospheres, however, the surface area decreases very slightly with increase in temperature. It is supposed that γ -lithium aluminate is available under the operating conditions of the cell.

3.1.2. Influence of time

As the above experimental results show, in the cathode gas condition at 923 K, γ -lithium aluminate particles are expected to be stable. In order to confirm the stability, immersion tests for 8000 h were conducted in a 70% air/30% CO₂ atmosphere at 923 K. Changes in surface area with time are shown in Fig. 2. As expected, it is found

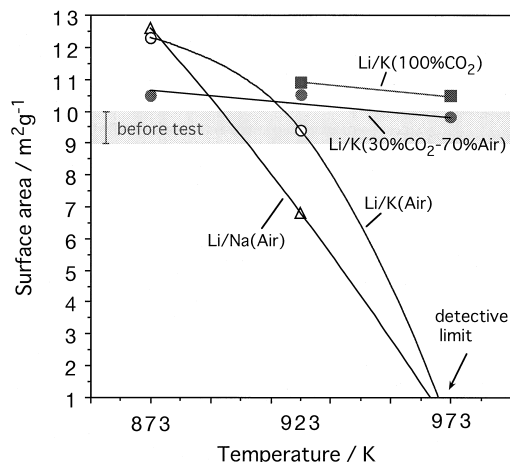


Fig. 1. Effect of temperature on surface area of γ -LiAlO₂ (HSA-10). Immersion time: 500 h.

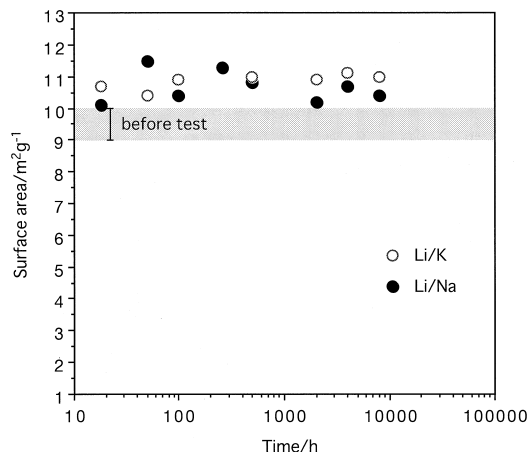


Fig. 2. Changes in surface area of γ -LiAlO₂ (HSA-10) at 923 K in 30% CO₂/70% air.

that γ -lithium aluminate particles are stable for 8000 h under the test conditions.

3.1.3. Influence of atmosphere

Changes in the surface area after immersion tests at 923 K in various environments. The surface area decreased significantly in air atmosphere (CO₂ partial pressure = 0.0003 atm) in comparison with air/CO₂ and CO₂ atmospheres (Fig. 3). It is considered that the particle growth is accelerated due to the dissolution of lithium aluminate (see below) in the low basic molten salt via a 'dissolution–deposition' mechanism. The difference in surface area between 30% CO₂ and 100% CO₂ is not, however, clearly discernible in the 500-h immersion test.

3.1.4. Influence of carbonate composition

The surface area of lithium aluminate after immersion for 500 h in Li/Na, Li/K and Li/Na/K eutectic salts is shown in Fig. 4. In an air atmosphere, the particle growth increases successively in Li/Na, Li/K and Li/Na/K

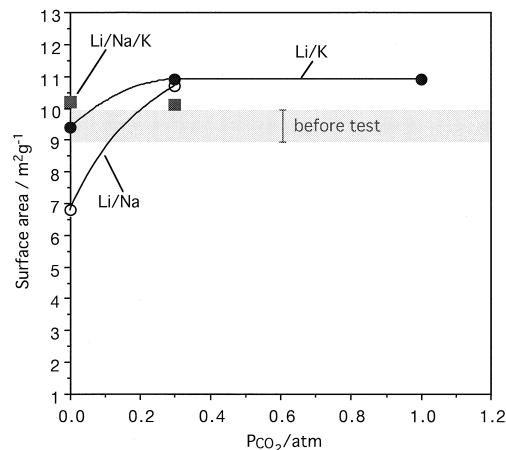


Fig. 3. Effect of partial pressure of CO₂ on surface area of LiAlO₂ (HSA-10) at 923 K. Immersion time: 500 h.

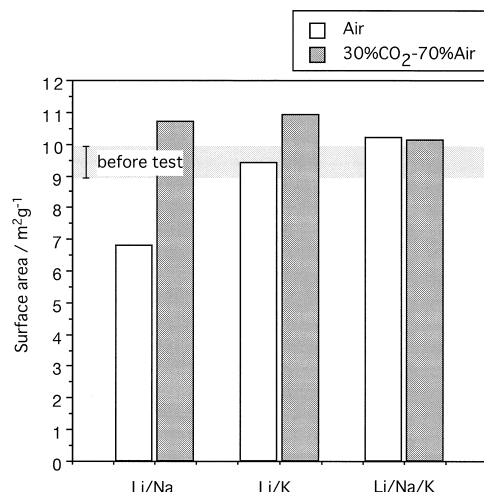


Fig. 4. Effect of electrolyte on surface area of γ -LiAlO₂ (HSA-10) at 923 K after 500 h.

melts. In 70% air and 30% CO₂ atmospheres, however, the difference in surface area is negligible in the 500-h immersion test with all three melts. This is considered to be due to inhibition of the dissociation of oxide ion from carbonate salt by the CO₂ atmosphere. The solubility of lithium aluminate decreases with increase in the partial pressure of CO₂.

By contrast, it is reported that the state-of-the-art NiO cathode undergoes increased dissolution with increase in the partial pressure of CO₂ [6]. Thus, for practical fuel cell operation, the pressure of CO₂ must be optimized.

Table 1
Effect of temperature on crystal phase of matrix

		α -LiAlO ₂ (kCPS)	β -LiAlO ₂ (kCPS)	γ -LiAlO ₂ (kCPS)	
		$2\theta = 18.7^{\circ a}$	$2\theta = 23.0^{\circ}$	$2\theta = 22.2^{\circ}$	$2\theta = 24.3^{\circ}$
Before test		0.86	2.1	1.6	0.23
After test	873 K	6.8	0.77	1.6	0.20
	923 K	9.2	0.00	2.6	0.34
	973 K	0.16	0.00	10.4	1.3

^a X-ray; Cu-K α .

kCPS: 1000 counts per second.

Immersion conditions: matrix HSA-19; electrolyte Li/KCO₃ (62/38); air; 500 h.

Table 2
Effect of gas on crystal phase of matrix

		α -LiAlO ₂ (kCPS)	β -LiAlO ₂ (kCPS)	γ -LiAlO ₂ (kCPS)	
		$2\theta = 18.7^{\circ a}$	$2\theta = 23.0^{\circ}$	$2\theta = 22.2^{\circ}$	$2\theta = 24.3^{\circ}$
Before test		0.86	2.1	1.6	0.23
After test	Air	9.2	0.00	2.6	0.34
	Air/CO ₂ (30%)	3.6	1.3	2.1	0.21
	CO ₂ (100%)	3.5	1.3	2.0	0.22

^a X-ray; Cu-K α .

kCPS: 1000 counts per second.

Immersion conditions: matrix HSA-19; electrolyte Li/KCO₃ (62/38); 923 K; 500 h.

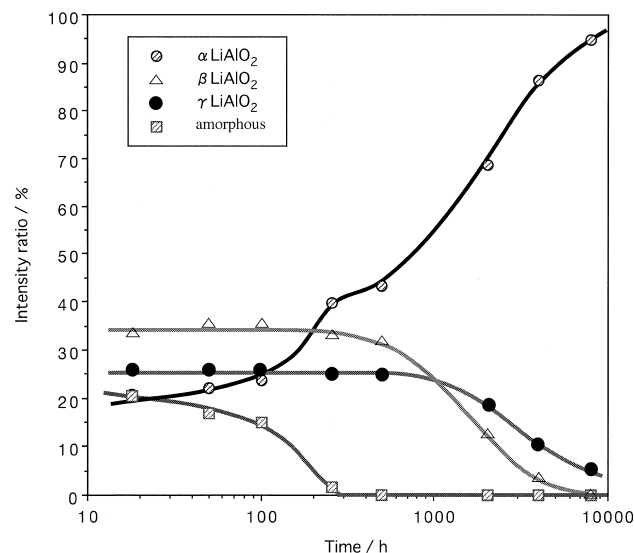


Fig. 5. Changes in intensity ratio of crystal phase in 30% CO₂ / 70% air.

3.2. Influence of environmental conditions on phase transformation of HSA-19

3.2.1. Influence of temperature

X-ray diffraction intensities of α , β and γ phases following immersion tests between 873 and 973 K are shown in Table 1. At least three different crystal structures, viz., α , β and γ , are known for LiAlO₂. The α phase is the low-temperature stable polymorph, the γ phase is the high-temperature stable one, and the β phase

Table 3
Effect of electrolyte on crystal phase of matrix

		α -LiAlO ₂ (kCPS)	β -LiAlO ₂ (kCPS)	γ -LiAlO ₂ (kCPS)	
		$2\theta = 18.7^\circ$ ^a	$2\theta = 23.0^\circ$	$2\theta = 22.2^\circ$	$2\theta = 24.3^\circ$
Before test		0.86	2.1	1.6	0.23
After test	Li/Na	5.0	0.12	5.3	0.58
	Li/K	7.3	0.51	2.1	0.26
	Li/Na/K	6.3	0.76	2.4	0.31

^a X-ray; Cu-K α .

kCPS: 1000 counts per second.

Immersion conditions; matrix HSA-19; 923 K; air; 250 h.

Table 4
Influence of additives on phase stability of matrix

		α -LiAlO ₂ (kCPS)	β -LiAlO ₂ (kCPS)	γ -LiAlO ₂ (kCPS)	
		$2\theta = 18.7^\circ$ ^a	$2\theta = 23.0^\circ$	$2\theta = 22.2^\circ$	$2\theta = 24.3^\circ$
Before test		0.86	2.1	1.6	0.23
After test	no additive	9.2	0.00	2.6	0.34
	1.4 wt.%—K ₂ WO ₄	0.86	0.00	10.8	1.2
	1.0 wt.%—MgO	2.4	0.00	10.4	1.1
	1.0 wt.%—Ga ₂ O ₃	5.9	0.00	6.3	0.75
	1.0 wt.%—CaCO ₃	7.7	0.00	3.9	0.50
	1.0 wt.%—Y ₂ (CO ₃) ₃	8.5	0.00	2.6	0.32

^a X-ray; Cu-K α .

kCPS: 1000 counts per second.

Immersion conditions: matrix HSA-19; electrolyte Li/KCO₃ (62/38); air; 923 K; 500 h.

is always metastable [7]. In these experiments, the β phase decreases throughout the range 873 to 923 K. The α phase increases significantly between 873 and 923 K and decreases at 973 K. The γ phase increases significantly at 973 K. In addition, it has been reported that the γ phase is transformed to the α phase after long-term (~ 10000 h) cell tests. From this point of view, the transformation temperature for the α phase to the γ phase, and vice versa, is considered to be between 923 and 973 K. The transformation temperature calculated by thermodynamics is, however, lower than this value. It is suggested that α -lithium aluminate should be an appropriate electrolyte-supporting material at a MCFC operating temperature of around 923 K.

3.2.2. Influence of time

In order to confirm the phase transformation of γ to α at a normal fuel-cell operating temperature of 923 K, a long-term study was conducted under an atmosphere of air/CO₂ = 70/30 in a Li/KCO₃ eutectic melt for 8000 h. The X-ray diffraction intensity ratios of α , β and γ phases, as well amorphous material, with time are given in Fig. 5. The intensity ratio at a given time is the calculated value based on the summation of intensities at 8000 h. The value for the amorphous material is calculated by subtracting from 100 the summation of the intensity ratios at 8000 h.

It is concluded that the increase in α phase is due to the decrease in amorphous material up to 300 h and due to the

decrease of β and γ phases after 500 h. In addition, it is found that the α phase is stable under an atmosphere of 70% air/30% CO₂ in a Li/KCO₃ eutectic melt at 923 K from the point of the decrease in the γ phase and the increase in the α phase after 1000 h.

3.2.3. Influence of environment and carbonate composition

The influence of the atmosphere and the composition of the molten salt on the phase transformation of lithium

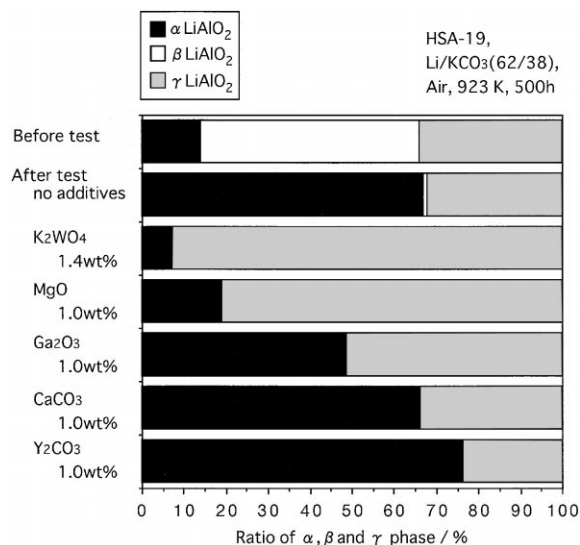


Fig. 6. Effect of additives on phase stability of matrix.

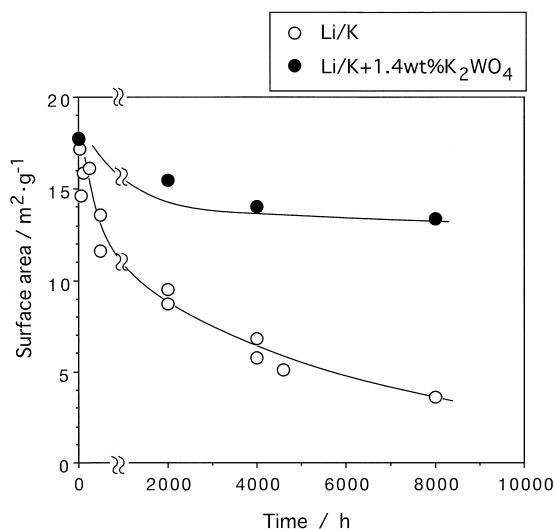


Fig. 7. Changes in surface area of HSA-19 at 923 K. Immersion conditions: (a) Li/K, 30% CO_2 /70% air; (b) HSA-19, electrolyte/ LiAlO_2 (HSA-19) = 70:30.

aluminate as shown in Tables 2 and 3, respectively. In all cases, the β phase decreases, and the α and γ phases increase. It is considered that the β phase is transformed to both α and γ phases simultaneously, although the α phase is reported to be stable at the temperature of 923 K. The transformation of the β phase increases with decrease in the CO_2 partial pressure and for melts in the order Li/Na, Li/K and Li/Na/K. The ratio of the transformation rate of α : γ before the immersion test is approximately 1:2 and becomes larger after the immersion test. This means that the transformation rate of β and α is larger than that of β to γ . The difference in the ratio is, however, slight in the Li/Na melt as well as in an air atmosphere. Although the phase transformation is considered to depend on the atmosphere and the composition of the melt, the relationship between the transformation rate and the basicity of the melt is not clear at present.

3.3. Effect of additives on inhibiting particle growth and phase transformation

The effect of additives on inhibiting particle growth and phase transformation of HSA-19 was investigated, since

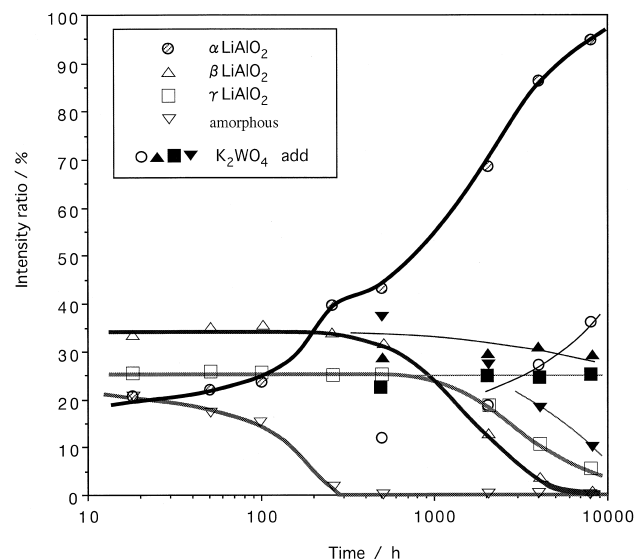


Fig. 8. Changes in crystal phase with K_2WO_4 at 923 K.

the rates of β to α and β to γ transformation are supposed to depend on the gas atmosphere and the composition of melt. The candidate materials were potassium tungstate, magnesium oxide, gallium oxide, calcium carbonate, and yttrium carbonate for controlling the basicity of melt. The amount of additive was 1.4 wt.% for potassium tungstate, which has been reported to be effective for preventing anode sintering [8], and 1.0 wt.% for the other compounds.

The X-ray diffraction intensities of the α , β and γ phases after immersion tests with the additives in the melt are given in Table 4 and Fig. 6. The ratio of the β to α and the β to γ transformation rate changes with some additives. The possibility of inhibiting particle growth and phase transformation is indicated by using an appropriate additive as well as by optimizing both the gas atmosphere and the melt composition.

Potassium tungstate is the most effective of the additives in the 500-h immersion test. Figs. 7 and 8 show the change with time of the surface area and the X-ray diffraction intensities of the α , β and γ phases of HSA-19 doped with potassium tungstate, respectively. It is found that adding potassium tungstate can inhibit both the particle growth and the phase transformation of HSA-19.

Table 5
Phase transition of α - and γ - LiAlO_2 matrix

		α - LiAlO_2 (kCPS)	β - LiAlO_2 (kCPS)	γ - LiAlO_2 (kCPS)	
		$2\theta = 18.7^\circ$ ^a	$2\theta = 23.0^\circ$	$2\theta = 22.2^\circ$	$2\theta = 24.3^\circ$
Before test		7.3	0.00	8.4	1.1
After test	Air	0.5	0.00	21.8	2.9
	CO_2 (100%)	11.4	0.00	9.2	1.2

^a X-ray; Cu-K α .

kCPS: 1000 counts per second.

Immersion conditions: matrix $\alpha + \gamma$; electrolyte Li/ KCO_3 (62/38); 923 K; 500 h.

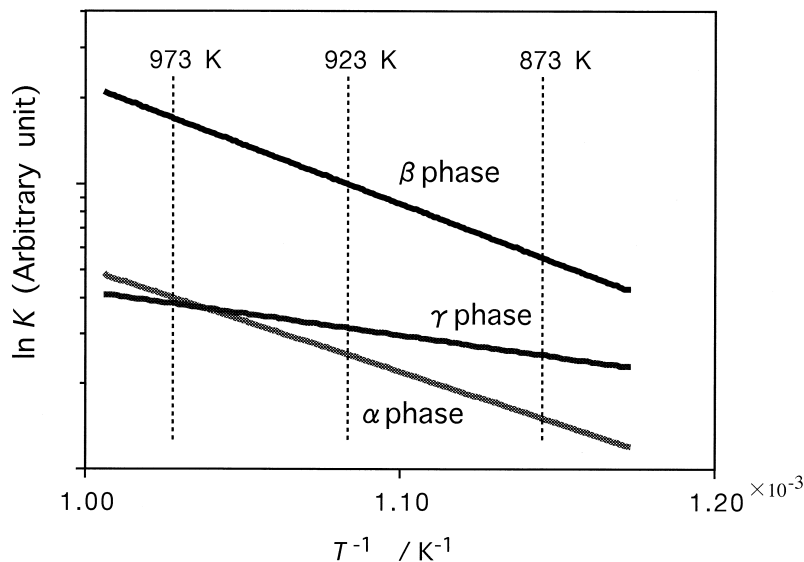


Fig. 9. Equilibrium constant of dissolution reaction of LiAlO_2 (predicted line).

3.4. Phase transformation of α - and γ -lithium aluminate

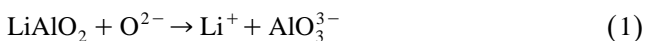
When using HSA-19 with β phase, it was not able to elucidate correctly which transformation occurred, γ to α or α to γ , due to the occurrence of the β to α transformation or the β to γ transformation in the initial stages. Therefore, a mixture of α and γ lithium aluminate instead of HSA-19 was used to investigate the phase transformation.

Table 5 shows the X-ray diffraction intensities of the α , β and γ phases after the immersion test with a mixture of α and γ particles at 973 K. In air, the α phase is transformed to the γ phase. In CO_2 atmosphere, the α phase increases but the γ phase show little change. Moreover, the α phase does not appear to transform to the γ phase.

3.5. Mechanism of particle growth and phase transformation

There are two mechanisms considered in particle growth and phase transformation. One is a 'grain boundary migration' mechanism and the other is a 'dissolution–precipitation' mechanism. The activation energy of particle growth is much larger than that of phase transformation. In a MCFC, the rates of particle growth and phase transformation are considered to depend on the rates of solubility, diffusion, and precipitation of the lithium aluminate.

The dissolution reaction of lithium aluminate is as follows [1]:



Describing the equilibrium constants of α -, β -, and γ -lithium aluminate as K_α , K_β , and K_γ , respectively, it is found from the test results that the order is $K_\beta > K_\gamma > K_\alpha$ at 873 K and $K_\beta > K_\alpha > K_\gamma$ at 973 K. The logarithm of

the equilibrium constant is proportional to the reciprocal of the absolute temperature, as shown in Fig. 9. This relationship can be used to explain the following test results.

(i) The equilibrium constants of the dissolution reaction for any kind of lithium aluminate are large at high temperature. In other words, the rate of particle growth is large at higher temperature.

(ii) The equilibrium constant of the meta-stable (β) phase is larger than that of the stable (α and γ) phase.

(iii) For a mixture with α , β , and γ phases, the meta-stable phase (β) with the larger equilibrium constant dissolves and precipitates as a stable phase (α and γ) with a smaller equilibrium constant. Then, the particle grows.

(iv) For a mixture including α and γ phases, the transformation of γ to α occurs at 873 K and α to γ at 973 K.

4. Conclusions

In order to prolong cell life, the behaviour of particle growth and phase transformation has been investigated. In addition, the effect of additives on inhibiting particle growth and phase transformation has been examined. The results are summarized as follows.

(i) Particle growth of lithium aluminate occurs faster at higher temperature, in low CO_2 gas atmospheres, and in strong basic melt.

(ii) The transformation of γ to α occurs at 873 K and that of α to γ at 923 K in air atmosphere and $\text{Li}/\text{KCO}_3 = 62/38$. It is found that like α phase is stable at 873 K, the γ phase is stable at 973 K, and the transformation temperature of α to γ is between 923 and 973 K.

(iii) In the case of lithium aluminate including the meta-stable phase (β) but not the stable phases (α and γ), the meta-stable (β) is transformed to α and γ phases. The

decrease in the β phase is larger in low CO_2 atmospheres and in CO_2 atmosphere; amorphous material changes to the α phase at 973 K.

(iv) The behaviour of particle growth and phase transformation can be explained by a ‘dissolution–precipitation’ mechanism.

(v) In order to operate a MCFC for a long time, low temperatures and high CO_2 atmospheres with a weak basic carbonate salt are preferable. The state-of-the-art NiO cathode, however, undergoes increased dissolution with increase in the partial pressure of CO_2 . Optimization of CO_2 pressure is needed for practical fuel cell operation.

The addition of potassium tungstate can inhibit particle growth and phase transformation of lithium aluminate with meta-stable phase (β).

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