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Kinetics of the $\alpha \rightarrow \gamma$ phase transformation in $LiAlO_2$ under various atmospheres within the 1073–1173 K temperatures range

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Stability of the $LiAlO_2$ crystallographic forms within given temperature limits, especially the occurrence of $\alpha \rightarrow \gamma$-$LiAlO_2$ phase transformation, is one of the crucial problems of application of this compound as solid phase matrix for electrolyte in molten carbonate fuel cells (MCFC). In this study, kinetics of this transformation has been investigated under atmospheres of CO_2 and N_2, both dehydrated and water vapor containing, at constant temperatures 1073, 1123 and 1173 K, in the α-$LiAlO_2$ powder prepared in a molten salts ambience. The increasing γ-$LiAlO_2$ phase concentration in the α-$LiAlO_2$ sample was determined by X-ray diffractometry as dependent on time of heating the sample. Similar measurements have been performed with α-$LiAlO_2$ samples after 5 h of heating at temperatures within 923–1223 K. The results of this investigation suggest the existence of some chemical steps of the overall phase transformation process, probably the decomposition of the double lithium-aluminum oxide at the α-$LiAlO_2$ particle surfaces *via* a surface-nucleation mechanism. This step determines the overall transformation rate, strongly depending on gas atmosphere and on molten carbonate ambience (solution-deposition mechanism). This transformation does not take place below 973 K, which is the upper temperature limit of the MCFC operation.

1. Introduction

Lithium aluminate, $LiAlO_2$, is used as solid matrix material for the fabrication of electrolyte tiles for molten carbonate fuel cells (MCFC). These devices operate within the 870–1000 K temperature range. The opinion about the phase composition of $LiAlO_2$ optimal for this purpose has evolved with the MCFC development. Forty years ago Lehmann and Hesselbarth have found that $LiAlO_2$ exists in two allotropic forms—α and γ ones [1]. Lejus and Collongues have determined the crystallographic structure of these phases [2]. The α-$LiAlO_2$ form is trigonal with a NaCl-like arrangement, elongated along 3-fold axis, where both cations have octahedral coordination (coordination number of both cations is 6, with equidistant oxygen neighbors). The structure consists of alternating sheets of LiO_6 and AlO_6 octahedra. Structural group is $R\underline{3}m$, the crystallographic density, $d_\alpha = 3.401$ g/cm^3 [3]. Poeppelmeier *et al.* have reported the recent values of the lattice parameters of this phase, $a = b = 2.7993$ Å and $c = 14.180$ Å. The observed Li—O and Al—O bond distances are 2.084 and 1.926 Å, whereas those predicted from the ionic radii are 2.16 and 1.94 Å, respectively [4]. The γ-phase is tetragonal, with an arrangement similar to the crystobalite where all atoms have tetrahedral coordination. Both cations have coordination number 4. The Al atoms are in place of the silicon and the lithium atoms occupy the tetrahedral holes in the array of the aluminum tetrahedra [3]. The crystallographic parameters of this form are $a = 5.169$ Å and $c = 6.268$ Å, the crystallographic density is $d_\gamma = 2.615$ g/cm^3. These parameters are very similar to those of sodium aluminate γ-$NaAlO_2$ [5]. Chang and Margrave have documented existence of the third allotropic form of $LiAlO_2$, the β one, where Al would show a mixed, both octahedral (α-phase) and tetrahedral (γ-phase) coordination (an inverse application by Chang and Margrave of α and γ symbols to the main forms of $LiAlO_2$ must be notified [6]). The lattice parameters of the monoclinic β-phase with HBO_2 arrangement would be $a = 8.147$ Å, $b = 7.941$ Å, $c = 6.303$ Å. The problem of the stability limits of all these phases is crucial for fabrication of the MCFC electrolytic tiles. Value of the $\alpha \rightarrow \gamma$-phase transformation temperature is still ambiguous. As early as Lehmann and Hesselbarth have discussed it, the α-form is called "the low-temperature phase," the γ-form—"the high-temperature" one [1]. These authors have claimed 873 K as the upper temperature limit of the α-$LiAlO_2$ stability and have found that in air and in the presence of Li_2CO_3, the calcination of the α-form above this temperature results by a fast transformation in the γ-phase. However, using X-rays diffraction method as well as by dilatometric and differential thermal analysis, Lejus have presented proves that the $\alpha \rightarrow \gamma$-$LiAlO_2$ transformation takes place at 1170 K—the lower temperature limit of α-$LiAlO_2$ to γ-$LiAlO_2$ transformation [7]. According to Marezio and Remeika, the inverse, $\gamma \rightarrow \alpha$-phase transformation would be possible at 1123 K only under high pressure of 35 kbar [8, 9]. Fisher has determined 1173 K as transformation temperature of β to γ-$LiAlO_2$ [10]. Distinct differences among stability limits reported by cited authors have given rise to further attempts of determination of the $\alpha \rightarrow \gamma$-$LiAlO_2$ transformation temperature in the MCFC operation conditions. Samples of $LiAlO_2$ investigated by them have been prepared by various methods and the established stability limits should be considered as characteristic for any kind of this material. Moreover, within these temperatures the solid phase transformations in $LiAlO_2$ are very slow and it is very difficult to distinguish between apparent stability—resulting only from the negligible rate of the phase transformation in curse- and the thermodynamic stability of the given crystallographic form of this phase. Hence, the respective part of the Li_2O-Al_2O_3 phase diagram reported in the literature [11] is not precisely determined and the temperature limits of the stability of two $LiAlO_2$ crystallographic forms—the upper limit of the α-phase stability and the lower one of the γ-phase—are not finally established until now. For $LiAlO_2$ prepared by a given method, the question what crystallographic form of $LiAlO_2$, the α- or γ- is practically the stable one in the MCFC operation conditions, may be resolved only by kinetic investigation. The pure γ-$LiAlO_2$ phase has been considered from long time as the only stable within MCFC operation temperatures (870–1000 K) and, therefore, as the must appropriate solid matrix material for MCFC electrolyte tiles. However, the nowadays development of these devices has furnished the data not consistent with the earlier results. After long time of the MCFC operation, in the electrolyte tiles fabricated using the γ-$LiAlO_2$ form as the solid component, some α-phase concentration has been detected. The resulting degradation in the $LiAlO_2$ morphology and, therefore, in the matrix porous structure increases the molten electrolyte losses during the MCFC stacks operation.

Some authors have shown that the surrounding gas atmosphere as well as the presence of liquid components influences the temperature at which the $\alpha \rightarrow \gamma$-$LiAlO_2$ transformation may take place. Finn [12] studied the influence of environment on the temperature of α-, β- and γ-allotropic transformations. In absence of molten carbonate, this author has not found the transformation of α-$LiAlO_2$ up to 1110 K. In air, within 1030–1110 K temperature range, the transformation of β-$LiAlO_2$ to γ-$LiAlO_2$ occurs after 24 h of heating; hence the β-phase seems to be less stable than the α-one. Finn has determined also the temperature of α-$LiAlO_2$ to γ-$LiAlO_2$ transformation in various atmospheres—in air, CO_2 and $8H_2 + 2CO_2$ mixture saturated with water. In air, powdered samples of α-$LiAlO_2$ have been transformed in the γ-phase at temperature as low as 875 K. The transformation temperature increased when the reducing atmosphere of humid $8H_2 + 2CO_2$ was applied. Finn has shown that the α-$LiAlO_2$ is less stable in air and in reducing atmosphere than in CO_2. In ambience of the molten carbonates, the β-$LiAlO_2$ transforms in the γ-$LiAlO_2$ at temperature lower than in absence of the liquid phase. One may conclude, however, that the α- and β-phases transform to the γ-$LiAlO_2$ above 975 K and the last allotropic form shows to be stable above this temperature. The rate of the transformation is highest in air and lowest in CO_2 atmosphere, because the last gas suppresses the hydrolysis of molten carbonate and OH^- ions concentration. Also the rate of crystal growth of the $LiAlO_2$ allotropic forms is higher in presence of molten carbonates, suggesting the solution-deposition mechanism.

Hydrolysis process of γ-$LiAlO_2$ has been widely studied by Rasneur and Charpin [13]. These authors have revealed the formation of complex hydroxide $LiOH \cdot 2Al(OH)_3 \cdot H_2O$ as the product of this hydrolysis at relative humidity ≥ 3. Below this humidity limit the water vapor corrosion of γ-$LiAlO_2$ is very low because the formation of a sorbed water monolayer on the solid phase is not complete. Kawamura *et al.* [14] have investigated adsorption and/or absorption of water on the porous $LiAlO_2$ samples in the 473–1073 K temperature range. These authors have concluded that both adsorption and absorption mechanisms play role in $LiAlO_2$—water vapor system. The amount of adsorbed/absorbed water decreases strongly with temperature.

Tomimatsu *et al*. have studied kinetics of this transformation [15]. They have proved that the lower limit of this transformation temperature depends on the CO_2 partial pressure above the solid $LiAlO_2$ sample and on the particle diameter and the powder morphology. The α-$LiAlO_2$ form has been shown stable up to ca. 1023 K in conditions corresponding to those in the MCFC electrolyte tiles i.e., when $LiAlO_2$ was wetted with molten alkali carbonates under CO_2 partial pressure from 0 to 1 atm. In air, within this temperature range the α-$LiAlO_2$ phase transforms in the γ-one after few hours. These authors have concluded that the α-$LiAlO_2$ is stable at temperature of 1023 K and under high partial pressure of CO_2, whereas the γ one is stable at higher temperatures and under low CO_2 partial pressure.

Ribeiro *et al.* have investigated the influence of temperature on the structural properties of $LiAlO_2$ prepared by various methods [16]. According to their results, the lowest temperature of γ-phase formation is about 1020 K. Suski and Tarniowy have shown that in the temperature range up to 1023 K the α-$LiAlO_2$ phase is the only product of the reaction

$$Li_2CO_3 + Al_2O_3 \rightarrow 2LiAlO_2 + CO_2, \qquad (1)$$

carried out in air, and that this phase is not transformed in the γ-crystallographic form, even when this transformation is performed in the excess of the molten $Li_2CO_3 + Na_2CO_3$ eutectic, where such transformation may be kinetically enhanced by the liquid ambience of the reaction [17]. The atmosphere above the mixture reacting according to Reaction 1, contains CO_2—the product of Li_2CO_3 decomposition. According to these authors, the temperature of the upper stability limit of the α-$LiAlO_2$ form prepared in Reaction 1 is higher than the temperature of the normal MCFC operation.

All studies of the kinetics of the $LiAlO_2$ allotropic form transformations give a rather complex picture of factors governing the temperature at which these transformations really may take place. In general, one may conclude that the solid phase transformation temperature limits reported in the cited articles are not the reversible phase transformation temperatures, but only kinetic parameters strongly depending on transformation conditions. Such parameters are characteristic for the material prepared by the given method.

It should be emphasized the way of the $LiAlO_2$ preparation in Reaction 1, because the presence of molten phase containing Li_2CO_3 and the CO_2 containing atmosphere, creates circumstances resembling those of the MCFC operation. Hence, it seems reasonable to investigate first of all the temperature stability limit for the α-$LiAlO_2$ produced by this way. Investigation described in this paper have been carried out in order to clarify some problems in this mater, namely the influence of gas atmosphere, as well as, partially, the influence of molten carbonate ambience, on these temperature limits. We present the results of the kinetic investigation of the $\alpha \rightarrow \gamma$-$LiAlO_2$ transformation performed within the 1073–1173 K, because within this temperature range this transformation may be evidently observed. Attention has been focused on the influence of the water vapor atmosphere on the transformation kinetics.

2. Experimental

2.1. Reagents

Li_2CO_3, Na_2CO_3, KCl and NaCl used in this study were reagents grade. Al_2O_3 was chromatography grade. γ-$LiAlO_2$ used for preparing X-ray standard has been produced by Aldrich Co. The pure α-$LiAlO_2$ crystallographic form has been prepared by an original method [18] of the synthesis according to Reaction 1, carried out in molten NaCl-KCl eutectic mixture. Reaction mixture and chlorides in weight ratio 1:3 was homogenized in the ball mill during 0.5 h and the synthesis has been carried out during 2 h at 1073 K. Chlorides have been dissolved in water and the obtained $LiAlO_2$ has been heated at 573 K during 3 h. It has been carefully verified by the X-ray diffraction method that the only product of this synthesis is the pure α-$LiAlO_2$ phase.

2.2. Procedure

Series of Pt crucibles (1.2 cm^3), each crucible containing 2 g sample of α-$LiAlO_2$, were heated at constant temperature in an electric furnace (VEB Electro Bad Frankenhausen), under controlled atmosphere. Depending on the temperature, various numbers of crucibles has been used in the given series. Temperature was controlled within $\pm 5^\circ$ by Pt-Pt10Rh thermocouple inserted in the sample. In regular time intervals adequate to the reaction temperature, the samples were taken out from the furnace one by one and their phase composition was analyzed by X-ray methods as described below. This procedure has been carried out at 1073, 1123 and 1173 K, under atmosphere of CO_2 and N_2 dehydrated on molecular sieves or saturated by the H_2O vapor at 343 K (water partial pressure was 31.2kN/m^2).

2.3. Determination of the phase composition of $LiAlO_2$ by X-ray reflects intensity

All X-ray diffraction measurements have been carried out using the Philips X'pert Polycrystal Diffractometer with the PW3020 goniometer. The Cu cathode has been applied. Throughout this work the $\alpha \rightarrow \gamma$-$LiAlO_2$ transformation factor, $S_\gamma(t)$, is defined as the time dependent mole fraction of this component in the reacting sample, X_γ, i.e., as the actual ratio of the number of γ-form moles, $n_\gamma(t)$, to the total number of $LiAlO_2$ moles, n, in the sample

$$S_\gamma(t) = X_\gamma(t) = n_\gamma(t)/n. \qquad (2)$$

In order to determine the values of this parameter in a given sample, standard mixtures of α- and γ-$LiAlO_2$ containing 0.2, 0.4, 0.6, and 0.8 mole fraction of α-$LiAlO_2$, respectively, have been prepared. In each of these mixtures, the intensities of characteristic peaks for α- and γ-$LiAlO_2$ phases have been determined, corresponding to crystallographic planes {*hkl* 104} and {*hkl* 101} for the α- and γ-form, respectively. Using these values as dependent on the mole fraction of γ-$LiAlO_2$ in the standard mixtures, two calibration curves have been constructed, permitting us the determination of the conversion factor values in the samples under study. Both calibration curves are presented in Fig. 1.

The first calibration curve corresponds to the function defined as

$$f_1(X_\gamma) = I_\gamma(101)/I_\gamma^0(101), \qquad (3)$$

where X_γ is the mole fraction of γ-$LiAlO_2$ in the sample, $I_\gamma(101)$ and $I_\gamma^0(101)$ are intensities of the diffraction peak corresponding to {*hkl* 101} plane for the given reacting mixture and of the pure γ-$LiAlO_2$ phase, respectively. As one can see in Fig. 1, the respective calibration relationship is linear with a sufficient approximation. Analogous procedure in respect to the dependence of the α-$LiAlO_2$ characteristic diffraction peak on the mole fraction of this crystallographic form, has not been applied because the inconvenient

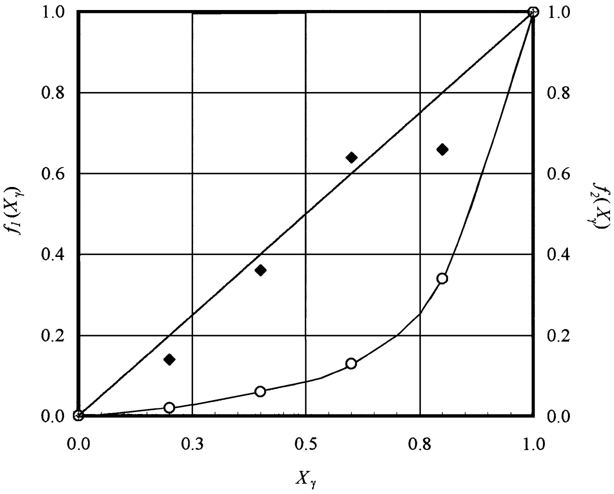

Figure 1 Dependencies of the $f_1(X_\gamma)$ and $f_2(X_\gamma)$ function values (see Equations 3 and 4) on the γ-$LiAlO_2$ mole fraction, X_γ, in standard $\alpha+\gamma$-$LiAlO_2$ phase mixtures. Solid rhombs—$f_1(X_\gamma)$, open circles—$f_2(X_\gamma)$.

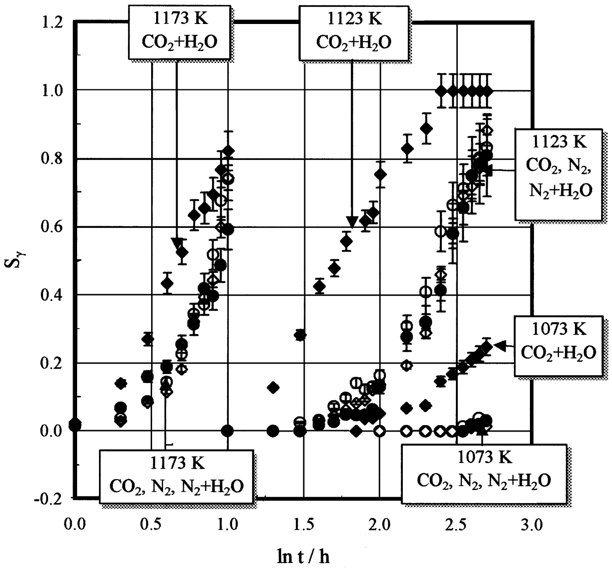

Figure 2 Dependencies of the α to γ-$LiAlO_2$ transformation parameter, S_γ, (mean values of determined by two methods) on the logarithm of transformation time, at 1073, 1123 and 1173 K, under CO_2 (open rhombs), humid CO_2 (solid rhombs), N_2 (open circles) and humid N_2 (solid circles) atmospheres, respectively. Max. percent errors are reported.

non-linearity of this relationship. The second calibration curve in Fig. 1 corresponds to the function defined as

$$f_2(X_\gamma) = I_\gamma(101)/I_\alpha(104), \tag{4}$$

where $I_\alpha(104)$ is the intensity of the diffraction peak corresponding to the $\{hkl\ 104\}$ crystallographic plane in the phase mixtures. In this study, the values of the $\alpha \rightarrow \gamma$-$LiAlO_2$ transformation factor have been determined from the characteristic peak intensity values using both calibration functions 3 and 4. The differences between the transformation factor values determined using these two methods, are within the accuracy limits of the X-ray diffraction method. Therefore, the results reported in the next sections of this article, are the mean values of parameters measured by both methods.

3. Results

3.1. Values of the α- to γ-$LiAlO_2$ conversion factor at 1073, 1123 and 1173 K, under dehydrated and humid CO_2 and N_2 atmospheres

The values of the $\alpha \rightarrow \gamma$-$LiAlO_2$ phase transformation factor, determined at three temperatures: 1073, 1123 and 1173 K, in CO_2 and N_2 atmosphere, both dehydrated and containing H_2O vapor, are compared in Fig. 2, as dependent on logarithm of time of heating the sample at a given constant temperature. One see that at 1073 K—the lowest temperature of investigation—the phase transformation process in CO_2, N_2 and humid N_2 atmospheres is very slow, but measurable after times as long as 300 h, whereas it is observable sooner (after ca. 100 h) in humid CO_2. At 1123 K, the γ-$LiAlO_2$ phase concentration starts to be measurable after 10 h in humid CO_2 and after ca 30 h in other 3 atmospheres. The conversion rates at 1173 K in humid CO_2 and in other atmospheres show similar difference, in humid CO_2 the concentration of the γ-$LiAlO_2$ phase increases already during first hour of transformation. This fact is certainly not a result of some uncontrolled differences in carrying out the series of measurements, because the investigation has been performed in the consequence: firstly all atmospheres at 1073 K, then at 1123 K and at 1173 K on the end. Dependencies for 1123 and 1173 K permit us to determine the values of the half-transformation time ($S_\gamma = 0.5$). Table I presents these values.

3.2. Values of the α- to γ-$LiAlO_2$ conversion factor in the α-$LiAlO_{2(Solid)}$ and α-$LiAlO_{2(Solid)}$ + $(0.53Li_2CO_3 + 0.47Na_2CO_3)_{(Liquid)}$ systems in air after 5 h of conversion, as dependent on temperature

In Fig. 3 are reported values of the α-$LiAlO_2$ concentration in samples after 5 h of isothermic conversion,

TABLE I Approximated values of the half-transformation (0.5 S_γ) time for the α to γ-$LiAlO_2$ phase transformation under dehydrated and humid CO_2 and N_2 atmospheres, respectively, at 1123 and 1173 K

	Values of the half-transformation factor (h)			
Temperature (K)	CO_2 dehydrated	CO_2 humid	N_2 dehydrated	N_2 humid
1123	225	55	225	225
1173	8	5	8	8

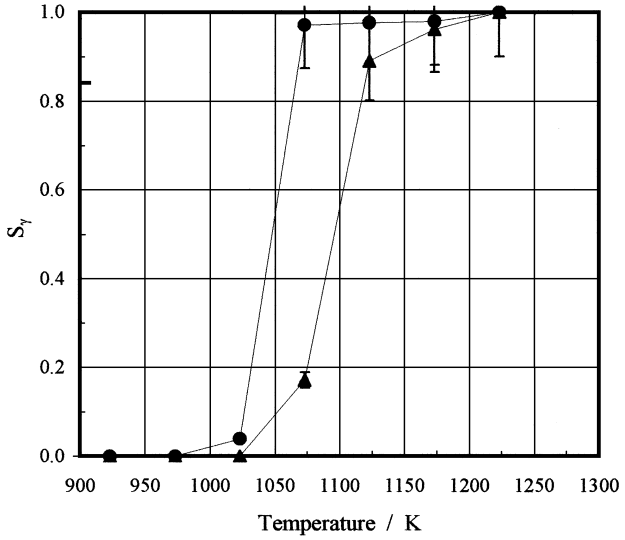

Figure 3 Values of the α to γ-LiAlO$_2$ transformation parameter after 5 h of heating in air, $S_\gamma(5)$, as dependent on temperature. Triangles—transformation in solid phase, circles—transformation in the molten $Li_2CO_3 + Na_2CO_3$ ambience.

as dependent on conversion temperature. These results correspond to conversion of the pure α-LiAlO$_2$ phase as well as of this phase dispersed in the $0.53Li_2CO_3$–$0.47Na_2CO_3$ molten eutectic mixture. The presence of molten carbonate liquid phase seems to enhance this transformation.

4. Discussion and conclusions

4.1. Approximate temperature of the $\alpha \rightarrow \gamma$-LiAlO$_2$ solid phase transformation

As it may be concluded on basis of the results presented in Fig. 1, at 1070 K, first traces of the γ-LiAlO$_2$ phase appear in the samples after a long time of heating. The dependencies presented in Fig. 3 prove that in the air atmosphere the $\alpha \rightarrow \gamma$-LiAlO$_2$ transformation is observable at temperature as low as ca 1020 K, i.e., at the upper temperature limit of the MCFC operation. This observation, allows us to place the approximate temperature of the $\alpha \rightarrow \gamma$-LiAlO$_2$ phase conversion not below 1020 K, i.e., above the upper limit of the MCFC operation temperature range. This result is approximately consistent with the previous observation [17] that in LiAlO$_2$ used by us the $\alpha \rightarrow \gamma$-LiAlO$_2$ transformation does not take place below ca. 1050 K. In other words, the α-LiAlO$_2$ phase may be stable up to this temperature.

4.2. Kinetic parameters of the $\alpha \rightarrow \gamma$-LiAlO$_2$ solid phase transformation

Let us describe the kinetics of the $\alpha \rightarrow \gamma$-LiAlO$_2$ phase transformation in terms of the empiric relationship, usually applicable to processes when the nucleation effect takes place in solids [19]

$$S_\gamma(t) = 1 - e^{-k^{\mathrm{n}}(t^{\mathrm{m}})}, \qquad (5)$$

where k (in sec^{-1}) and m (dimensionless) are constant parameters informing us about the nucleation mechanism. The values of both parameters may be determined from the dependence of the transformation factor $S_\gamma(t)$ on time under the form of the linear relationship resulting from a simple rearrangement of Equation 5

$$\ln\left[\ln\frac{1}{1 - S_\gamma(t)}\right] = \ln k + m \ln t, \qquad (6)$$

In Figs 4–7, values of the transformation factor at three temperatures and in four various atmospheres are presented in respective coordinate system, according to Equation 6. The values of logarithm of the k and of the m parameters, calculated for respective experimental relationships, are reported in Table II. The values of m parameter placed within limits $1.0 \leq m \leq 2.3$ merit comments. These results seem to indicate rather the phase-boundary, one dimensionally controlled mechanism than the diffusion controlled one. This is consistent with the established influence of the gas atmosphere and the molten carbonate ambience on the kinetics of the $\alpha \rightarrow \gamma$-LiAlO$_2$ transformation process.

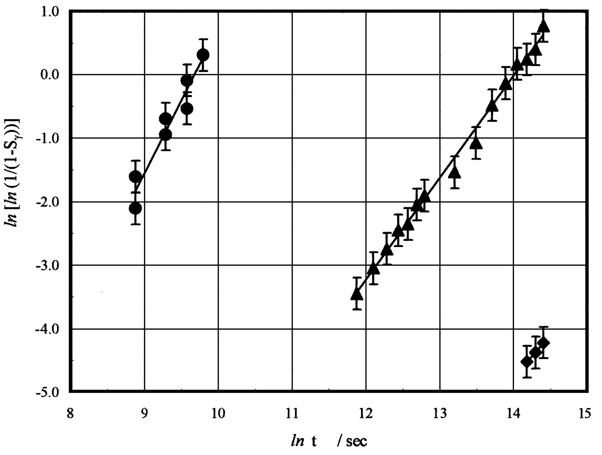

Figure 4 Values of the ln[ln1/(1 − S_γ)] functions as dependent on the logarithm of time of the α to γ-LiAlO$_2$ transformation under dehydrated CO$_2$ atmosphere. Rhombs—1073 K, triangles—1123 K, circles—1173 K. Max. percent errors are reported.

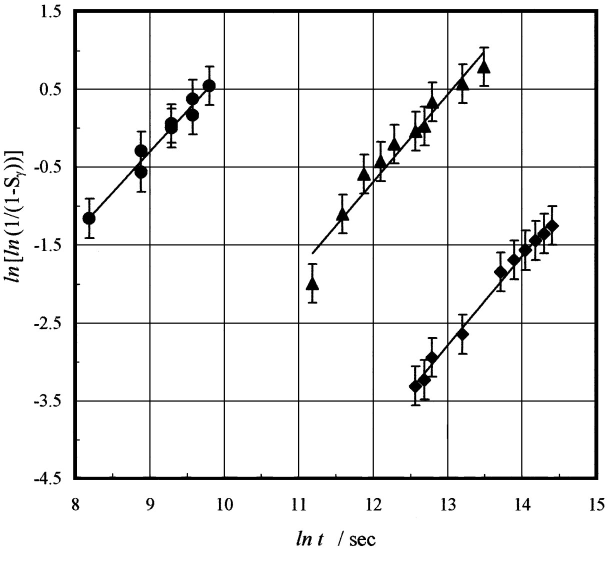

Figure 5 Values of the ln[ln1/(1 − S_γ)] functions as dependent on the logarithm of time of the α to γ-LiAlO$_2$ transformation under humid CO$_2$ atmosphere. Rhombs—1073 K, triangles—1123 K, circles—1173 K. Max. percent errors are reported.

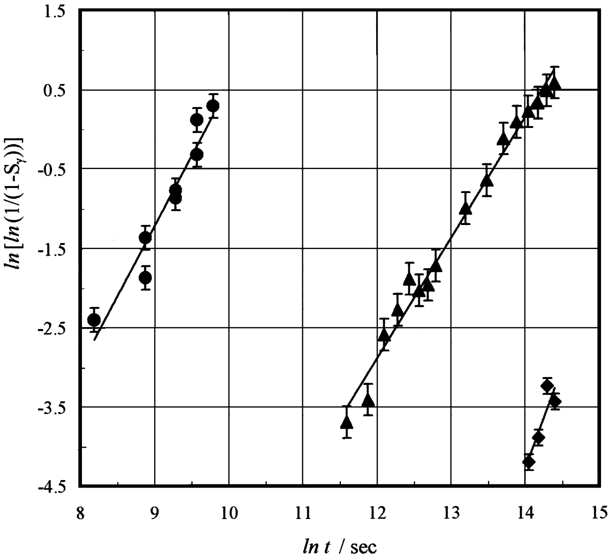

Figure 6 Values of the $\ln[\ln 1/(1-S_\gamma)]$ functions as dependent on the logarithm of time of the α to γ-LiAlO$_2$ transformation under dehydrated N$_2$ atmosphere. Rhombs—1073 K, triangles—1123 K, circles—1173 K. Max. percent errors are reported.

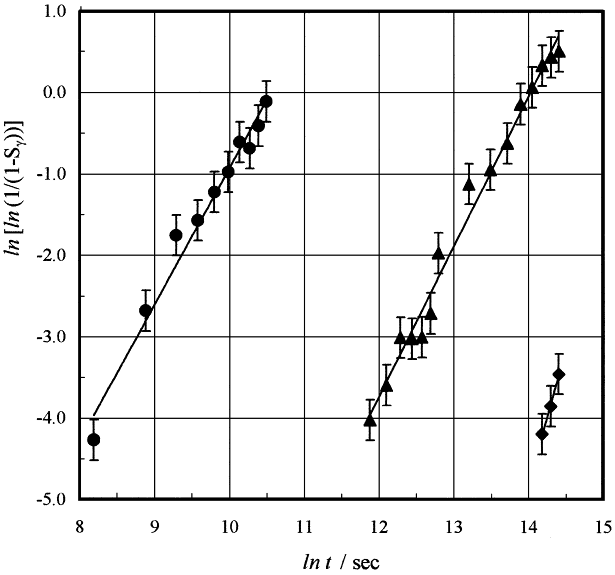

Figure 7 Values of the $\ln[\ln 1/(1-S_\gamma)]$ functions as dependent on the logarithm of time of the α to γ-LiAlO$_2$ transformation under humid N$_2$ atmosphere. Rhombs—1073 K, triangles—1123 K, circles—1173 K. Max. percent errors are reported.

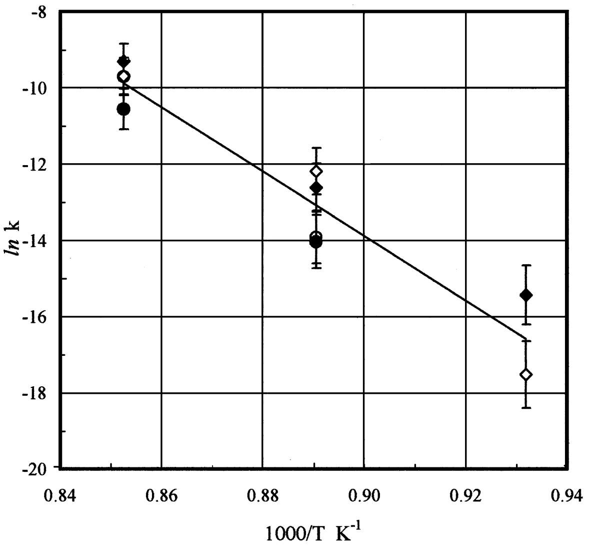

Figure 8 Dependence of the logarithm of k values for the α to γ-LiAlO$_2$ transformation process, calculated by Equation 11, on the inverse temperature, $1/T$. Atmospheres: dehydrated CO$_2$—open rhombs, humid CO$_2$—solid rhombs, dehydrated N$_2$—open circles, humid N$_2$—solid circles, respectively.

4.3. Apparent activation energy of the $\alpha \rightarrow \gamma$-LiAlO$_2$ phase transformation

Values of the k parameter determined at three temperatures permit us to estimate approximately, according to Arrhenius linear relationship, the apparent activation energy of the $\alpha \rightarrow \gamma$-LiAlO$_2$ phase conversion,

$$\ln k = B - \frac{E_a}{RT}, \tag{7}$$

where E_a (Jmol^{-1}) is the apparent activation energy, B is the experimental constant, R—gas constant, T—absolute temperature. In Fig. 8 are reported values of ln k for the $\alpha \rightarrow \gamma$-LiAlO$_2$ phase transformation at three temperatures under four gas atmospheres, as dependent on $1/T$. The approximated values of the apparent activation energy of the $\alpha \rightarrow \gamma$-LiAlO$_2$ phase transformation are within 550 (humid CO$_2$)–730 (CO$_2$) kJmol^{-1}. The precision of the determination of this parameter is estimated as ±10%.

4.4. General remarks and conclusions

In the previous work, the evidence of some $\alpha \rightarrow \gamma$-LiAlO$_2$ transformation has been searched in the product of Reaction 1 carried out up to 1023 K [17]. This reaction has been performed in air, the partial pressure of CO$_2$—the reaction product—was nearly 1 atm and the α-LiAlO$_2$ form has not been transformed in the γ-one up to 1023 K, consistently with Tomimatsu results [15]. However, it has been shown in this investigation that the

TABLE II Values of parameters of Equation 6 determined at temperatures 1073, 1123 and 1173 K, under dehydrated and humid CO$_2$ and N$_2$ atmospheres, respectively

Temperature	1073 K		1123 K		1173 K	
Parameters of Equation 6	m	$\ln k'$	m	$\ln k'$	m	$\ln k'$
CO$_2$ dehydrated	1.358	−23.776	1.849	−22.529	2.290	−22.169
CO$_2$ humid	1.152	−17.764	1.124	−14.179	1.048	−9.734
N$_2$ dehydrated	2.520[a]	−39.552[a]	1.513	−21.043	1.757	−17.028
N$_2$ humid	3.312[a]	−51.176[a]	1.848	−25.921	1.682	−17.739

[a] Imponderable statistics.

dependence of the α-$LiAlO_2$ stability temperature limits on atmosphere is more complicated than Tomimatsu *et al.* have suggested. In the present study the $\alpha \rightarrow \gamma$-$LiAlO_2$ has been investigated both under pure CO_2 and under pure N_2 atmospheres. Consistently with results of Finn [12], in the ambience of both gases, the lowest temperature at which γ-$LiAlO_2$ has been found in the transforming mixture after some hundred hours, was ca. 1073 K. The presence of water has not influenced the kinetics of the transformation in N_2 atmosphere. The rates under dehydrated CO_2 and N_2, as well as under $N_2 + H_2O$ are the same within the limits of the measurement precision. As it has been reported above, the rate increases approximately ten times, when this transformation is carried out in CO_2 with water vapor content.

The phase boundary nucleation mechanism of the $\alpha \rightarrow \gamma$-$LiAlO_2$ transformation, as well as all results of this investigation indicate, that there are some steps in the overall phase transformation process in the $LiAlO_2$ prepared by Reaction 1 for the need of this investigation. During the $\alpha \rightarrow \gamma$-$LiAlO_2$ transformation, the observed Al—O and Li—O distances in the α-$LiAlO_2$, equal 1.92 and 2.08 Å [4], respectively, become shortened to 1.76 and 2.06 Å in the γ-phase lattice [20]. One can believe that during the rearrangement in the $LiAlO_2$ lattice some Li_2O is evolved. Evidently, the $\alpha \rightarrow \gamma$-$LiAlO_2$ phase transformation, in the given ambience of gases and—like in the MCFC electrolytes—in presence of molten carbonates, is a stepwise chemical process. The decomposition of the double lithium-aluminium oxide taking place on the surface of α-phase grains seems to be the one of steps of this phase transformation. This surface is in contact with gas and with the liquid carbonate and the products of the $LiAlO_2$ decomposition are absorbed by gas and liquid phases. The last step would be the reconstruction of the $LiAlO_2$ compound and crystallization of γ-phase with more compact network structure. In presence of water, the transient, surface products of the α-$LiAlO_2$ grains decomposition are LiOH and $Al(OH)_3$ (Rasneur and Charpin claim the formation of double hydroxide [14]). However, as we have proved, the transient hydrolysis product formation does not influences the rate of the $\alpha \rightarrow \gamma$-$LiAlO_2$ phase transformation; its rate is the same in both dehydrated and humid N_2 atmospheres. Moreover, nearly the same rate of this process has been determined in dehydrated CO_2 atmosphere. The excess of CO_2 gives not the best conditions for this transformation, because this gas suppresses the formation OH^- ion in the surface layer. This results show, that neither the formation of solid Li_2CO_3—which is possible due to the surface reaction of Li_2O and CO_2—nor the surface hydrolytic decomposition of α-$LiAlO_2$ are sufficient to enhance the phase transformation. In the humid CO_2 atmosphere, however, the double system Li_2CO_3—LiOH may be formed, liquid at the temperature above 1070 K. The transformation takes place more easily throughout the layer of this liquid. For that reason, the highest rate of the transformation process has been observed in the air atmosphere, with some partial pressure of both CO_2 and water vapor.

It seems to us very probable that this mechanistic hypothesis formulated in respect to $LiAlO_2$ used in this investigation may be extended also on other powders of this compounds when produced by the high-temperature method according to Reaction 1. The results of this investigation prove also that for the appropriate conditions of the α-$LiAlO_2$ preparation one may expect stability of this phase within all temperature range of the MCFC operation.

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