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The phase stability of solid $LiAlO_2$ used for the electrolyte matrix of molten carbonate fuel cells

LESZEK SUSKI, MIROSLAWA TARNIOWY
Institute of Physical Chemistry of the Polish Academy of Sciences, Molten Salts Laboratory, Zagrody 13, 30-318 Kraków, Poland
E-mail: nbsuski@cyf-kr.edu.pl

$LiAlO_2$ is used as a solid matrix for molten carbonate fuel cell (MCFC) electrolyte tiles. These devices operate within the temperature range of 870–970 K. The γ-crystallographic form of this compound is commonly used for fabrication of these matrix tiles. The thermodynamic stability of this phase within the above temperature range is not clear and it is reasonable to consider the $\gamma \rightarrow \alpha$ transformation to take place in solid $LiAlO_2$ in presence of molten alkali carbonates. In order to establish the crystallographic form of the compound that forms as a product of reaction between the liquid Li_2CO_3 and solid Al_2O_3, the kinetics of $LiAlO_2$ formation has been investigated. Values of conversion factor as a function of the reaction time have been determined both for a stoichiometric reaction mixture and for mixtures with an excess of the liquid $0.53\ Li_2CO_3 + 0.47\ Na_2CO_3$ eutectic. The simultaneous determination of the reaction conversion factor and the relative intensity of the characteristic x-ray peak for the $\alpha - LiAlO_2$ form in the reaction mixture have shown that, within 843–973 K, in experiments of ca 100–10 hours, respectively, only this phase of $LiAlO_2$ is formed. These results may explain the presence of some $\alpha - LiAlO_2$ amount in the MCFC electrolyte tiles after long run tests of these devices.

1. Introduction

In molten carbonate fuel cells (MCFC) a ceramic material, chemically stable in alkali carbonates melt, is used as a matrix to support the molten carbonate electrolyte. The state-of-the-art technology consists in preparing this matrix from a slurry composed of submicron particles of this ceramic material and of organic solvent and binder [1]. Thin sheets of the slurry undergo drying and burning out of organic component followed by impregnation with an appropriate alkali carbonate mixture. Sandwiched between two porous electrodes, the impregnated sheet forms the electrolyte plate for the MCFC. Lithium metaaluminate ($LiAlO_2$), in the form of a submicron powder with high surface area, is used commonly as the ceramic matrix. Any changes in the properties of its particles during the MCFC operation may alter seriously the ability of the matrix to retain molten electrolyte and, therefore, decrease the operation parameters of the cell.

Within the temperature range of 870–970 K, the equilibrium

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

is strongly shifted to the right. This is the basis of the methods of the metaaluminate synthesis. In early studies of the kinetics of this reaction, it was assumed that $LiAlO_2$ formation takes place in two steps. The first is lithium carbonate decomposition according to the acid-base equilibrium

$$Li_2CO_3 \Leftrightarrow Li_2O + CO_2, \qquad (1a)$$

whereas the second one is the reaction between two solid oxides

$$Li_2O + Al_2O_3 = 2\,LiAlO_2. \qquad (1b)$$

The rate of the first step is controlled by the CO_2 partial pressure above the reaction mixture, or in other words by the rate of CO_2 transport from the reactor. The kinetics of the second step should be discussed in terms of solid state reactions in the mixture of the powdered grains of two solid reagents. Usually, the rates of such reactions are controlled by diffusion of reaction components through the product layer formed on the reagent grains. It seems evident to the authors that, if the transport of CO_2 is established by a good flushing of the reactor atmosphere, the rate of the overall process according to reaction (1) should be controlled by the diffusion of the solid reactants through the $LiAlO_2$ solid layer covering the grains.

As has been shown by many authors, $LiAlO_2$ may exist in three crystallographic forms, α, β and γ [2]. The temperature and pressure limits of the thermodynamic stability of these phases are still not sufficiently clear, in spite of a number of studies devoted to this problem [3–5]. The phase diagrams of $Li_2O + Al_2O_3$ system, proposed by Byker *et al.* [6] and by Weirauch and Grady [7], consider temperatures above 1000 K. On the basis of short term tests, performed by MCFC developers in the last decade, the γ-$LiAlO_2$ has been considered to be the most stable form in molten alkali carbonate melts at the typical MCFC operation temperature (ca 870 K).

According to some authors, however, the $\alpha \rightarrow \gamma$ transformation does not seem to be irreversible, as it should be in case of the thermodynamic stability of γ-phase at this temperature. Moreover, recently a reverse transformation of $\gamma \rightarrow \alpha - LiAlO_2$ has been observed in MCFC electrolyte plates after 2-years test [1, 8]. Therefore, the thermodynamic stability of γ-$LiAlO_2$ up to 970 K may be considered doubtful and its apparent stability a results of very slow kinetics of phase transformations in the solid metaaluminate. The presence of the molten alkali carbonates may accelerate transport of solid reactants and the kinetics of the overall processes taking place in small, submicron particles of the solid $LiAlO_2$ matrix.

The $0.62Li_2CO_3 + 0.38K_2CO_3$ eutectic melt has been used by the majority of MCFC developers in recent years and most of the results relevant to $LiAlO_2$ have been obtained with electrolyte plates containing this liquid electrolyte. Some developers have recently experienced success with electrolyte plates containing the alternative, $0.53Li_2CO_3 + 0.47Na_2CO_3$ eutectic melt [9–11]. Different acid-base equilibria in these two molten electrolytes affect the solubility of $LiAlO_2$. The solubility is higher in the molten Li/Na carbonate eutectic system than in the Li/K one. Therefore, in the former electrolyte, one can expect a greater reactivity of solid $LiAlO_2$ submicron particles than in the last one.

The purpose of this work is the identification of the crystallographic form of $LiAlO_2$, produced in reaction (1) within the MCFC operation temperature range as well as the solid phase transformation, in excess of molten Li/Na carbonate eutectics. It is expected that the thermodynamically stable crystallographic form of $LiAlO_2$ should appear in course of this reaction. Therefore, we assume that even if the α-$LiAlO_2$ is the first product of reaction (1), the γ-phase, if it is really stable at these temperatures, should appear already before the conversion according to reaction (1) is complete. Consequently, the kinetics of reaction (1) is to be followed parallel to the identification of the crystallographic form.

2. Experimental procedure

In the first part of this investigation the kinetics of the overall reaction (1) has been studied in order to identify what kinetic model is adequate to describe this reaction under isothermal conditions. The time dependency of the reaction conversion factor in the $Li_2CO_3 + Al_2O_3$ system has been determined by measurement of the mass of CO_2 evolved. The reaction mixtures were prepared by mixing Li_2CO_3 (chemical grade) and Al_2O_3 (chromatography grade) in a vibrating mill with alundum balls during 0.5 hour. The resulting mixtures were composed of 10–20 μm grains. Reactions between Li_2CO_3 and Al_2O_3 were performed in alundum crucibles at constant temperatures. 17.6 g of the equimolar $Al_2O_3 + Li_2CO_3$ mixture was held at a constant temperature ($\pm 1^\circ$) in an alundum crucible inserted in a tubular electric furnace under a dried nitrogen atmosphere, flowing through the furnace at 2.5 ml/min rate. Temperature was controlled directly in the reaction mixture with the 10PtRh-Pt thermocouple in an alundum tube. CO_2 evolved in the reaction was flushed by the flowing nitrogen and was absorbed in 38% KOH solution in water. The mass of the cylinder containing this solution was continuously determined with an accuracy of ± 0.01 g. At the end of the reaction the final mass of reacting mixture was also determined.

A continuous determination of the reaction (1) conversion factor by weighting the evolved CO_2 does not permit simultaneous monitoring of the phase transformation by the X-ray diffraction method. In the second part of this study a separate investigation of the phase transformation was conducted. The alundum crucible with 1 mole of the reaction mixture was placed in the electric furnace at the reaction temperature. After a determined heating time, a specimen for X-ray analysis was taken from the reaction mixture. Then the reaction mixture was returned to the furnace. Reactions between Li_2CO_3 and Al_2O_3 have been performed in alundum crucibles at constant temperatures. The same reactants as in first part of this investigation have been used. The sample of reaction mixture was put in the furnace at reaction temperature, after some time taken out, weighted, a specimen for X-ray investigation was extracted from the reaction mixture, and then the reaction mixture returned to the furnace. X-ray diffraction measurements have been carried out using the CPS 120 type (IMEL Co.,) counter and the Siemens rotating anode. This procedure permitted us to follow the progress of reaction (1) and this of the $\alpha \rightarrow \gamma$ phase transformation in the reaction product, simultaneously.

3. Kinetics of the reaction in the $Al_2O_3 + Li_2CO_3$ system within the temperature range 873–1023 K

3.1. Results

Dependencies of the reaction (1) conversion factor on reaction time, as determined at 873, 973 and 1023 K, respectively, are presented in Fig. 1. The conversion factor has been defined as

$$S(t) = \frac{\Delta m_{CO_2}(t)}{m_{CO_2}}; 0 \leq S(t) \leq 1, \qquad (2)$$

where $S(t)$ and $\Delta m_{CO_2}(t)$ denote the conversion factor and the increment of the KOH solution mass as dependent on the reaction time t, respectively, m_{CO_2} is the mass of CO_2 corresponding to the full conversion of reacting mixture.

The values of $S(t)$ parameter at three temperatures are presented in Fig. 1 as 1-$S(t)$ functions. For these results correlation equations of the type

$$(1-S(t)) = a(t)^6 + b(t)^5 + c(t)^4 + e(t)^3 + f(t)^2 + g(t) + 1 \qquad (3)$$

have been calculated. The a–g constant values are reported in Table I up to 10 decimal places.

3.2. Applicability of the nucleation model to reaction (1)

According to classical review published by Hulbert 1969 [12], the nucleation model would be applicable

TABLE I Constant values of the correlation polynomial $(1 - S) = a\,t^6 + b\,t^5 + c\,t^4 + d\,t^3 + e\,t^2 + + f\ t + 1$ for the conversion factor of the reaction $Li_2CO_3 + Al_2O_3 = 2\ LiAlO_2 + CO_2$, ($S$), as dependent on reaction time (t), at three temperatures. R – correlation coefficient

Temperature/K	873	973	1023
R^2	0.9988	0.9968	0.9905
a	$-4.0277501171.10^{-25}$	$8.83370258460.10^{-23}$	$-4.0444422350.10^{-21}$
b	$1.4153409250.10^{-20}$	$-2.44913670970.10^{-18}$	$6.4586666355.10^{-17}$
c	$-5.9294681538.10^{-17}$	$2.6804963831.10^{-14}$	$-3.9360154685.10^{-13}$
d	$-3.2369787556.10^{-12}$	$-1.4687157997.10^{-10}$	$1.1148436789.10^{-9}$
e	$5.1791941283.10^{-8}$	$4.2945727626.10^{-7}$	$-1.3463286060.10^{-6}$
f	$-3.2411414335.10^{-4}$	$-7.4637518447.10^{-4}$	$1.4896233586.10^{-4}$

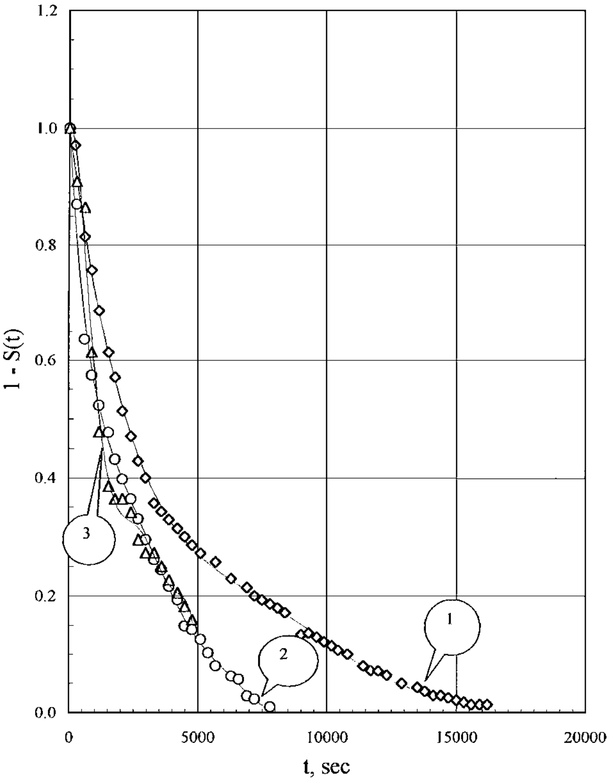

Figure 1 Values of $1 - S(t)$ functions at 873 K (diamonds), 973 K (circles) and 1023 K (triangles). Lines 1, 2 and 3 correspond to the polynomial correlation functions in Table I.

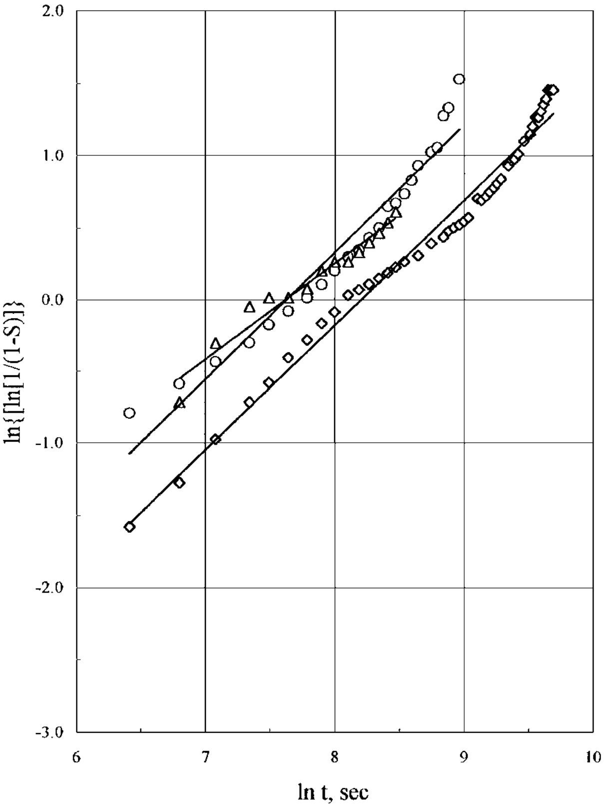

Figure 2 Equation 4 applied to the results in Fig. 1 at 873 K (diamonds), 973 K (circles) and 1023 K (triangles), respectively.

to the reaction (1) if a dependency of the conversion factor on time, the Avrami equation, of the form

$$\ln \frac{1}{1 - S(t)} = kt^m \tag{4}$$

is observed. Here, m is a parameter dependent on the reaction mechanism, nucleation rate and geometry of nuclei. Plots of the logarithmic form of those relationships, constructed on base of the data reported in Table I, are presented in Fig. 2.

These plots show a satisfying linearity permitting us the estimation of the m parameter values, which are 0.87, 0.88 and 0.67 at 873, 973 and 1023 K, respectively. According to Hulbert, these values indicate diffusion control of the decreasing nucleation rate up to conversion factor of ca 0.8. The diagrams presented in this figure do not cover the period of the first 500 seconds of nuclei formation. The values of the m parameter indicate rather two-dimensional growth of nuclei. The increase of the slope values in final stage of the reaction is the result of decrease of the nucleation rate.

3.3. Kinetic model of the reaction (1)

Dependencies of the conversion factor on reaction time presented in Fig. 1, have been analyzed in terms of kinetic–mechanistic models presented in the review of Hulbert [12], namely those of Jander, Kröger and Ziegler, Zhuravlev, Lisokhin and Tempelman and Ginstling – Braunstein. It has been find that only the last model [13] based on the modified parabolic law of the product layer on reacting grains, (GB), is adequate to these dependencies. According to this model the $S - t$ function should fulfill the equation

$$k't = 1 - 0.67S - (1 - S)^{0.33}, \tag{5}$$

where constant k' equals 2 $kD/(r_o)^2$. In the last definition, D denotes diffusion constant of the reactant throughout the product layer, r_o is the initial mean grain radius of the reactants.

Linear representations of the functions according to Equation 5, for three temperatures, may be seen in Fig. 3. The values of the correlation coefficients R^2 of the respective linear dependencies are 0.997, 0.980 and 0.973 at 873, 973 and 1023 K, respectively and

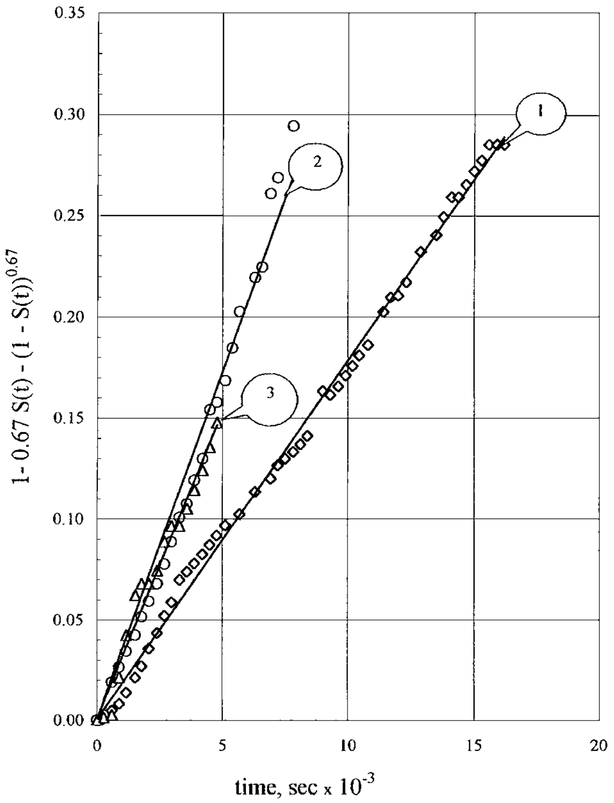

Figure 3 Equation 5 applied to the results in Fig. 1 at 873 K (diamonds), 973 K (circles) and 1023 K (triangles), respectively.

support the applicability of this model to the kinetics of reaction (1).

3.4. Kinetic order of the reaction (1)

Kinetic order (γ) values of the reaction (1) at three temperatures has been calculated using the dependencies of the (3) type in the kinetic formula under logarithmic form

$$\log\left[-\frac{d(1-S(t))}{dt}\right] = \log k - \gamma(1 - S(t)). \qquad (6)$$

As calculated by differentiation of the regression functions (see Table I.), the respective plots are very sensitive to all, even smallest, irregularities of the experimental dependencies. Therefore, only on base of the general trends shown by these plots, one can very roughly estimate the reaction order values at three temperatures as nearly 1. This is generally consistent with conclusion on the diffusion control of reaction (1).

4. Identification of the crystallographic form of LiAlO$_2$ as a product of reaction (1) within the temperature range of 843–1023 K

4.1. Determination method of the conversion factor of reaction (1)

In this part of the study, the conversion factor of reaction (1) after the n-th run of reaction mixture heating, S_n, may be calculated according to equation

$$S_n \cong S_{n-1} + \frac{m_{n-1} - m_n - \Delta m_{n-1}}{m_0^{\mathrm{Al_2O_3}}} \cdot \frac{m_{n-1}}{m_{n-1} - \Delta m_{n-1}} \cdot \frac{M^{\mathrm{Al_2O_3}}}{M^{\mathrm{CO_2}}}; 0 \le S_n \le 1, \qquad (6)$$

where n is the number of the heating run, S_{n-1} - the conversion factor after the $(n-1)$-th heating run, m_n- the mass of the reaction mixture after n-th heating run, $\Delta m_{(n-1)}$ - the mass of the X-rays specimen extracted after the $(n-1)$-th heating run, $m_0^{\mathrm{Al_2O_3}}$ - the mass of Al$_2$O$_3$ in the initial reaction mixture, $M^{\mathrm{Al_2O_3}}$ and $M^{\mathrm{CO_2}}$ are mole masses of Al$_2$O$_3$ and CO$_2$, respectively.

4.2. Determination method of the relative intensity of x-rays diffraction peak characteristic for α-LIALO$_2$

In this work, relative concentrations of α-LiAlO$_2$ vs. the maximum values of this parameter obtained at the end of reaction (1) were established using the intensities of the X-rays peaks on diffractograms. In this purpose the following procedure has been applied.

On diffractograms obtained for n-th specimens of the reaction mixture, peaks corresponding to the α-LiAlO$_2$ crystallographic plane *hkl* {104} were selected and their intensities were measured as intensity counts. Let us define the relative intensities, I_α^r, as

$$I_\alpha^r = \frac{I_\alpha(104)}{I_\alpha^{\max}(104)}, \quad 0 \le I_\alpha^r \le 1; \qquad (7)$$

where $I_\alpha(104)$ is the intensity of respective peak as determined in the probe corresponding to the given conversion factor value, $I_\alpha^{\max}(104)$ - the highest value of the $I_\alpha^r(104)$ parameter obtained in the given reaction mixture. The $I_\alpha^{\max}(104)$ parameter should decrease when phase transformation $\alpha \rightarrow \gamma$ will take place in LiAlO$_2$ as product of reaction (1). Only dependencies of $I_\alpha^r(104)$ dimensionless intensity parameter on reaction time have been determined in this work.

4.3. Results

The dependencies of the conversion factor S_n on time for reaction (1) have been determined at 843, 893, 943 and 973 K. These determinations have been carried out for reaction mixtures with stoichiometric initial ratios of Al$_2$O$_3$ to Li$_2$CO$_3$, as well as for those containing an excess of 38 mole of 0.53 Li$_2$CO$_3$ + 0.47 Na$_2$CO$_3$ eutectic. In case of stoichiometric reaction mixtures, the synthesis of LiAlO$_2$ was a reaction between two solids, whereas in case of reaction mixtures with molten carbonates surplus, Li$_2$CO$_3$ was a liquid component over all the experimental temperature range.

At temperature of 973 K the measurements have been performed also with reaction mixtures with 45, 52 and 59 mole% excess of the 0.53 Li$_2$CO$_3$ + 0.47 Na$_2$CO$_3$ eutectic system.

In all these measurements, the determinations of the relative X-rays intensities, I_α^r, have been performed according to the procedure already described, in order to evaluate the concentration of the α-phase in the LiAlO$_2$ produced in reaction (1). Values of the $(1 - S_n)$ parameters, as dependent on the reaction time at four temperatures are presented in Fig. 4. In the same figure, the respective dependencies for the parameter $1 - I_\alpha^r$ values may be seen. The presented dependencies show, that a full conversion of the reaction (1) reagents, i.e. $(1 - S_n) = 0$, are difficult to be obtained when the procedure of the discontinuous heating run has been applied.

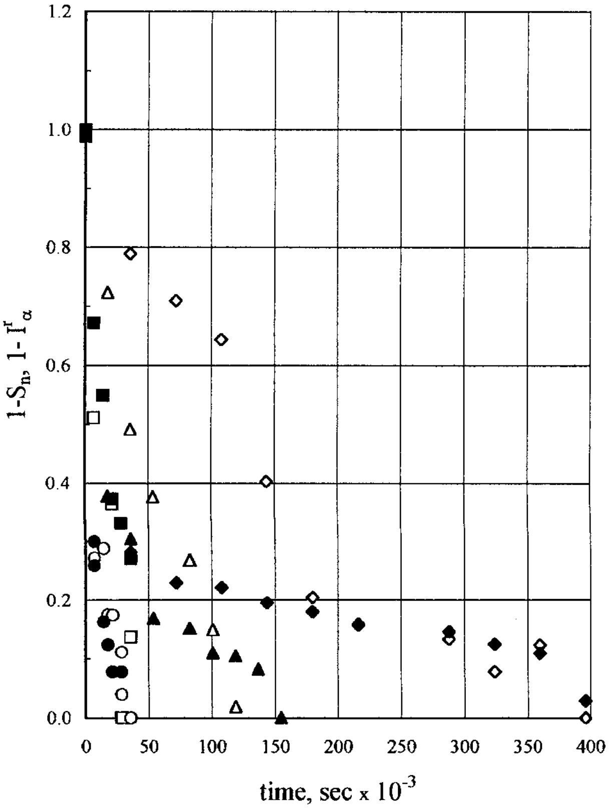

Figure 4 Values of $1 - S_n$ (solid symbols) and $1 - I^r_\alpha$ (open symbols) for reaction (1) in the stoichiometric $Li_2CO_3 + Al_2O_3$ mixture. Diamonds, triangles, circles and squares – 843, 893, 943 and 973 K, respectively.

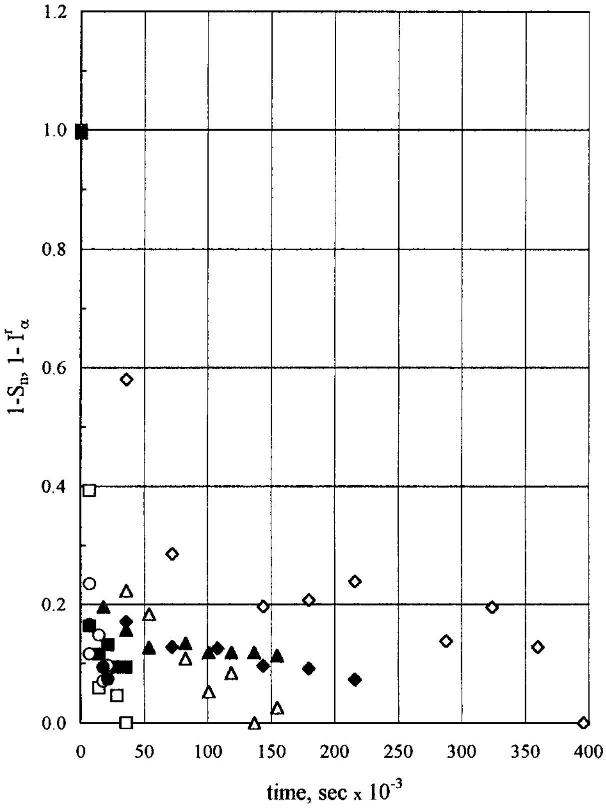

Figure 5 Values of $1 - S_n$ (solid symbols) and $1 - I^r_\alpha$ (open symbols) for reaction (1) in the $Li_2CO_3 + Al_2O_3$ mixture with excess of 38 Li_2CO_3 mole percent. Diamonds, triangles, circles and squares — 843 K, 893, 943 and 973 K, respectively.

The I^r_α parameter values show that the crystallographic form of the product of reaction (1) is the α-$LiAlO_2$ phase and that this phase is not converted to γ-$LiAlO_2$, at least as long as the reaction (1) takes place.

Similar results have been obtained when the reaction (1) had been performed with the $0.53\ Li_2CO_3 + 0.47\ Na_2CO_3$ eutectic excess in the reaction mixture, i.e. when the ambient of reaction (1) was liquid within all the temperature range of the experiments. This may be seen in Fig. 5.

In order to establish, what is the role of the amount of the $0.53\ Li_2CO_3 + 0.47\ Na_2CO_3$ eutectic on time dependencies both of the $1 - S_n$ and of the $1 - I^r_\alpha$ parameters at 973 K, the respective data are shown in Fig. 6.

These diagrams show that in the presence of liquid carbonate conversion rate of reaction (1) increases with the amount of excess liquid. Within the limits of the experimental accuracy, there is no evidence for appearance of the γ-$LiAlO_2$ phase under these conditions.

5. Discussion and conclusions

The results of this investigation indicate that within ca 850–970 K the γ-$LiALO_2$ phase is not the stable crystallographic form of this compound. When produced by the reaction of solid Li_2CO_3 with Al_2O_3, as well as in the presence of molten Li/Na carbonates, $LiAlO_2$ appears in the α-crystallographic form. It seems to be unjustified to suppose that this is not the thermodynamically stable phase at temperatures up to ca 1000 K. This conclusion is consistent with observation of some

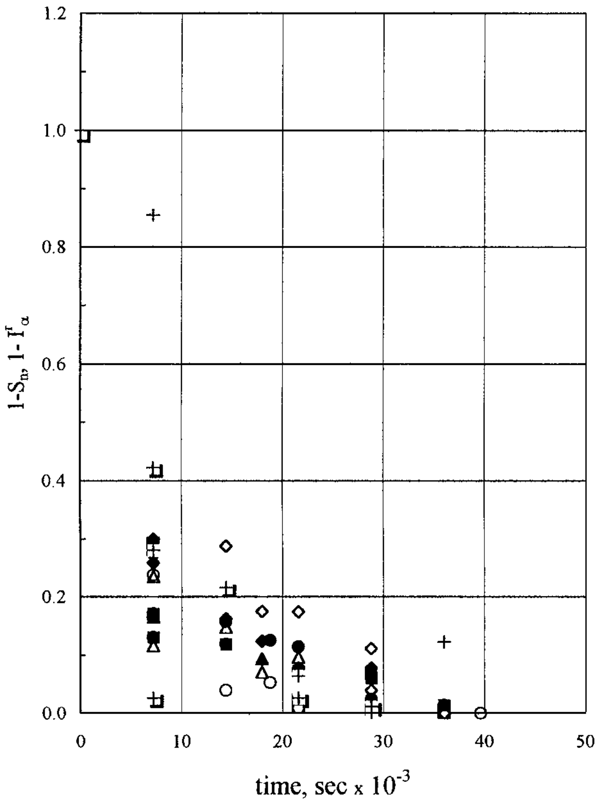

Figure 6 Values of $1 - S_n$ (solid symbols) and $1 - I^r_\alpha$ (open symbols) for reaction (1) in the $Li_2CO_3 + Al_2O_3$ mixture with the excess of $Na_2CO_3 + Li_2CO_3$ eutectic, at 973 K. Diamonds, triangles, circles, crosses with shadow and crosses: excess of 0, 38, 45, 52 and 59 mole percent of $Na_2CO_3 + Li_2CO_3$ eutectic, respectively.

partial conversion of the γ to α-$LiAlO_2$ phase in the MCFC after a long operation of the cell. The rate of such conversion is probably very slow and the γ-$LiAlO_2$, commonly used as the solid component of the MCFC electrolytic tiles, may be easily considered as apparently stable at the discussed temperature range.

One can expect that the presence of the molten carbonate phase should accelerate reactions with solid $LiAlO_2$. As is commonly known, this compound is in some, very small extent soluble in the molten carbonate electrolyte, and more soluble in the alternative Li/Na carbonate eutectic than in the classic Li/K one. $LiAlO_2$ dissolved in the molten carbonate phase enhances grain - to - grain transport during solid phase transformation. However, it seems to us doubtful the appearance of $LiAlO_2$ product of reaction (1) under the unstable crystallographic form, which after would be converted to the stable one in a slow, solid phase transformation. Therefore, the α-$LiAlO_2$ phase seems to be the allotropic form of this oxide stable up to ca 970 K. A very slow conversion of the γ-phase of this compound to the α-one, notified by some MCFC developers, confirms this conclusion.

Acknowledgments

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