Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 699-705

INVESTIGATION OF KINETICS OF SOLID-PHASE SYNTHESIS OF LITHIUM ORTHOSILICATE

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Abstract

The kinetics of the interaction between lithium carbonate and silica with various degrees of dispersion was investigated by TG and DTA methods. It was found that the utilization of pyrogenic silica with a specific surface area of about 300 $m^2 g^{-1}$ instead of aerosil with one of 175 $m^2 g^{-1}$ leads to an increase of the reaction rate between lithium carbonate and silica, which depends on the formation and growth of lithium orthosilicate crystals in the first stage, and is conditioned by the diffusion of lithium and oxygen ions through the lithium orthosilicate layer formed at temperatures above 800 K. This supposition is supported by the kinetic analysis results obtained with the use of the different models. The optimal regime of heating is recommended.

Keywords: interaction in solid phase, lithium carbonate, lithium orthosilicate, kinetics, solid electrolytes

Introduction

Electrochemical devices for the solution of scientific and technological tasks can be designed on the basis of solid electrolytes, and this undoubtedly stimulates interest in investigations of materials of this nature. They are of particular importance in numerous practical situations where liquid electrolytes cannot be used, e.g. at high temperature or low pressure.

The potential of new batteries based on solid electrolytes is a stimulus for the investigation of these materials. The rapid progress in electronics has led to the creation of a great variety of battery-powered portable devices. Small devices such as hearing aids or heart stimulators demand miniature batteries. The possibilities for decreasing the dimensions of traditional batteries with liquid electrolytes are limited by the technological conditions of manufacturing. One of the most perspective methods for the solution of this task is the utilization of solid electrolytes which can be prepared as thin films and which ensure ionic conduc-

1418–2874/99/ $ 5.00

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tivity and separation of the electrodes without separators. The physical requirements for these batteries are essentially lower than those involving liquid electrolytes, which may leak or dry out if the battery is broken.

No gas is formed in solid batteries and there is no self-discharge. Moreover, solid batteries may be operated at temperatures up to 373 K and pressures lower than 1 atm.

Batteries with lithium anodes have the highest specific characteristics. The efforts of many investigators are therefore directed to the search for solid electrolytes with high conductivity based on the lithium ion. Among the best are the solid solutions based on lithium orthosilicate.

Li_4SiO_4 has moderate conductivity (10^{-4} ohm^{-1} cm^{-1} in the temperature range 700–800 K). Its structure is built up of isolated SiO_4 tetrahedra connected in a network with polyhedral sites with common facets, inside which Li^+ is situated; this is a convenient matrix for the insertion of different ions.

Li_4SiO_4 is prepared by heating a mixture of Li_2CO_3 and SiO_2 powders. A considerable number of papers have been devoted to investigations of the conductivity of Li_4SiO_4 [1–9], but papers relating to investigations of the kinetics of the interaction between solid Li_2CO_3 and SiO_2 were not found in the literature accessible to us. The purpose of the present paper is to fill this gap.

Experimental

For sample preparation, fine powders of Li_2CO_3 and SiO_2 in stoichiometric proportion were pounded in an agate mortar to obtain a homogeneous mixture, and then pressed at 300 MPa. Pyrogenic SiO_2 samples with specific surface areas of 175 and 300 m^2 g^{-1} were taken. After this, the samples were again pounded in a mortar and pressed once more. Samples of 230–250 mg were taken in a platinum crucible. The reaction was carried out in the isothermal regime at a heating rate of 10 K min^{-1} up to the set temperature. The degree of conversion was determined via the mass loss of the sample with a Q-1500 D derivatograph (Hungary).

X-ray spectra were recorded with a DRON-3M diffractometer.

Results and discussion

The example of a thermoanalytical curve obtained by heating a pressed mixture of Li_2CO_3 and dispersed SiO_2 is shown in Fig. 1.

The reaction can be seen to begin at 573 K. A correction of 30 min was therefore made when the calculations were carried out.

The DTA curves revealed an endothermal effect at 800 K, which may be connected with the appearance of liquid phase in the reaction zone [10]. However, investigations of the systems Li_2CO_3–Li_4SiO_4 and Li_4SiO_4–SiO_2 did not confirm this supposition: the magnitudes of the endothermal effect were practically the

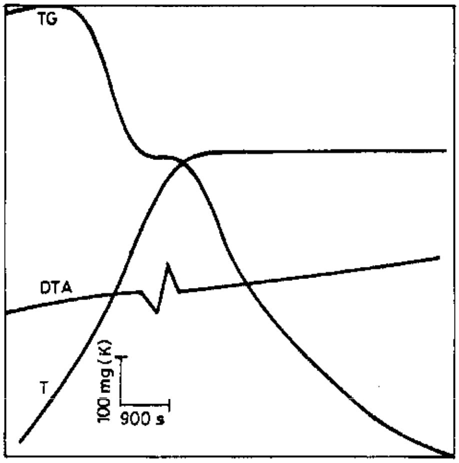

Fig. 1 Thermoanalytical curve of a mixture of the pressed powders $2Li_2CO_3–SiO_2$

same and did not depend on the composition. This endothermal effect must therefore be attributed to the polymorphous transformation of Li_4SiO_4 which occurs at 883 K [1].

The dependences of the degree of conversion (α) on time are typical for solid-phase reactions, with sigmoidal curves. At higher temperatures, a degree of conversion of 1 was achieved more rapidly, but at temperatures higher than 1000 K (the melting point of Li_2CO_3) a sharp decrease in reaction rate occurred. This is connected with exfoliation of the system and flotation of the SiO_2 particles on the surface of melted Li_2CO_3, with the evolution of CO_2, and as result the area of contact of the interacting particles decreases.

Reactions of the type $A_s+B_s=C_s$ can involve the following processes:

a) A reaction product can be formed on the surface of the particles and separate the initial substances. After that, further reaction may be achieved by diffusion of one or both initial substances through the layer of the reaction product only.

b) Growth of the crystals of the reaction product into the volume of the particles of the initial substances, and an unbroken layer is not formed.

The complicated character of the conversion rate dependence $d\alpha/d\tau$ against time (or against α) (Fig. 2) points to the reaction rate being determined by different processes in the initial and final stages.

In the initial stage (20–30 min), the reaction rate increase is connected with the temperature rise. On heating, an unbroken layer of product is formed and the reaction rate decreases, being governed by the diffusion rate.

On the basis of the ideas of Wagner [10] concerning the dependence of the solid-phase reaction rate on the ionic conductivities of the initial substances and

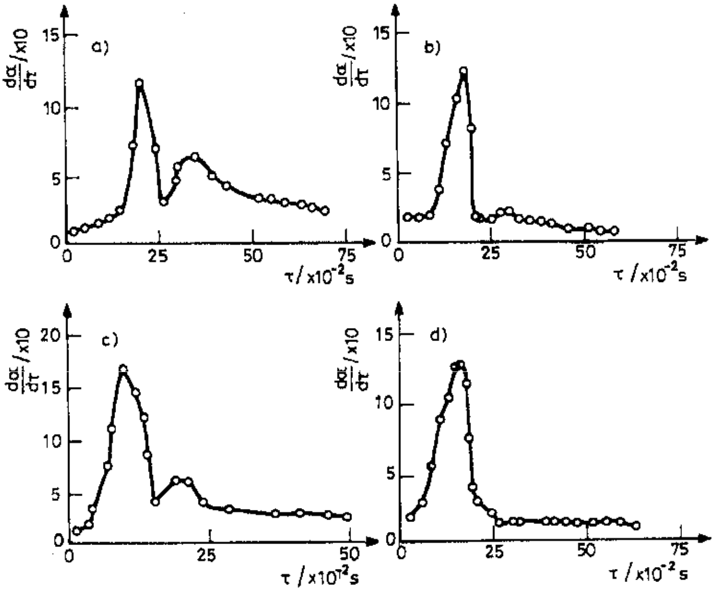

Fig. 2 Dependence of reaction rate on time: a – $2Li_2CO_3$–SiO_2 (A-175); b – $3Li_2CO_3$–SiO_2 (A-175); c – $2Li_2CO_3$–SiO_2 (A-300); d – $2Na_2CO_3$–SiO_2 (A-175)

the products, the appearance of the second peak in the curves at temperatures up to 800 K can be explained. At this temperature, the polymorphous transformation of Li_4SiO_4 and an essential rise in conductivity occur [1]. The reaction rate then decreases monotonously at constant temperature in consequence of the increase in the layer thickness of the Li_4SiO_4, which must be crossed by the lithium and oxygen ions. This supposition is confirmed by the results of the interaction between highly dispersed SiO_2 and Na_2CO_3 (Fig. 2d). Accordingly, the polymorphous transformation does not occur in Na_4SiO_4; the second peak is absent from the curve. Replacement of Li^+ by the larger and less mobile Na^+ leads to a regular decrease in the reaction rate in the stage where it is determined by diffusion.

Utilization of more dispersed silica leads to a 1.2-fold rise in the reaction rate in the initial stage, and 1.4-fold rise in the final stage, due to the increase in contact surface area of the reagents (Fig. 2c).

Comparison of the results obtained when a surplus of Li_2CO_3 was introduced into the initial mixture (Fig. 2b) and when more dispersed SiO_2 was utilized (Fig. 2c) leads to the conclusion that Li_4SiO_4 crystals grow deep into the SiO_2 particles, and not into the Li_4SiO_4 particles, because the Li_2CO_3 surplus has practically no influence on the reaction rate, but decrease of the SiO_2 particle dimensions leads to a rise in the rate.

This reasoning is confirmed by comparing the experimental data with Avrami-Erofeev equation:

$$\alpha = 1 - \exp(-k\tau^{n}) \tag{1}$$

where α is the degree of conversion, k is a constant, n is the kinetic parameter, and τ is time.

Taking the logarithm of this equation gives

$$-\ln(1-\alpha) = k\tau^{n} \tag{1a}$$

Repetition of this operation yields the equation

$$\ln(-\ln(1-\alpha)) = \ln k + n\ln\tau \tag{lb}$$

which in the coordinates $\ln(-\ln(1-\alpha))$ *vs.* $\ln\tau$ is the equation of a straight line with slope n.

The magnitude of n provides information on the reaction rate [11–13]. If $n>1$, the reaction rate is controlled by the rate of formation and growth of the reaction product crystals. If $n\sim0.5$, the reaction proceeds under diffusion control. Figure 3 reveals a straight-line dependence with $n=1$ in the initial stage.

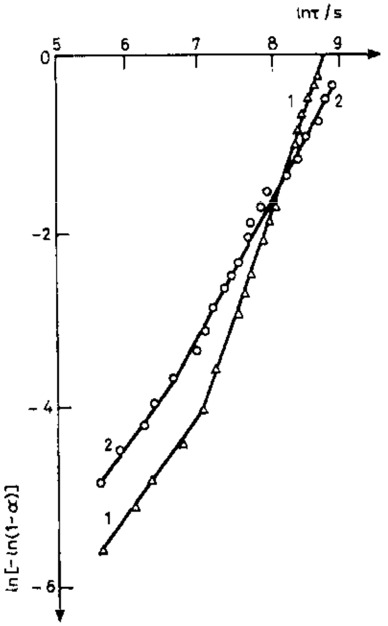

Fig. 3 Fit of the experimental data to the Avrami-Erofeev equation: 1 $-2Li_2CO_3-SiO_2$; 2 $-$ $2Na_2CO_3-SiO_2$

Deviation from this dependence points to the transition of the reaction to the regime of diffusion control. In this case, the dependence of the degree of conversion must obey the Yander equation:

$$(1-\sqrt[3]{1-\alpha})^2=\frac{2k}{r_0^2\tau}=k'\tau \qquad (2)$$

where k' is a constant and r_0 is the average radius of the initial component particles.

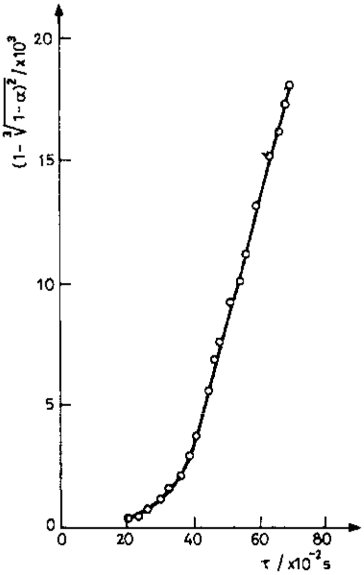

Fig. 4 Fit of the experimental data to the Yander equation

It follows from Fig. 4 that the degree of conversion *vs.* time function is described by the Yander equation in the final reaction stage.

Conclusions

Through the interaction of Li_2CO_3 and highly dispersed SiO_2 powders, Li_4SiO_4 can be prepared. X-ray analysis confirmed the formation of Li_4SiO_4 and the absence of unreacted initial reagents and lithium metasilicate. The electrical conductivity of the prepared Li_4SiO_4 in the temperature range 373–543 K coincides with that published in the literature.

– The reaction rate is conditioned by the rates of formation and growth of Li_4SiO_4 in the initial stage ($\alpha<0.1$) and the reaction proceeds under diffusion control in the final stage.

– The synthesis of Li_4SiO_4 is recommended by heating pressed powders of Li_2CO_3 and highly-dispersed SiO_2 at a rate of 10 K min^{-1} up to 573 K; the rate must then be lowered to 5–7 K min^{-1}. When the temperature reaches 973 K, the reaction is carried out in the isothermal regime up to a degree of conversion of 0.8. After that, the temperature can be raised, but not higher than 1273 K.

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