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Short communication

Kinetic study on solid state reaction for synthesis of LiBOB

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Abstract

The process of preparing lithium bis(oxalato)borate (LiBOB) was studied by TG/DTA and XRD methods. Five DTA plots were obtained at five different heating rates. According to the DTA plots, the Ozawa integral method and the Kissinger differential method were employed in the study on kinetics of solid state reaction. The result showed that to increase the heat preservation time at 100–120 °C was advantageous to the synthesis of LiBOB. The stages of solid state reaction for preparing LiBOB were analyzed by XRD method. The optimum conditions of synthesis LiBOB were first heat preservation at 100–120 °C, and then heat preservation at 240–280 °C.

Keywords: TG/DTA; XRD; LiBOB; Solid state reaction

1. Introduction

Lithium bis(oxalato)borate (LiBOB) was reported as the most promising potential salt for lithium-ion battery electrolytes in recent years [1,2]. The synthesis methods of LiBOB reported so far were all organic solution reactions including some steps such as dissolution, reflux, evaporation, etc. These methods could not be carried out and be commercialized easily, thus making production very expensive. Recently, a novel method to get LiBOB with solid state reaction has been developed in our group [3]. Oxalic acid dihydrate, lithium hydroxide and boric acid were mixed at mole ratio of 2:1:1, then the mixture was treated in an oven at proper temperature in air to prepare LiBOB. This method was easier, cheaper and more environment-friendly than the organic solution reaction method. In this article, in order to further understand clearly the solid state reaction and to optimize the process of preparing LiBOB, the mixture of the oxalic acid dihydrate, lithium hydroxide and boric acid was heated and analyzed with TG/DTA method and XRD method.

2. Exprimental

2.1. Materials

The starting chemicals were oxalic acid dihydrate (≥99.5%), lithium hydroxide (≥95%) and boric acid (≥99.5%). They were mixed at mole ratio of 2:1:1 in blender for 1 min. The mixture was for TG/DTA analysis. It was first heated at 120 °C for 4 h and then heated at 240 °C for 6 h to get LiBOB. The sample was taken at regular intervals for XRD analysis.

2.2. Measurements

Thermogravimetric/differential thermal analysis (TG/DTA) of the mixture of oxalic acid dihydrate, lithium hydroxide and boric acid was performed on a Pyris Diamond TG/DTA Analyzer. The mixture was heated from room temperature to 400 °C with 5 °C min^{-1}, 10 °C min^{-1}, 15 °C min^{-1}, 20 °C min^{-1} and 25 °C min^{-1} rate in air atmosphere.

XRD analysis was performed on XD2618N X-ray diffraction analyzer (Japan).

3. Results and discussion

Oxalic acid dihydrate and lithium hydroxide easily react each other to produce lithium hydrogen oxalate at room temperature. Therefore, after oxalic acid dihydrate, lithium hydroxide and boric acid were mixed at mole ratio of 2:1:1, the mixture became a three-component mixture of oxalic acid dihydrate, lithium hydrogen oxalate and boric acid. The new mixture was analyzed with TG/DTA method at different heating rate. The DTA plots were shown in Fig. 1. There were five exothermic peaks in each DTA plot, corresponding to five reactions, respectively. The temperature of exothermic peaks changed with the rising of heating rate (Table 1). Among five exothermic reactions, the

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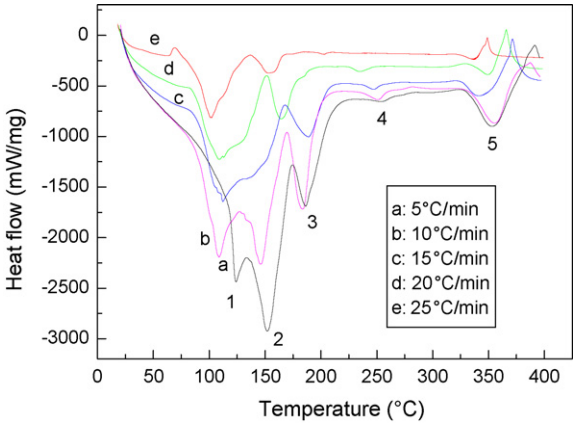

Fig. 1. DTA plots of the mixture of oxalic acid dihydrate, lithium hydrogen oxalate and boric acid in air atmosphere at five different heating rate at 25–400 °C.

peak temperature of the reaction (1) had minimum change from 101 °C to 123 °C when the heating rate rose from 5 °C min^{-1} to 25 °C min^{-1}. Reaction (1) was an exothermic reaction, and the reactants, $H_2C_2O_4{\cdot}2H_2O$ and $HC_2O_4Li{\cdot}H_2O$, would melt and release crystal water. The crystal water released would be as a medium which made the reactants contacted enough and reacted completely. The details of the reactions were displayed in Table 2. The analyses of reactions (1)–(4) were the same to those in literature [3].

It must be pointed out that reaction (5) was the decomposition of LiBOB. In literature [3], the solid decomposing products were regarded as lithium carbonate and diboron trioxide, but in fact, it was confirmed that the products were lithium oxalate and diboron trioxide after analyzed using XRD. Based on the DTA plots, the Ozawa integral method [4] and the Kissinger differential method [5] were employed to study the kinetics of solid state reaction. The activation energies of reactions (1)–(4) could be calculated (Table 3) by two methods, and some similar results were obtained. Based on these results, it can be seen that the reaction (1) had highest activation energy. That was to say, comparing with other four reactions, the dehydration of the reactants was the most difficult step to process. According to the DTA analysis, dehydration of the reactants was endothermic reaction. Therefore, to increase the heat preservation time at 100–120 °C was advantageous to the synthesis of LiBOB. Literature [3] considered that the temperature range for preparing LiBOB was from 240 °C to 280 °C. Therefore, the processes of preparing LiBOB by solid state reaction should be first heat preservation at 100–120 °C for a period of time and then heating to 240–280 °C for several hours.

Table 3
The reaction energies calculated by Ozawa and Kissinger methods

	Activation energy (kJ mol)			
	E_1	E_2	E_3	E_4
Ozawa method [4]	90.0	57.1	61.7	57.4
Kissinger method [5]	88.2	53.2	54.5	52.0

According to the above analysis, the mixture of the oxalic acid dihydrate, lithium hydrogen oxalate and boric acid was heated at 120 °C for 4 h and then heated at 240 °C for 6 h to prepare LiBOB. The sample was taken at regular intervals for XRD analysis (Fig. 2). The XRD spectrum at 60 °C indicated the mixture was still lithium hydrogen oxalate, oxalic acid dihydrate and boric acid. After keeping 2 h at 120 °C, a lot of water was observed and solid–liquid state coexisted in the whole reactive system due to dehydration and melting of oxalic acid dihydrate and lithium hydrogen oxalate. In the XRD spectrum, the diffract peaks of LiBOB were found, but the intensity was very low. Along with the processing of the reaction, the diffract peak intensity of the mixture became lower while the diffract peak intensity of LiBOB was getting higher and higher. After keeping 4 h at 120 °C, water and solid mixture coexisted in the system and the water became less than that of keeping 2 h at 120 °C due to evaporation. After keeping 2 h at 240 °C, only white solid existed in the system. The XRD spectrum belonged to LiBOB and a little reactants. After 6 h at 240 °C, all the diffract peaks of the mixture disappeared, and the XRD spectrum indicated LiBOB. The

Table 1
The temperatures of five reaction peaks

Heating rate (°C/min)	Reaction (1) (°C)	Reaction (2) (°C)	Reaction (3) (°C)	Reaction (4) (°C)	Reaction (5) (°C)
5	101.76	115.95	155.21	202.44	348.50
10	109.40	127.48	164.1	234.59	365.41
15	111.65	133.65	188.35	246.99	371.05
20	115.04	146.05	183.27	250.38	381.28
25	123.50	151.69	186.09	255.45	390.79

Table 2
The corresponding possible reactions of the five peaks

Possible reaction	
$H_2C_2O_4 \cdot 2H_2O \rightarrow H_2C_2O_4 + 2H_2O$; $HC_2O_4Li \cdot H_2O \rightarrow HC_2O_4Li + H_2O$	(1)
$H_3BO_3 \rightarrow HBO_2 + H_2O$	(2)
$H_3BO_3 + HC_2O_4Li + H_2C_2O_4 \rightarrow LiB(C_2O_4)_2{\cdot}2H_2O + H_2O$	(3)
$LiB(C_2O_4)_2{\cdot}2H_2O \rightarrow LiB(C_2O_4)_2 + 2H_2O$	(4)
$2LiB(C_2O_4)_2 \rightarrow Li_2C_2O_4 + B_2O_3 + 3CO_2 + 3CO$	(5)

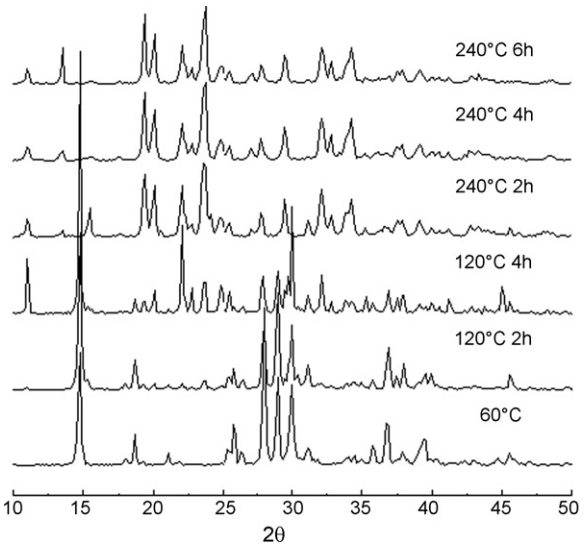

Fig. 2. The XRD spectrum of products prepared by solid state reaction at different time.

results of XRD supported the opinion to hold for a period of time at 100–120 °C.

Solid state reaction usually includes four stages; they are diffusion stage, reaction stage, nucleation stage and growth stage. Firstly, oxalic acid dihydrate and lithium hydrogen oxalate lost their crystal water and diffused to the crystal lattice of boric acid due to their low melting point and low decomposition temperature. The reactants contacted each other and produced LiBOB. It was considered that nucleation and growth of LiBOB were both faster, because there was no any gibbosity which implied intermediate substances existed as the local ordered amorphous phase in XRD spectrum. In the reaction process crystal reactants and crystal products coexisted when LiBOB was synthesized. With the processing of the reaction the intensity of the diffract peaks of the reactants weaken gradually and disappeared at last.

4. Conclusions

The DTA plots of the mixture of the oxalic acid dihydrate, lithium hydrogen oxalate and boric acid were obtained using TG/DTA with different heating rate in order to study the process of LiBOB synthesis with solid state reaction. The activation energies of reactions in the process were calculated by the Ozawa integral method and the Kissinger differential method. The reactions losing crystal water from oxalic acid dihydrate and lithium hydrogen oxalate had highest activation energy in all reactions of synthesis process. The different stages of solid state reaction for preparing LiBOB were analyzed by XRD method. The optimum conditions of synthesis LiBOB were first heat preservation at 100–120 °C, and then heat preservation at 240–280 °C.

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