Studies on the thermal decomposition kinetics of LiPF$_6$ and LiBC$_4$O$_8$

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Abstract. Thermal decomposition of LiPF$_6$ and LiBC$_4$O$_8$ (lithium *bis*(oxalate)borate, abbreviated as LiBOB) were studied using TG (thermogravimetry)-DTG (derivative thermogravimetry) method with different heating rate β of 5, 10, 20 and 40°C min^{-1} or at different constant temperature θ_C (109·80, 118·79, 148·41, 176·86°C for LiPF$_6$ and 278·51, 298·13, 317·65, 336·13 for LiBOB). From the non-isothermal kinetics we calculate that n_{LiPF_6} is 1·01, n_{LiBOB} is 1·04, E_{LiPF_6} is 91907·61 J/mol, and E_{LiBOB} is 205179·88 J/mol; from the isothermal kinetics we calculate that n for both LiPF6 and LiBOB are 1, E_{LiPF_6} is 91907·61 J/mol, E_{LiBOB} is 205179·88 J/mol, lnA_{LiPF_6} is 16·89 s^{-1}, and lnA_{LiBOB} is 31·96 s^{-1}. The results obtained from the two ways have minor differences and can validate each other.

Keywords. LiPF$_6$; LiBOB; TG–DTG; non-isothermal kinetics; isothermal kinetics.

1. Introduction

Electrolyte which plays a crucial role in ion transport is one of the most important components of lithium-ion batteries. The current electrolyte generally used in lithium-ion batteries is mainly composed of LiPF$_6$ and a blend of alkyl carbonates. LiPF$_6$ has been widely adopted for more than a decade, owing to its necessary pre-requisites for use in lithium ion batteries, for example, it is easily soluble in various solvents, can lead to electrolytes having high conductivities, and has a high level of electrochemical stability. However, hazardous reactions of LiPF$_6$ are widely reported recently.[1,2] Even if only slight, LiPF$_6$ decomposes to LiF and PF$_5$, and the latter not only can lead to a cationic polymerization, but also readily hydrolyses to form HF and PF$_3$O which can lead to the dissolution of the transition-metal oxides.[3,4]

Recently, LiBC$_4$O$_8$ (lithium *bis*(oxalate)borate, abbreviated as LiBOB) has been reported as a promising candidate for lithium-ion batteries, with non-halogen, high decomposition temperature (302°C), effective electrochemical stability to Fe-based and Mn-based metal oxide, and improved cycling performance. More important is that it can effectively stabilize the graphite structure even in pure propylene carbonate (PC).[5,6] But as a new candidate for lithium-

ion chemistry, it still has many disadvantages. For example, it is difficult to dissolve in solvents of carbonates, and is less conductive in typical carbonate mixtures when compared with LiPF$_6$.[7]

Considering that LiPF$_6$ and LiBOB both have their own characters, and neither of them is absolutely suitable for lithium-ion batteries, LiPF$_6$ and LiBOB, as two most important lithium salts for lithium-ion batteries, will exist together in a certain period. So, it is necessary to study on these two salts. Electrochemical performances of these two salts have been reported extensively, but the reports about their thermodynamic performances are absent, especially about the thermal decomposition kinetics. In these limited reports, most of them are about LiPF$_6$ on which thermal decomposition reaction has been mentioned in two steps shown as (1) and (2),[8–10] only a few reports about LiBOB.[11]

$$LiPF_6(s) + H_2O(g, \text{trace}) \rightarrow$$
$$LiF(s) + OPF_3(g) + 2HF(g). \quad (1)$$

$$LiPF_6(s) \rightarrow LiF(s) + PF_5(g). \quad (2)$$
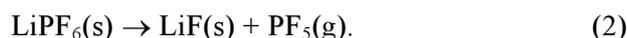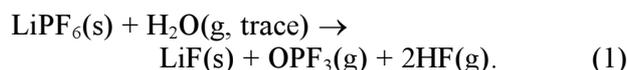
In our work, we studied on the thermal decomposition kinetics of LiPF$_6$ and LiBOB by TG–DTG method, and obtained many useful thermodynamic and kinetic information that can help us to understand their characters such as the condition of preparation and preservation.

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2. Experimental

LiPF$_6$ (99·99%) was obtained from Sigma-Aldrich, Inc. LiBOB was synthesized in our laboratory following a solid-state reaction,[11] and purified to above 99·5% by repeated recrystallizations with anhydrous CH$_3$CN. High purity (99·999%) argon was obtained from Qinghai Laoqian Gas Limited Corporation.

The *in situ* TG (thermogravimetry)-DTG (derivative thermogravimetry) measurements were conducted using a TA Instruments SDT Q600 in argon atmosphere. The samples were first measured in 90 μL ceramic pans from room temperature to 400°C with the average heating rate β of 5, 10, 20 and 40°C min^{-1}, then were measured at different constant temperature θ_C. The room temperature was about 25°C and the relative humidity was about 45% during the experiments.

3. Results and discussion

3.1 *Thermal decomposition*

Figure 1 shows TG–DTG curves of LiPF$_6$ and LiBOB from room temperature 400°C with β of 10°C min^{-1}. Table 1 shows their thermal analysis dates (I and II respectively to represent the two thermal decomposition steps shown in figure 1). Similar with LiPF$_6$, LiBOB's thermal decomposition also includes two reactions shown as (3) and (4). That does not support the view that LiBOB is much inerter than LiPF$_6$

when in contact with H$_2$O, but similar to the view of Wu that LiBOB can be readily hydrolysed by ambient moisture.[7]

$$\text{LiBOB(s)} + \text{H}_2\text{O(g, trace)} \rightarrow$$

$$\text{LiHC}_2\text{O}_4\text{(s)} + \text{CO(g)} + \text{CO}_2\text{(g)} + \text{HBO}_2\text{(s)}. \quad (3)$$

$$2\text{LiBOB(s)} \rightarrow \text{Li}_2\text{CO}_3\text{(s)} + 4\text{CO(g)} +$$

$$3\text{CO}_2\text{(g)} + \text{B}_2\text{O}_3\text{(s)}. \quad (4)$$
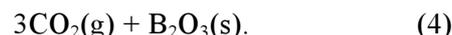
3.2 *Studies on the non-isothermal kinetics of thermal decomposition*

The decomposition peak temperature θ_m depends on the β, that has been observed during many experiments.[10] Figure 2 shows θ_m of the second decomposition step in DTG curve of LiPF$_6$ and LiBOB with various β of 5, 10, 20 and 40°C min^{-1}, and reveals that for the two salts, θ_m increases along with the increasing of β. The reason is that with the increasing of β, more and more sample is decomposed at higher temperature; that may cause the deviation from equilibrium conditions.

Further, relationship between β and θ_m could be displayed by the (5) given by Kissinger:[12]

$$d\ln(\beta'/T_m^2)/d(1/T_m) - E_a/R, \quad (5)$$

where T_m is the peak temperature ($T_m = \theta_m + 273\cdot15$, with the unit of K), β' the average heating rate
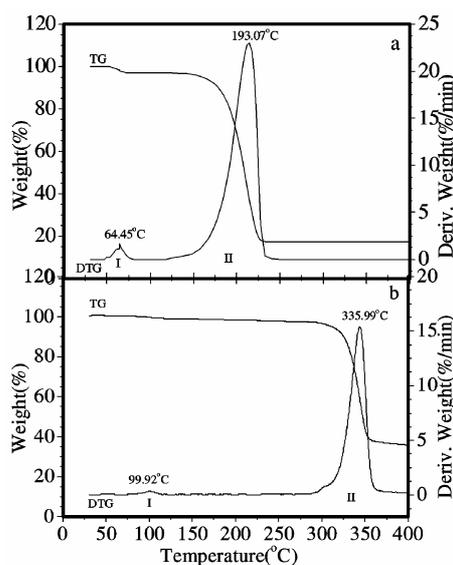
Figure 1. TG–DTG curves of thermal decomposition ($\beta = 10$°C/min). (**a**) LiPF$_6$, (**b**) LiBOB.
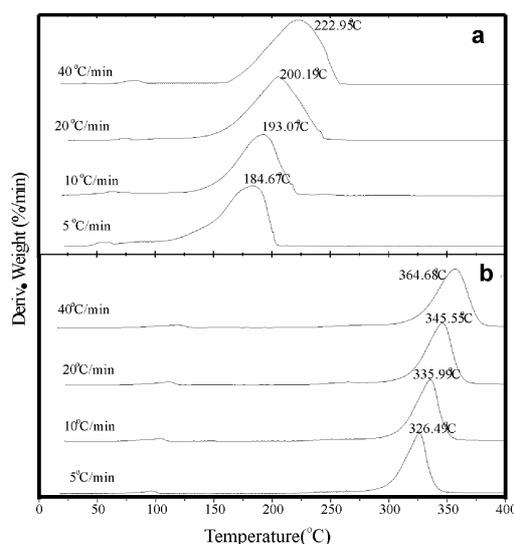
Figure 2. θ_m of the second decomposition step in DTG curve with various β. (**a**) LiPF$_6$, (**b**) LiBOB.

Table 1. The thermal analysis data of LiPF$_6$ and LiBOB.

Sample	Decomposition reaction	Range of temperature (°C)	θ_p (°C)	Rate of the mass loss (%)
LiPF$_6$	I	49·42~77·80	64·45	2·980
	II	125·06~250·25	193·07	79·87
	I + II			82·85 (82·93)*
LiBOB	I	71·66~118·85	99·92	2·768
	II	288·15~382·41	335·99	60·76
	I + II			63·53 (62·97)*

*Rate of the theoretical mass loss

($\beta' = \beta/60$, with the unit of K/s), R the molar gas constant ($R = 8·314$ J mol^{-1} K^{-1}) and E_a the apparent activation energy with the unit of J/mol. If we construct the curve of $\ln(\beta'/T_m^2)$ with $1/T_m$, we should get a line, with the slope value of $-E_a/R$. So from figure 2 and (5), (6) for LiPF$_6$ and (7) for LiBOB can be obtained using linear regression analysis technique:

$$\ln(\beta'/T_m^2) = 9·61 - 11054·56/T_m \quad (r = 0·9674), \quad (6)$$

$$\ln(\beta'/T_m^2) = 25·79 - 24678·84/T_m \quad (r = 0·9761), \quad (7)$$

where r is the linear related coefficient. Then E_a for LiPF$_6$ E_{LiPF_6} and E_a for LiBOB E_{LiBOB} could be accounted as $E_{\text{LiPF}_6} = 11054·56*R = 91907·61$ J/mol, $E_{\text{LiBOB}}=24678.84*R = 205179·88$ J/mol.

Kissinger also claimed that the relationship between peak-type index S and reaction order n could be displayed as[12]

$$S = 0·63n^2, \quad (8)$$

where S could be obtained from figure 2 using the method given by reference 12. The average n of LiPF$_6$ and LiBOB respectively accounted as 1·01 and 1·04.

3.3 *Studies on the isothermal kinetics of thermal decomposition*

For thermal decomposition reaction A → Products, the common rate equation is

$$dx/dt - k(1 - x)^n, \quad (9)$$

where x is the sample's thermal decomposition rate at the time of t (in the unit of s), k the rate constant, and n equals to 1 in most occasions while the other few equals to 2.[13] If $n = 1$, the integral equation of (9) is

$$-\ln(1 - x) = kt + C, \quad (10)$$

where C is a constant, and when construct the curve of $-\ln(1 - x)$ with t, a line would be obtained with the slope value of k. But if $n = 2$, the integral of (9) will change to

$$1/(1 - x) = kt + C, \quad (11)$$

with the line curve of $1/(1 - x)$ with t.

From (2) and (4), we know that the loss mass Δm is caused by the product of gas (PF$_5$ or CO and CO$_2$). Then x can be expressed as

$$x_{\text{LiPF}_6} = \frac{\Delta m_{\text{LiPF}_6} \cdot M_{\text{LiPF}_6}}{m_{\text{LiPF}_6} \cdot M_{\text{PF}_5}} = \frac{\omega_{\text{LiPF}_6} M_{\text{LiPF}_6}}{M_{\text{PF}_5}}, \quad (12)$$

$$x_{\text{LiBOB}} = \frac{\Delta m_{\text{LiBOB}} \cdot M_{\text{LiBOB}}}{m_{\text{LiBOB}} \cdot M_{\text{C}_{3.5}\text{O}_5}} = \frac{\omega_{\text{LiBOB}} M_{\text{LiBOB}}}{M_{\text{C}_{3.5}\text{O}_5}}, \quad (13)$$

where m is the sample mass with the unit of g, M is the molecular weight with the unit of g, ω is the rate of the mass loss at the time of t which could be gotten from TG curve, and $M_{\text{C}_{3.5}\text{O}_5}$ equals to $(4M_{\text{CO}} + 3M_{\text{CO}_2})/2$.

Figure 3 shows ω_{LiPF_6} and ω_{LiBOB} at the time of t with different θ_C. When we construct the curve of

Table 2. k of LiPF$_6$ and LiBOB at different θ_C.

Sample	θ_C (°C)	k(s^{-1})	r
LiPF$_6$	109·80	7·31E-5	0·9995
	118·79	1·14E-4	0·9991
	148·41	6·85E-4	0·9956
	176·86	3·7E-3	0·9979
LiBOB	278·51	3·82E-4	0·9746
	298·13	1·82E-3	0·9851
	317·65	4·50E-3	0·9956
	336·13	1·87E-2	0·9984
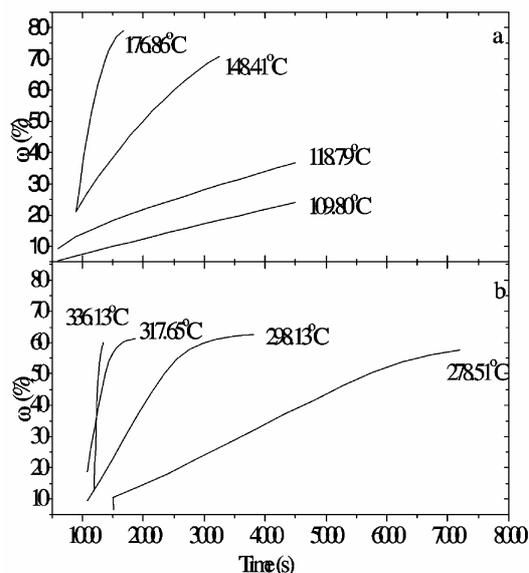
Figure 3. ω at the time of t with different θ_C. (**a**) LiPF$_6$, (**b**) LiBOB.

$-\ln(1 - x)$ or $1/(1 - x)$ with t, only the former has the linear shape that is shown in table 2. It proves that both n of LiPF$_6$ and LiBOB are 1 which is approximate to the results obtained from the non-isothermal kinetics of thermal decomposition.

Considering the Arrhenius equation

$$\ln k = \ln A - E_a/RT, \qquad (14)$$

where A is the pre-exponential factor, T the temperature with the unit of K ($T = \theta_C + 273\cdot15$), if we construct the curve of $\ln k$ with $1/T$ using data in table 2, a line would be gotten with the slope value of $-E_a/R$ and the interception of $\ln A$. The linear equation for LiPF$_6$ (15) and LiBOB (16) respectively is that

$$\ln k_{\mathrm{LiPF_6}} = 16\cdot89 - 10150\cdot77/T \quad (r = 0\cdot9986), \qquad (15)$$

$$\ln k_{\mathrm{LiBOB}} = 31\cdot96 - 21949\cdot48/T \quad (r = 0\cdot9951), \qquad (16)$$

from which we can get the E_a for LiPF$_6$ $E_{\mathrm{LiPF_6}}$ is $10150\cdot77*R = 84393\cdot50$, $\ln A$ for LiPF$_6$ $\ln A_{\mathrm{LiPF6}}$ is 16.89 s^{-1}; E_a for LiBOB E_{LiBOB} is $21949\cdot48*8\cdot314 = 182488\cdot00$ J/mol, $\ln A$ for LiBOB $\ln A_{\mathrm{LiBOB}}$ is $31\cdot96$ s^{-1}.

4. Conclusions

Thermal decomposition of LiPF$_6$ and LiBOB are studied from their non-isothermal and isothermal kinetics. From the former, we calculate that $n_{\mathrm{LiPF_6}}$ is $1\cdot01$, n_{LiBOB} is $1\cdot04$, $E_{\mathrm{LiPF_6}}$ is $91907\cdot61$ J/mol, and E_{LiBOB} is $205179\cdot88$ J/mol; from the latter we calculate that n for both LiPF$_6$ and LiBOB are 1, $E_{\mathrm{LiPF_6}}$ is $84393\cdot50$ J/mol, E_{LiBOB} is $182488\cdot00$ J/mol, $\ln A_{\mathrm{LiPF_6}}$ is $16\cdot89$ s^{-1}, and $\ln A_{\mathrm{LiBOB}}$ is $31\cdot96$ s^{-1}. The results obtained from these two ways have minor differences and can be validated each other. And then, the mechanism of decompositions of both LiPF$_6$ and LiBOB were obtained to be Mample Power theorem, with random nucleation and later growth mechanism function.[14]

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