

Thermal behavior and decomposition kinetics of six electrolyte salts by thermal analysis

Zhenrong Lu¹, Li Yang*, Yaju Guo

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, No. 800 Dongchuan Road, Minhang District, Shanghai 200240, China

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Abstract

The thermal behavior of five lithium salts commonly used in the electrolytes of lithium-ion battery and one non-lithium salt used as a dominant salt of electrochemical capacitor was studied using simultaneous thermogravimetry (TG)–derivative thermogravimetry (DTG)–differential scanning calorimetry (DSC) under a dynamic nitrogen atmosphere. The results showed that the amount of free acid remained in the five lithium salts and their initial revolution temperature are different and the stability of all six salts falls in the order $\text{LiClO}_4 > \text{LiCF}_3\text{SO}_3 > \text{LiTFSI} > \text{TEABF}_4 > \text{LiBF}_4 > \text{LiPF}_6$. In addition, the reaction heat values associated with their decomposition processes were measured, which showed the stages for the evolution of free acid are endothermic with lower reaction heat, while for the decomposition of salts either endo- or exothermic, mainly depending on their chemical compositions. Kinetic parameters for these decomposition reaction processes were obtained by jointly using two thermal kinetic analysis methods.

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1. Introduction

The lithium-ion battery is an attractive alternative to other batteries due to its excellent characteristics including high cell voltage, high energy density, light weight, etc. [1–4].

However, large-scale lithium-ion batteries are not yet used in practice, primarily owing to safety consideration. It is well known that abuse conditions such as over charge/discharge, short circuits and operation at high temperatures accelerate the rate of heat generation in a Li-ion battery, which can lead to safety problems. In order to improve the safety of lithium-ion batteries, it is necessary to understand the thermal stability of the materials within the cell. For this reason, many researchers have carried out thermal studies on these batteries [2,5,6]. Most of the thermal studies have been focused on the

electrode materials [7–9] as well as electrolytes composed of lithium salt and organic solvents [3,4,10]. So far as we know, however, there has been little investigation on lithium salt itself. In fact, the lithium salts also play an important role in the thermal stability of the cell. Information about thermal properties of lithium salt alone without organic solvents is actually essential in design of novel electrolytes for safe and high performance lithium-ion batteries.

In the present paper, therefore, a systematic study on the thermal properties of a group of lithium salts widely used in lithium-ion batteries: lithium trifluoromethyl sulfonate LiCF_3SO_3 , lithium hexafluorophosphate LiPF_6 , lithium fluoroborate LiBF_4 , lithium perchlorate LiClO_4 , lithium bis (trifluoromethyl(sulfonyl))imide LiTFSI has been performed using simultaneous thermogravimetry (TG)–derivative thermogravimetry (DTG)–differential scanning calorimetry (DSC) technique. In addition, for the purpose of comparison, a non-lithium salt used as a dominant salt for non-aqueous electrochemical capacitor, i.e. tetraethylammonium tetrafluoroborate TEABF_4 has also been studied. Their thermal

* Corresponding author. Tel.: +86 21 54748917; fax: +86 21 54741297.

E-mail address: liyancee@sjtu.edu.cn (L. Yang).

¹ Permanent address: Testing and Analysis Center, Suzhou University, Suzhou, Jiangsu 215006, China.

behavior, thermal stability, together with all the kinetic analysis results of their decomposition, such as the activation energy E and pre-exponential factor A calculated by jointly using two data processing approaches have been presented.

2. Experimental

2.1. Materials

All the samples studied in this paper were commercially obtained from Morita Chemical Industries Co. Ltd., Japan. They were used as received.

2.2. Methods

TA Instrument's, SDT module 2960 model was used for both thermal stability and decomposition kinetic studies for the electrolyte salts. This apparatus allows TG and DSC measurements to be taken simultaneously [11,12]. Crucibles were made from alumina. The instrument was previously calibrated against standard substances provided by TA Instruments. Multiple heat rate runs (2.5, 5, 7.5, 10 °C min⁻¹) were performed with the following conditions: sample size 3–5 mg, purge gas N₂ at a flow rate 100 mL min⁻¹.

3. Kinetic methodology

The kinetic heterogeneous decomposition of solids is customarily described by the basic kinetic equation [13]:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (1)$$

or

$$\frac{d\alpha}{dT} = \left(\frac{k}{\beta}\right) (1 - \alpha)^n \quad (2)$$

where α represents the extent of reaction, t the time, $\beta = dT/dt$ is heating rate, T temperature, k the rate constant and n is reaction order. The value of α is experimentally derived from the global mass loss in TG experiments. The temperature dependence of k can be commonly described by the Arrhenius equation:

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where E , A and R are the activation energy, the pre-exponential factor and the gas constant (8.134 J mol⁻¹ K⁻¹), respectively.

Two iso-conversional kinetic methods are used in the paper to calculate both the activation energy and the pre-exponential factor as these methods have been recommended by International Committee of Thermal Analysis Calorimetry (ICTAC) due to the fact that they allow the E and A values

to be independently obtained [14–16]. These equations are as follows:

Kissinger equation [17] (adopted as ASTM 698-79 [18]):

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_p} \quad (4)$$

Flynn–Wall–Ozawa (F–W–O) equation [19,20]:

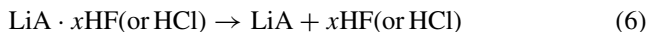
$$\log\beta = \log\left[\frac{AE}{Rg(\alpha)}\right] - 2.315 - \frac{0.4567E}{RT} \quad (5)$$

where β is heating rate, T_p the peak temperature of DTG curve and $g(\alpha)$ is a conversion functional relationship. It is obvious that by using least squares multiple regression of the data and from the slope and the intercept of the plot of $\ln \beta/T_p^2$ versus $1/T_p$ (or $\log \beta$ versus $1/T$), E and A can be calculated, respectively.

4. Results and discussion

4.1. Thermal behavior

The TG–DTG–DSC curves for all six salts are given in Figs. 1–6, respectively. The general information about their thermal behaviors, in terms of stability range, peak temperature and percentage mass loss and reaction heat, is presented in Table 1. As seen from them, LiCF₃SO₃, LiPF₆, LiBF₄, LiTFSI and LiClO₄ show a two-step decomposition mode. The first mass loss, which generally completes before 100 °C is related to the hydrogen fluoride (or hydrogen chloride in the case of LiClO₄) removal and is due to the thermal decomposition reaction:



where A is CF₃SO₃⁻, PF₆⁻, BF₄⁻, TFSI⁻ or ClO₄⁻ corresponding to appropriate salts compounds. The HF (or HCl)

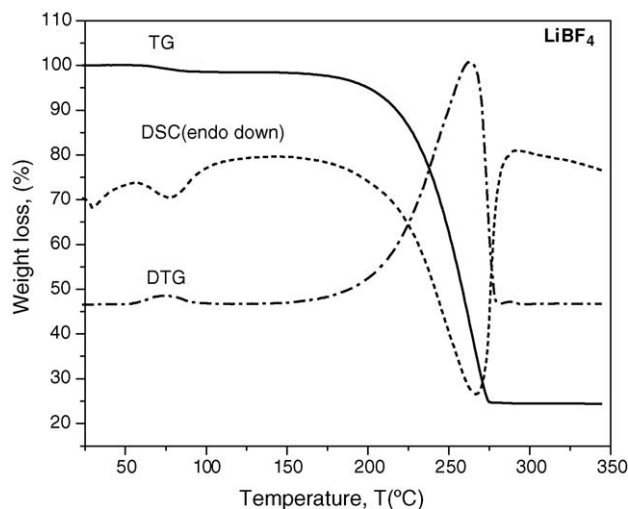


Fig. 1. TG–DTG–DSC curves for LiBF₄, $\beta = 5$ °C min⁻¹.

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