

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

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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

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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]:

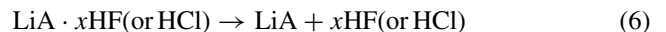
$$\log\beta = \log\left[\frac{AE}{Rg(\alpha)}\right] - 2.315 - \frac{0.4567E}{RT} \quad (5)$$

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)

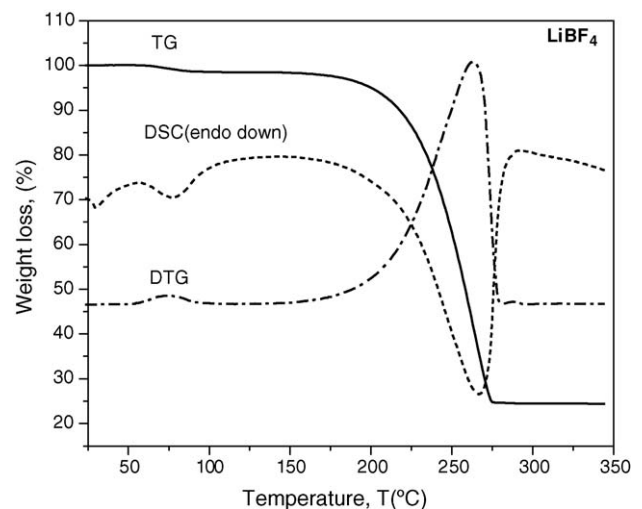
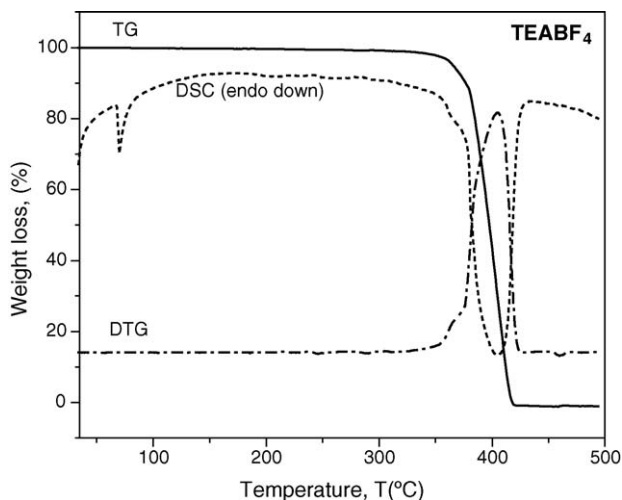
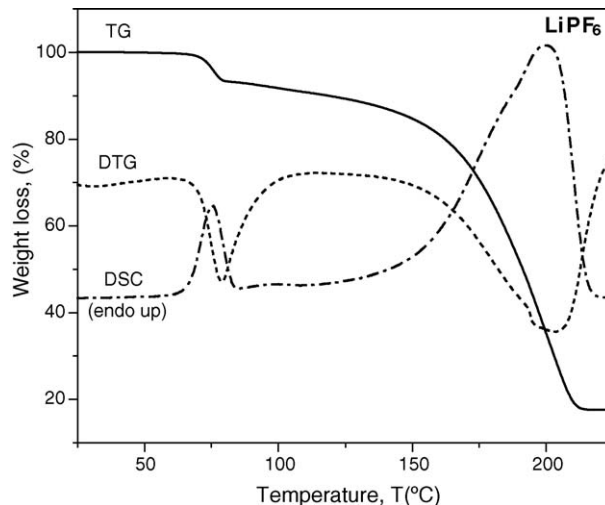
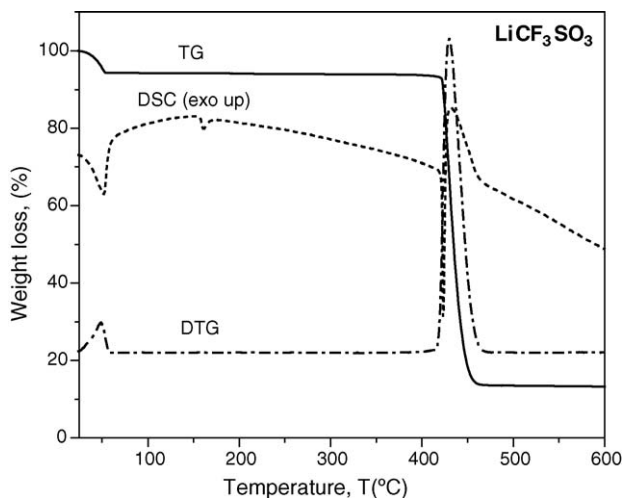
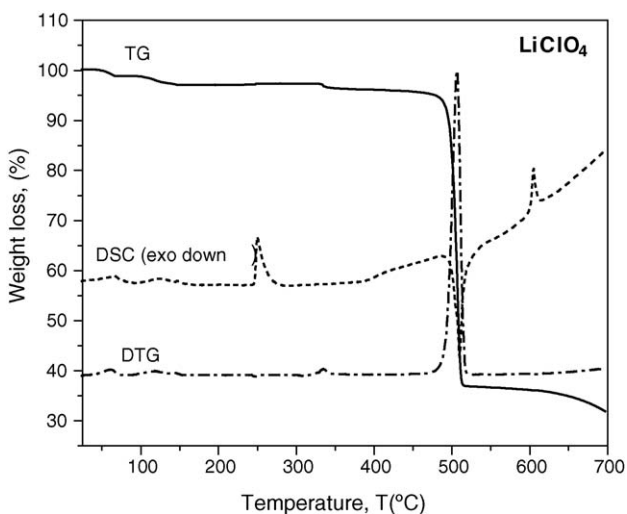
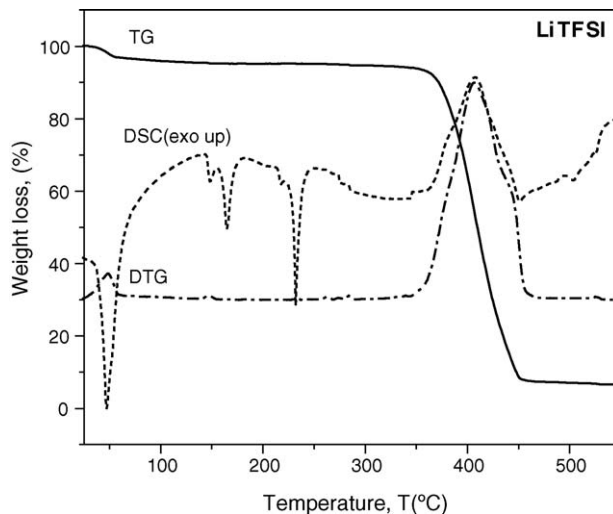


Fig. 1. TG–DTG–DSC curves for LiBF₄, $\beta = 5$ °C min⁻¹.

Fig. 2. TG–DTG–DSC curves for TEABF₄, $\beta = 5^\circ\text{C min}^{-1}$.Fig. 5. TG–DTG–DSC curves for LiPF₆, $\beta = 5^\circ\text{C min}^{-1}$.Fig. 3. TG–DTG–DSC curves for LiCF₃SO₃, $\beta = 5^\circ\text{C min}^{-1}$.Fig. 4. TG–DTG–DSC curves for LiClO₄, $\beta = 5^\circ\text{C min}^{-1}$.Fig. 6. TG–DTG–DSC curves for LiTFSI, $\beta = 5^\circ\text{C min}^{-1}$.

is a free acid, which often inevitably remains, more or less, in the above salt products during their production; x is used to express its amount mainly depending on its productive technology. A low content of this acid in lithium salts is demanded for high-quality lithium-ion battery because the existence of free acid promotes severe corruptions of the current collectors, and leads to further deterioration of the battery performance [21]. The present work shows that the amount of it in these salt compounds falls in the order $\text{LiPF}_6 > \text{LiCF}_3\text{SO}_3 > \text{LiTFSI} > \text{LiClO}_4 > \text{LiBF}_4$. In addition, the initial temperature for the release of free acid is also different, arranged in the order $\text{LiTFSI} > \text{LiCF}_3\text{SO}_3 > \text{LiClO}_4 > \text{LiBF}_4 > \text{LiPF}_6$. However, TEABF₄ shows no stage of HF removal because of its unique chemical composition and production process.

The main mass loss stage for all the salts compounds is the decomposition of their base materials. It can be observed from Table 1 that the stability of these salt compounds, according to the temperatures at which their

Table 1
Thermal decomposition data for the electrolyte salts under an atmosphere of dynamic nitrogen (heating rate $\beta = 5^\circ\text{C}$)

Salt	Stage	TG ^a ($^\circ\text{C}$)			Mass loss (%)	DSC ($^\circ\text{C}$)	
		T_i	T_p	T_f		T_p	H (J/g) ^b
LiClO ₄	I	51	62	149	2.89	64	83.1
	II	430	501	698	63.9	503	−446
LiCF ₃ SO ₃	I	41	49	62	5.77	51	164
	II	425	429	470	81.2	430	−299
LiTFSI	I	36	49	116	4.27	48	74.3
	II	340	407	415	87.7	407	−218
TEABF ₄		308	406	424	100	405	1350
LiBF ₄	I	63	75	97	2.08	77	31.3
	II	162	263	277	73.9	265	747
LiPF ₆	I	68	77	91	7.14	75	70.7
	II	91	201	225	74.8	204	282

^a T_i , T_p and T_f represent the initial decomposition temperature, the peak temperature of DTG and the final decomposition temperature, respectively.

^b Negative values indicate exothermic process.

main decompositions begin, can be described in the order LiClO₄ > LiCF₃SO₃ > LiTFSI > TEABF₄ > LiBF₄ > LiPF₆. All the salt compounds show stable within a certain temperature range after their first decomposition stage, with an exception of LiPF₆, which decomposes immediately after its previous stage.

The DSC profiles of the salt compounds show that their peak temperatures T_p generally match the corresponding ones of DTG curves very well and suggest that all the HF (or HCl) removal stages be associated with an endothermic behavior. It is very interesting to note that their main decomposition stages are different: it is exothermic for LiClO₄ or LiTFSI, and endothermic for LiBF₄, LiPF₆ or TEABF₄, while endothermic first and then exothermic for LiCF₃SO₃.

In view of the composition of the salts compounds studied in the present paper, the phenomenon from their DSC curves seems chemically reasonable. Usually, decomposition of a

compound requires energy to break its some chemical bands, the process, therefore, shows an endothermic behavior, this is the case of LiBF₄, LiPF₆ or TEABF₄. Actually, these salts are ate-complex of LiF + BF₃, LiF + PF₅ and TEAF + BF₃, respectively. Therefore, they separate to original composition at a high temperature, and the process is endothermic. If a compound molecule, however, contains the element oxygen which is to be expelled during decomposition process, oxygenation sometimes would occur in the meantime even under a nitrogen atmosphere, resulting in an overall exothermic effect [22], which is the case of LiClO₄, LiTFSI or LiCF₃SO₃. Furthermore, for LiCF₃SO₃, it melts (mp 423 $^\circ\text{C}$) shortly before its decomposition (425 $^\circ\text{C}$), which exhibits an endothermic peak first and immediately followed by an exothermic one. Besides, some small endothermic peaks on the DSC curves of LiClO₄ and LiTFSI which correspond to no mass loss on their TG curves may arise from the melt-

Table 2
Kinetic parameters of thermal decomposition for the electrolyte salts

Salt	Stage	E (kJ mol ^{−1})		log A	r^b		S.D. ^c	
		Kissinger	F–W–O ^a		Kissinger	F–W–O	Kissinger	F–W–O
LiClO ₄	I	72.68	73.21	8.544	0.9985	0.9988	0.02310	0.01256
	II	68.36	68.84	10.03	0.9989	0.9992	0.02236	0.01132
LiCF ₃ SO ₃	I	92.44	93.01	12.94	0.9988	0.9989	0.03436	0.01496
	II	223.9	224	14.30	0.9991	0.9992	0.02934	0.01269
LiTFSI	I	94.65	95.11	13.28	0.9962	0.9967	0.06034	0.02611
	II	156.3	159.4	9.543	0.9981	0.9984	0.04224	0.01836
TEABF ₄		262.6	260.5	17.96	0.9982	0.9984	0.04214	0.01834
LiBF ₄	I	74.99	76.82	9.031	0.9985	0.9987	0.03699	0.01604
	II	73.59	78.41	4.595	0.9964	0.9971	0.05555	0.01442
LiPF ₆	I	62.88	65.33	7.091	0.9975	0.9979	0.04781	0.02084
	II	106.2	108.2	9.362	0.9958	0.9963	0.06287	0.02741

^a F–W–O represents the Flynn–Wall–Ozawa method.

^b r is linear coefficient.

^c S.D. is the standard deviation.

ing or possible solid state phase transition [23] for these salt compounds. As seen from Table 1, by comparison, the reaction heat for the decomposition stage of the salts is generally more than that for the removal of the free acid.

The mass loss values indicate that the final residue at the end of decomposition for all the salt compounds is LiF or LiCl (for LiClO₄) except that of TEABF₄, with no residue left.

4.2. Decomposition kinetics

The kinetic parameters in Eq. (3), i.e. the activation energy E and the pre-exponential factor A (in terms of $\log A$) together with their appropriate linear correlation coefficient r and standard deviation, S.D., obtained from Eqs. (4) and (5) are summarized in Table 2. It can be seen that the E values by these two methods are not only in a relatively good agreement, but also corresponding to quite ideal r and S.D. values. Besides, the reaction heat values for the decomposition stages, i.e. H , calculated using software of the TG–DSC instrument, are also presented in this table.

If the decomposition processes for the studied salts compounds are assumed to be first-order reactions (i.e. $n = 1$) [21], the relationship among the conversion factor α , time t and temperature T could be established based on Eqs. (1)–(3).

Once more, the activation energy values for the decomposition of salts are generally larger than that for the revolution of the free acid. TEABF₄ shows unusually high activation energy like its reaction heat (Table 1).

5. Conclusions

From the results of the present study, the following conclusions may be drawn:

- (1) The five lithium salts show a two-step decomposition mode. The initial decomposition is related to the release of free acid and the followed step is due to the decomposition of the salts. The amount of free acid contained in the five lithium salts falls in the order LiPF₆ < LiCF₃SO₃ < LiTFSI < LiClO₄ < LiBF₄. Besides, their initial decomposition temperatures are different, arranged in the order: LiTFSI < LiCF₃SO₃ < LiClO₄ < LiBF₄ < LiPF₆.
- (2) The reaction heat values associated with two decomposition stages for the five salts are different. Generally, the processes of the free acid evolution are endothermic with lower reaction heat; while the salt decomposition are either endo- or exothermic, mainly depending on their chemical compositions.
- (3) The thermal stability of these salt compounds can be described in the order LiClO₄ < LiCF₃SO₃ < LiTFSI < TEABF₄ < LiBF₄ < LiPF₆.
- (4) The kinetic parameters for the decomposition processes for six salts studied have been obtained, which may be helpful to further understanding the thermal properties of these electrolyte salts.
- (5) Compared with five lithium salts, TEABF₄ shows different behaviors, involving no stage of free acid removal, higher activation energy and larger reaction heat.

References

- [1] Y. Baba, S. Okada, J. Yamaki, *Solid State Ionics* 148 (2002) 311–316.
- [2] G.G. Botte, R.E. White, Z. Zhang, *J. Power Sources* 97–98 (2001) 570–575.
- [3] D.D. MacNeil, J.R. Dahn, *J. Electrochem. Soc.* 150 (1) (2003) A21–A28.
- [4] E.S. Hong, S. Okada, T. Sonoda, S. Gopukumar, T. Yamaki, *J. Electrochem. Soc.* 151 (11) (2004) A1836–A1840.
- [5] T. Kawamura, A. Kimura, M. Boba, S. Okada, J. Yamaki, *J. Power Sources* 104 (2002) 260–264.
- [6] N. Katayama, T. Kawamura, Y. Baba, J. Yamaki, *J. Power Sources* 109 (2002) 321–326.
- [7] Y. Sato, K. Kanari, T. Masuda, *Thermochim. Acta* 296 (1997) 75–85.
- [8] Z. Zhang, D. Fowchard, J.R. Rea, *J. Power Sources* 70 (1998) 16–20.
- [9] J.R. Dahn, E.W. Fuller, M. Obrovac, U. von Sacken, *Solid State Ionics* 69 (1994) 265–270.
- [10] T. Kawamura, A. Kimura, M. Egashira, S. Okada, J. Yamaki, *J. Power Sources* 104 (2002) 260–264.
- [11] Z. Lu, Y. Ding, Y. Xu, S. Chen, Y. Yu, *J. Therm. Anal. Calorim.* 73 (2003) 333–340.
- [12] Z. Lu, Y. Ding, Y. Xu, Z. Yao, Q. Liu, J. Lang, *J. Therm. Anal. Calorim.* 70 (2002) 985–994.
- [13] J.A.F.F. Rocco, J.E.S. Lima, A.G. Frutuoso, K. Iha, M. Ionashiro, J.R. Matos, E.V. Suarez-Jha, *J. Therm. Anal. Calorim.* 77 (2004) 803–813.
- [14] M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Desseyn, C.R. Li, T.B. Tang, B. Roduit, J. Malek, T. Mitsuhashi, *Thermochim. Acta* 355 (2000) 125–143.
- [15] A.K. Burnham, *Thermochim. Acta* 355 (2000) 165–170.
- [16] Z. Lu, *Chin. J. Inorg. Chem.* 14 (2) (1998) 119–125.
- [17] H.E. Kissinger, *Anal. Chem.* 29 (1957) 1702–1705.
- [18] ASTM E698-79 Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials, 1984.
- [19] J.H. Flynn, L.A. Wall, *J. Polym. Sci. Part B, Polym. Lett.* 4 (1966) 323–328.
- [20] T. Ozawa, *Bull. Chem. Soc. Jpn.* 38 (1965) 1881–1886.
- [21] A.A. Smagin, V.A. Matyukha, V.P. Korobtsov, *J. Power Sources* 68 (1997) 326–327.
- [22] Z. Lu, Y. Ding, Y. Xu, B. Li, Y. Zhang, *Chin. J. Chem.* 22 (2004) 1087–1090.
- [23] Z. Lu, S. Chen, Y. Yu, J. Sun, S. Xiang, *J. Therm. Anal. Cal.* 55 (1999) 197–203.