Journal of Thermal Analysis and Calorimetry, Vol. 89 (2007) 1, 245–250

EFFECT OF $LiPF_6$ ON THE THERMAL BEHAVIORS OF FOUR ORGANIC SOLVENTS FOR LITHIUM ION BATTERIES

Q.-S. Wang[1], *J.-H. Sun*[1*], *G.-Q. Chu*[1], *X.-L. Yao*[2] *and C.-H. Chen*[2]

[1]State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei 230026, P.R. China
[2]Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, P.R. China

The thermal behaviors of four organic solvents with/without $LiPF_6$ were measured by C80 microcalorimeter at a 0.2°C min^{-1} heating rate. With the addition of 1 M $LiPF_6$, the ethylene carbonate (EC) and propylene carbonate (PC) show the exothermic peaks at elevated temperature, which lessen their stabilities. The exothermic peak temperatures of EC and PC based $LiPF_6$ solutions are at 212 and 223°C, respectively, in argon filled vessel. However, two endothermic peak temperatures were detected in diethyl carbonate (DEC) based $LiPF_6$ solution at 182 and 252.5°C, respectively, in argon filled vessel. Dimethyl carbonate (DMC) based $LiPF_6$ solution shows two endothermic peak temperatures at 68.5 and 187°C in argon filled vessel at elevated temperature. Consequently, it is concluded that $LiPF_6$ play a key role in the thermal behavior of its organic solution.

Keywords: *C80 microcalorimeter, lithium ion battery, organic solvents, thermal behavior*

Introduction

The cyclic and chain carbonates have been most widely used in lithium ion batteries, such as the ethylene carbonate (EC, $C_3H_4O_3$), propylene carbonate (PC, $C_4H_6O_3$), dimethyl carbonate (DMC, $C_3H_6O_3$), diethyl carbonate (DEC, $C_5H_{10}O_3$), and combinations thereof. Lithium hexafluorophosphate ($LiPF_6$) is by far the most widely used electrolyte salt in lithium ion batteries. It has high solubility in polar aprotic solvents, thus yielding highly conductive solutions, a wide electrochemical window and good anodic stability, and acceptable safety features, which is nonexplosive and relatively nonpoisonous. However, under appropriate conditions, $LiPF_6$ may be a source of the powerful Lewis acid PF_5 by the way of the following equilibrium decomposition [1–3].

$$LiPF_6 \Leftrightarrow LiF + PF_5 \qquad (1)$$

Both the PF_5 and the fluoride ion may react with solution species. Furthermore, the P–F bonds are highly susceptible to hydrolysis by even trace amounts of moisture yielding HF and POF_3, etc. A rise in temperature will, of course, accelerate the formation of these species and their further reaction with the solvents.

Cyclic alkyl carbonate and chain alkyl carbonate mixed solvent systems with $LiPF_6$ as a salt are used in lithium ion batteries because of their electrochemical stability and highly ionic conductivity. The thermal stability of electrolytes is very important, which has been widely studied by using differential scanning calorimeter (DSC) and accelerating rate calorimeters (ARC) [4–7]. The electrolytes are mixtures of organic solvents with electrolyte salt are generally well known, so the thermal behavior research of single solvent is necessary and important for further researches. Ravdel *et al.* [8] investigated 1 M $LiPF_6$ in DMC and DEC heated at 85°C for 500 h, and the products were observed by gas chromatography with mass selective detection (GC-MS) and nuclear magnetic resonance (NMR) spectroscopy. MacNeil *et al.* [9] simply reported DSC results of 1 M $LiPF_6$ in EC, PC and DEC at a 5°C min^{-1} heating rate. However, the endothermic reaction cannot be detected by ARC because of its inherent shortcoming, and then the result may deviate from the real reaction [10–12]. As to DSC, the vessel obturation is a key problem to be solved [12–16]. While C80 microcalorimeter can make up above shortcomings for the thermal study of electrolytes [17–20]. In this paper, the thermal behaviors of four organic solvents and their $LiPF_6$ solutions were studied detailedly by C80 microcalorimeter with low heating rate.

Experimental

The C80 calorimeter used in this study belongs to the CALVET calorimeters family distinguished by their accurate and reproducible calorimetric measurements. It is made by Setaram Scientific and Industrial Equipment Company and commercialized since 1975. The C80 calorimeter is a sturdy and high-per-

---

[*] Author for correspondence: sunjh@ustc.edu.cn and pinew@ustc.edu

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

formance instrument that makes possible a very large amount of application in varied fields. The instrument was designed to study materials transformation over the temperature range from room temperature to 300°C. The calorimeter is connected to a data acquisition and control unit, as well as to a personal computer equipped with the SETSOFT software, which can be used to calculate thermodynamics and kinetic data [12, 20–23]. In this study, all the samples were heated in the high pressure vessel at a 0.2°C min^{-1} heating rate from room temperature to 300°C.

The organic solvents are commercially available products (Zhangjiagang Guotai-Huarong Co., Ltd.). The salt $LiPF_6$ was purchased from another chemical company (Tianjin Jinniu Co. Ltd.). From these chemicals, we prepared four solutions, i.e. 1 M $LiPF_6$ in EC, PC, DEC and DMC, respectively, in argon filled gloved box. In the thermal analysis experiments, each sample was put into a high-pressure sample vessel, sealed, and taken out from the argon filled glove box. In the air filled vessel test, the vessel was opened for few minutes to let air in and then sealed again.

Results and discussion

Figure 1 presents the heat flow curves of 1 M $LiPF_6$/EC and pure EC in argon filled vessel at elevated temperature. It clearly indicates that the existence of $LiPF_6$ impacts the thermal behavior of EC. The pure EC express itself a weak exothermic peak at 198°C between the range 158–241°C with a heat of reaction of 43.8 J g^{-1}, followed by an increasing heat flow trend. With the addition of $LiPF_6$, two exothermic peaks is observed, a pronounced sharp one between 192 and 226°C and the peak temperature is 212°C with a heat of reaction 355.4 J g^{-1}. The following broad and lower one is between about 225 and 280°C and the peak temperature is 253.7°C with a heat of reaction 226.8 J g^{-1}.

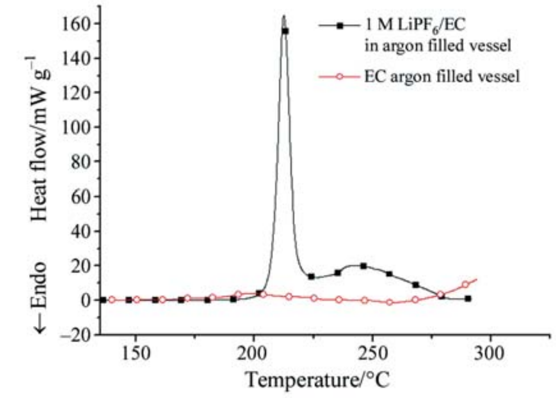


Fig. 1 C80 heat flow curves of 1 M $LiPF_6$/EC and EC in argon filled vessel

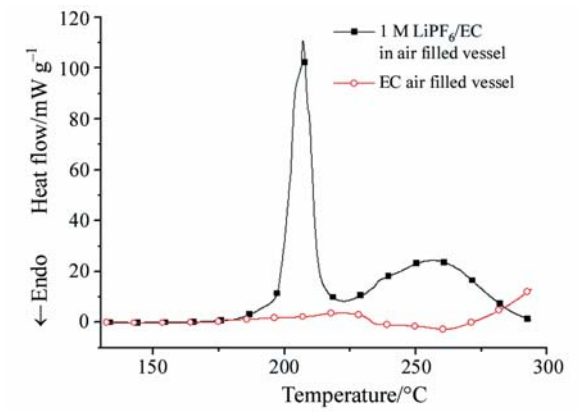
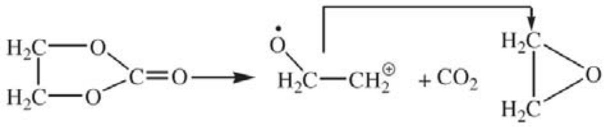


Fig. 2 C80 heat flow curves of 1 M $LiPF_6$/EC and EC in air filled vessel

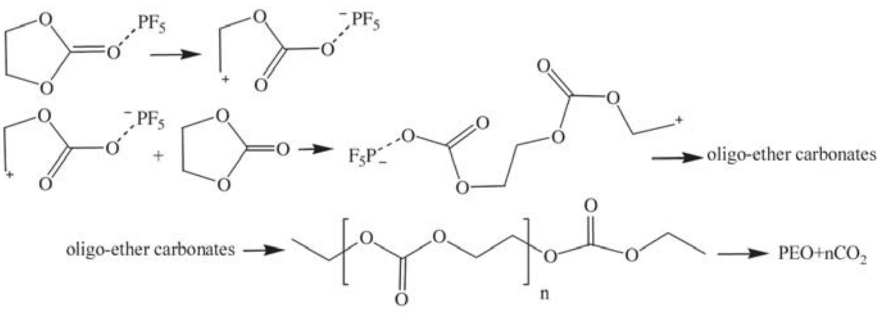
In the air filled vessel, the 1 M $LiPF_6$/EC and EC exhibit the similar thermal behavior in argon filled vessel, Fig. 2 shows the results. The pure EC exhibit a broad and lower exothermic process in the range 175–233°C, the peak temperature is 222°C with a reaction heat 38.3 J g^{-1}, then followed by endothermic process ended at 271°C, and then to release heat again. Botte *et al.* [4] found the exothermic peak temperature is 220°C with a heat generation of 23 J g^{-1} by using DSC with 10°C min^{-1} heating rate, but the endothermic process was not found. It shows another thermal behavior once 1 M $LiPF_6$ is added to EC solvent, two exothermic peaks, 207 and 259°C, respectively, were observed with the heat of generation 366.3 and 323.7 J g^{-1}.

By comparing the thermal behavior of EC in air and argon filled vessel, oxygen has little effect on this cyclic carbonate. At the elevated temperature, before the boiling point 238°C, EC is stable and with little heat generation. After the temperature is over 260°C, EC decomposes and generate gases such as CO_2, O_2 and H_2 [7]. The gases ratio reported by using a gas chromatograph, CO_2 was the major component (15.15%), with the formation of some O_2 (422 ppm) and traces of H_2 (33 ppm). Combining their results, the possible main reaction can be proposed as Scheme 1 [24].

The few O_2 and H_2 may be generated by other unknown reactions. When the temperature is over 192°C, $LiPF_6$ acts as a Lewis acid with EC solvents to generate transesterification products, polyethylene oxide (PEO) polymers and CO_2 [25]. Under the attack of PF_5 in higher temperature, the ring is broken. Then the possible ring-opening polymerization process is as Scheme 2 [24].



Scheme 1 The possible main reaction of EC



Scheme 2 The possible PF_5 effect on EC ring broken

Furthermore, Li^+ will react with EC in rising temperature, too. Mogi *et al.* [26] detected the thermal decomposition products such as CO, C_2H_4 and so on by pyrolysis-gas (300°C) chromatography-mass spectroscopy (Py-GC-MS). Then the possible processes are proposed as following [26, 27]:

$$CH_2OCOOCH_2(EC)+2Li^++2e^-\rightarrow(CH_2OLi)_2+CO \quad (2)$$

$$CH_2OCOOCH_2(EC)+Li^++e^-\rightarrow{}^{\cdot}CH_2CH_2OCO_2Li \quad (3)$$

$$2\,{}^{\cdot}CH_2CH_2OCO_2Li\rightarrow LiOCO_2CH_2CH_2OCO_2Li+C_2H_4 \quad (4)$$

with comparision of the heat flow curves of PC and 1 M $LiPF_6$/PC in Fig. 3, PC is more stable with two small endothermic peak temperatures at 130 and 163°C, and the endothermic heat is 3.1 and 3.6 J g^{-1}, respectively. However, the addition of $LiPF_6$ changes the thermal behavior greatly. A large and sharp exothermic is observed from 214 to 233°C, the sharp peak temperature is 223.3°C with the reaction heat 565.1 J g^{-1}. Katayama *et al.* [28] also found the exothermic phenomenon by using DSC with 5°C min^{-1} heating rate, but the peak temperature is at about 274°C, which is 51°C higher than that one detected by C80.

PC changes its thermal behavior in air filled vessel at elevated temperature, which is shown in Fig. 4. Although PC release little heat comparing with 1 M $LiPF_6$/PC, it presents an exothermic peak temperature at 154°C with heat of reaction 39.6 J g^{-1} instead of endothermic process that presents in argon filled atmosphere. 1 M $LiPF_6$/PC shows a sharp and large exothermic peak, which is similar with that in argon filled atmosphere, the peak temperature is 202°C with the reaction heat 582.9 J g^{-1}.

The pure PC both in argon and air filled vessel are stable although it has different thermal behavior and may be influenced by oxygen. With the effect of $LiPF_6$ at high temperature, PC solvent generates transesterification products. Just like EC, $LiPF_6$ acts as a Lewis acid, and the products were detected by Arakawa and Yamaki [29] using GC-MS. The possible processes are as Scheme 3.

DEC shows its thermal behavior in argon filled vessel in Fig. 5. The pure DEC is stable until 245°C, and then exothermic process following. The addition of 1 M $LiPF_6$ changes its thermal behavior obviously. Three endothermic peak temperatures locate at 173, 182 and 252.5°C, and the exothermic peak between the second and third exothermic peaks is 202°C with the heat of reaction 62.7 J g^{-1}. Between the front two endothermic peaks, there is an endothermic rate decreasing process with the peak temperature at 176.5°C, and form a 'W' style with the heat of reaction 112 J g^{-1}. The last endothermic process heat is 112.3 J g^{-1}, which almost equates to the former one.

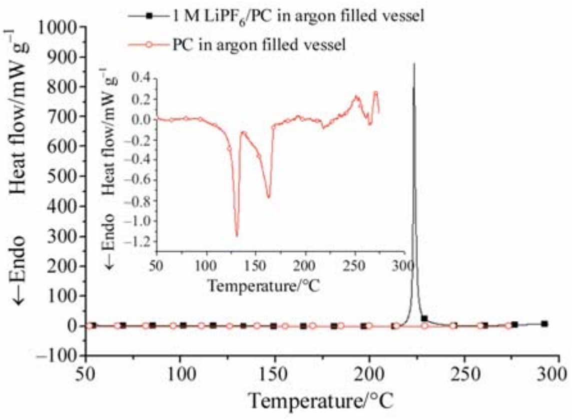


Fig. 3 C80 heat flow curves of 1 M $LiPF_6$/PC and PC in argon filled vessel

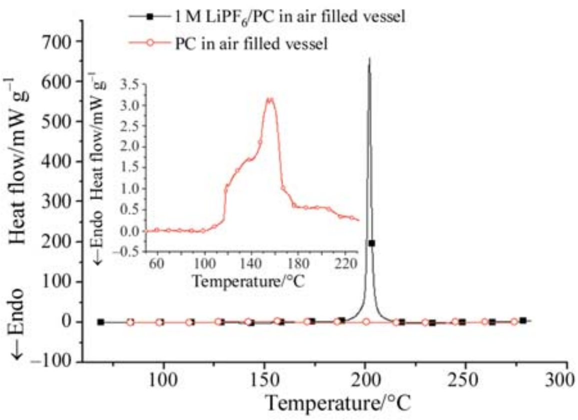


Fig. 4 C80 heat flow curves of 1 M $LiPF_6$/PC and PC in air filled vessel

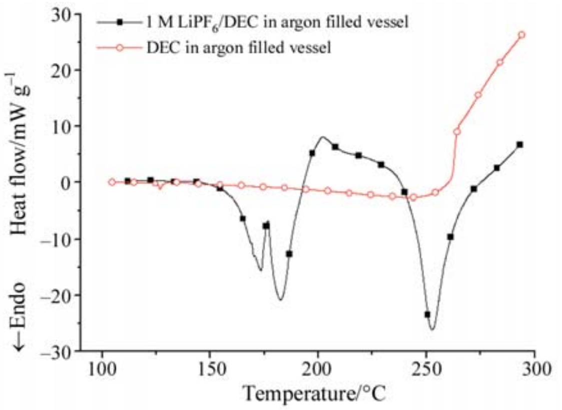
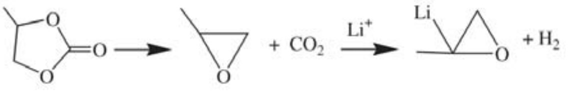


Fig. 5 C80 heat flow curves of 1 M LiPF$_6$/DEC and DEC in argon filled vessel



Scheme 3 The possible main reaction of PC

The oxygen, sealed in the vessel, will participate to the DEC reaction at elevated temperature, which can be illustrated by Fig. 6. The DEC has an exothermic peak temperature at 167°C with the heat of release 30.2 J g^{-1}, and then followed by a slow endothermic process and undergoes a sharp exothermic process at 246°C, it may be the bonds broken in DEC. The 1 M LiPF$_6$ in DEC solution undergoes endothermic and exothermic process alternately. The first endothermic peak temperature is 167.3°C with the heat of reaction 49.7 J g^{-1}, and then a sharp exothermic peak temperature appears at 171°C with the heat of reaction 22.8 J g^{-1}. A cuspidal endothermic peak temperature is observed at 176°C with the heat of reaction 84 J g^{-1}, then following with a broad exothermic process and reached to peak temperature at 206°C with the heat 57.9 J g^{-1}. The last process is endothermic and the peak temperature is 252.7°C with the heat of reaction 251 J g^{-1}, which is consistent with that in argon filled vessel but the amount of endothermic heat is larger.

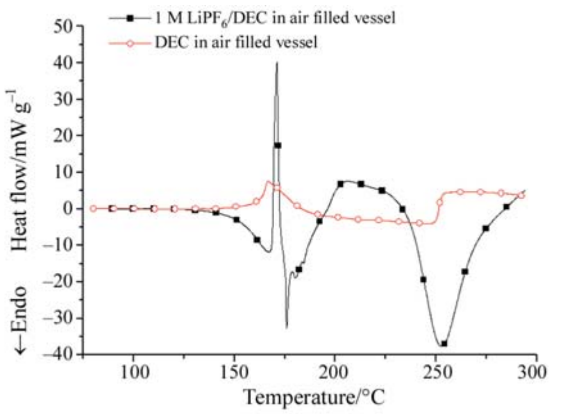
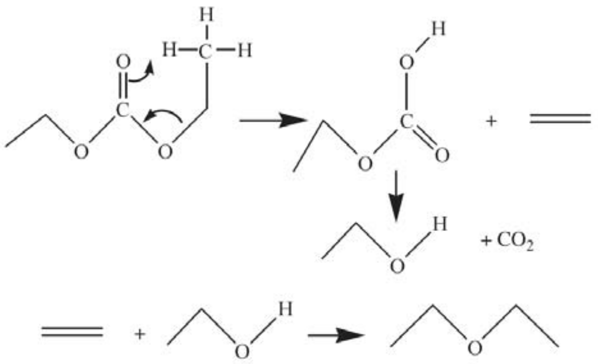


Fig. 6 C80 heat flow curves of 1 M LiPF$_6$/DEC and DEC in air filled vessel

When the temperature of DEC is over 245°C, transesterification may be occurring and yielding methyl ethyl carbonate either in argon or in air filled vessel. The possible transesterification is shown in Scheme 4 [1]. It is sure that oxygen affects their thermal behaviors with an exothermic process, which may be caused by DEC oxidation reaction with little oxygen sealed in the vessel.



Scheme 4 The possible main transesterification of DEC

NMR measurements by Gnanaraj *et al.* [1, 6] on LiPF$_6$ solutions after different stages of thermal reaction revealed that the solutions are stable up to 140°C and upon heating to 180°C undergo an elimination reaction of DEC and followed by transesterification. Further heating leads, by stages, to complete decomposition. The major reaction products detected in the condensed and gas phases are CH_3CH_2F, CH_3F, FCH_2CH_2Y (Y is OH, F, etc.), H_2O, and polymer. From the results, the possible LiPF$_6$/DEC reactions were proposed as following [5, 30]:

$$C_2H_5OCOOC_2H_5+PF_5\rightarrow C_2H_5OCOOPF_4+HF+C_2H_4 \qquad (5)$$

$$C_2H_5OCOOC_2H_5+PF_5\rightarrow C_2H_5OCOOPF_4+C_2H_5F \qquad (6)$$

$$C_2H_5OCOOPF_4\rightarrow PF_3O+CO_2+C_2H_4+HF \qquad (7)$$

$$C_2H_5OCOOPF_4\rightarrow PF_3O+CO_2+C_2H_5F \qquad (8)$$

$$C_2H_5OCOOPH_4+HF\rightarrow PF_4OH+CO_2+C_2H_5F \qquad (9)$$

Figure 7 shows that DMC has an endothermic peak temperature at 91°C, which is according with its boiling point 90°C with the endothermic heat 1.5 J g^{-1}. DMC shows stable characteristics with slow endothermic phenomenon in argon filled vessel at elevated temperature, and a sharp exothermic occurs at 223°C. An endothermic peak appears at 68.5°C in 1 M LiPF$_6$/DMC solution with the endothermic heat 15.4 J g^{-1} in Fig. 7, then, it undergoes a fluctuant process till to 187°C. The followed zigzag endothermic process reaches to peak temperature at 219°C with heat of reaction 41.7 J g^{-1}.

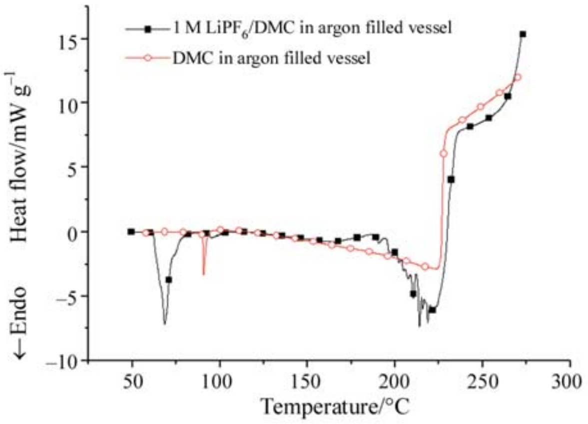


Fig. 7 C80 heat flow curves of 1 M $LiPF_6$/DMC and DMC in argon filled vessel

In lower temperature, DMC shows stable characteristic in air filled vessel at elevated temperature in Fig. 8. An exothermic process of DMC occurs at 191°C and followed by a sharp exothermic process with a broad range around 209°C with the heat of 104.2 J g^{-1}. There shows a different thermal behavior with the addition of $LiPF_6$ in DMC, and an endothermic peak temperature is detected at 202°C with the decalescence of 37.2 J g^{-1}. Then, it is followed by a sharp exothermic process and the peak temperature is 208.7°C with the heat of reaction 10.2 J g^{-1}. The later endothermic peak temperature is 210°C with the heat of 1.8 J g^{-1}, and then goes to exothermic process.

The exothermic process of pure DMC both in air and argon filled vessel may be caused by the cleavage of C–O bond in higher temperature, then the possible reactions as Scheme 5 [24].

The molecule of DMC possesses two active centers (alkyl and carbonyl carbons), whose reactivity can be tuned with the temperature. In particular, two distinct pathways can be recognized in the reaction of DMC with a generic anionic nucleophile (Y^-) [31]. When PF_6^- nucleophile attacks at carbonyl carbon of DMC, the cleavage of acyl-oxygen bond generates a methoxycarbonyl product at lower temperature (100°C) [32]. Then, the possible reactions can be proposed to illustrate the first endothermic peak in Fig. 7 as Scheme 6.

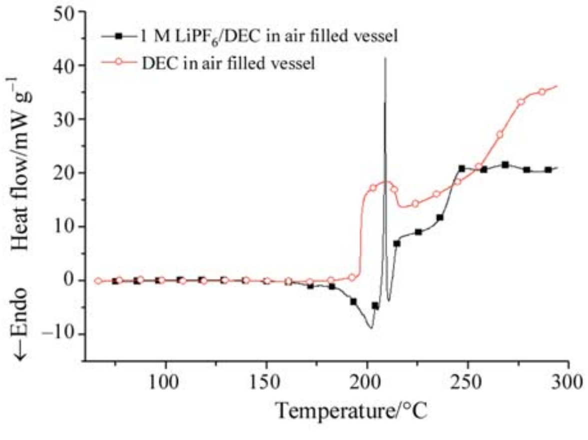
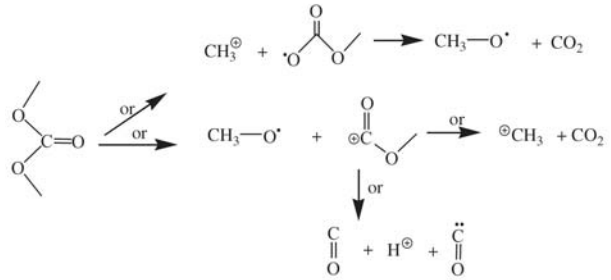


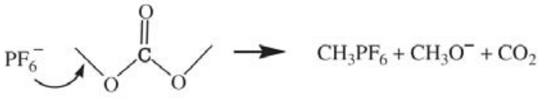
Fig. 8 C80 heat flow curves of 1 M $LiPF_6$/DMC and DMC in air filled vessel



Scheme 5 The possible main reactions of DMC

Scheme 6 The possible PF_6^- effect on DMC below 100°C

When temperature is over 187°C, PF_6^- nucleophile attacks at DMC and undergoes a methylation reaction to generate methoxide and CO_2 as Scheme 7.



Scheme 7 The possible PF_6^- effect on DMC over 187°C

At the elevated temperature, the endothermic processes show that Li^+ also react with DMC and the possible reactions as following [27, 33]:

$$CH_3OCO_2CH_3+2e^-+2Li^+\rightarrow 2CH_3OLi+CO \quad (10)$$

$$CH_3OCO_2CH_3+2e^-+2Li^++H_2\rightarrow Li_2CO_3+2CH_4 \quad (11)$$

$$2CH_3OCO_2CH_3+2e^-+2Li^++H_2 \rightarrow 2CH_3OCO_2Li+2CH_4 \quad (12)$$

All above reactions with heat release or decalescence will disturb the normal characteristics of electrolytes, and the exothermic reaction is more dangerous for the safe use of lithium ion batteries usage, as the generated heat can be accelerated inner the batteries to induce more reactions till to thermal runaway. On the other hand, gas generation will increase the inner pressure in the sealed batteries, which also is a threat to the batteries. Hereby, the corresponding technologies or measures should be taken to delay or eliminate the reactions and to suppress gases generation.

Conclusions

The thermal behavior of $LiPF_6$ in carbonates was investigated by C80 microcalorimeter. It is found that $LiPF_6$ plays a major role in the thermal decomposition of the solution components both in the endothermic and the exothermic reactions.

The pure cyclic alkyl carbonates show good stability at elevated temperature, with the addition of 1 M $LiPF_6$ in argon filled vessel, the large exothermic peak temperature is detected at 212 and 223°C in EC and PC, respectively. It is thought that $LiPF_6$ acts as a Lewis acid and transesterification is occurring in EC and PC with the generation of CO_2 and others.

The pure chain alkyl carbonates appear sharp exothermic process at higher temperature. The exothermic process of DEC is almost at about 245°C both in argon and air filled vessel. The addition of $LiPF_6$ changes its thermal behavior greatly, two endothermic peaks is detected at 182 and 252.5°C, respectively, in argon atmosphere. DMC is less stable than DEC, and its onset exothermic temperature is at 223 and 191°C in argon and air filled vessel, respectively. The effect of $LiPF_6$ is shown by two endothermic peak temperatures at 68.5 and 219°C, which makes DMC unstable. The unstable may be caused by the PF_5, Li^+ and PF_6^-, as well as with gases generation.

Acknowledgements

This study was supported by National Science Foundation of China (grant no. 20603034) and ‘100 Talents Project’ of Chinese Academy of Sciences. A financial support from Anhui Provincial Natural Science Foundation (no. 050450403) and youth funds of USTC are also appreciated.

References

1 J. S. Gnanaraj, E. Zinigrad, L. Asraf, H. E. Gottlieb, M. Sprecher, M. Schmidt, W. Geissler and D. Aurbach, J. Electrochem. Soc., 150 (2003) A1533.
2 K. S. Gavritchev, G. A. Sharpataya, A. A. Smagin, E. N. Malyi and V. A. Matyukha, J. Therm. Anal. Cal., 73 (2003) 71.
3 Q. S. Wang, J. H. Sun, L. S. Xiang, X. L Yao and C. H. Chen, Solid State Ionics, 177 (2006) 137.
4 G. G. Botte, R. E. White and Z. M Zhang, J. Power Sources, 97–98 (2001) 570.
5 T. Kawamura, A. Kimura, M. Egashira, S. Okada and J. I. Yamaki, J. Power Sources, 104 (2002) 260.
6 J. S. Gnanaraj, E. Zinigrad, L. Asraf, H. E. Gottlieb, M. Sprecher, D. Aurbach and M. Schmidt, J. Power Sources, 119–121 (2003) 794.
7 G. G. Botte and T. J. Bauer, J. Power Sources, 119–121 (2003) 815.
8 B. Ravdel, K. M. Abraham, R. Gitzendanner, J. DiCarlo, B. Lucht and C. Campion, J. Power Sources, 119–121 (2003) 805.
9 D. D. MacNeil and R. Dahn, J. Electrochem. Soc., 150 (2003) A21.
10 M. Odlyha, Q. Wang, G. M. Foster, J. de Groot, M. Horton and L. Bozec, J. Therm. Anal. Cal., 82 (2005) 627.
11 F. Xu, L. X. Sun, Z. C. Tan, J. G. Liang and T. Zhang, J. Therm. Anal. Cal., 83 (2006) 187.
12 J. H. Sun, X. R. Li, K. Hasegawa, and G. X. Liao, J. Therm. Anal. Cal., 76 (2004) 883.
13 J. Pak, W. Qiu, M. Pyda, E. Nowak-Pyda and B. Wunderlich, J. Therm. Anal. Cal., 82 (2005) 565.
14 M. Rodríguez de Rivera and F. Socorro, J. Therm. Anal. Cal., 80 (2005) 769.
15 A. Raemy, C. Appolonia Nouzille, P. Frossard, L. Sagalowicz and M.-E. Leser, J. Therm. Anal. Cal., 80 (2005) 439.
16 S. P. Sivapirakasam, M. Surianarayanan, F. Chandrasekaran and G. Swaminathan, J. Therm. Anal. Cal., 78 (2004) 799.
17 Y. Chen, J. Q. Xie, B. Zhang and X. C. Zeng, J. Therm. Anal. Cal., 75 (2004) 847.
18 Q. S. Wang, J. H. Sun, X. L Yao and C. H. Chen, J. Electrochem. Soc., 153 (2006) A329.
19 Q. S. Wang, J. H. Sun, X. L Yao and C. H. Chen, J. Solution Chem., 35 (2006) 179.
20 J. H. Sun, Y. F. Li and K. Hasegawa, J. Loss Prevent. Proc., 14 (2001) 331.
21 T. Kamiyama, Y. Toshima, T. Matsushita and T. Kimura, J. Therm. Anal. Cal., 82 (2005) 207.
22 J. M. Criado and L. A. Pérez-Maqueda, J. Therm. Anal. Cal., 80 (2005) 27.
23 H. X. Chen, N. A. Liu, L. F. Shu and R. W. Zong, J. Therm. Anal. Cal., 78 (2004) 1029.
24 M. Moshkovich, M. Cojocaru, H. E. Gottlieb and D. Aurbach, J. Electrochem. Soc., 497 (2001) 84.
25 S. E. Sloop, J. B. Kerr and K. Kinoshita, J. Power Sources, 119–121 (2003) 330.
26 R. Mogi, M. Inaba, Y. Iriyama, T. Abe and Z. Ogumi, J. Power Sources, 119–121 (2003) 597.
27 H. Yoshida, T. Fukunaga, T. Hazama, M. Terasaki, M. Mizutani and M. Yamachi, J. Power Sources, 68 (1997) 311.
28 N. Katayama, T. Kawamura, Y. Baba and J. I. Yamaki, J. Power Sources, 109 (2002) 321.
29 M. Arakawa and J. I. Yamaki, J. Power Sources, 54 (1995) 250.
30 Q. S. Wang, J. H. Sun, X. L Yao and C. H. Chen, Thermochim. Acta, 437 (2005) 12.
31 P. Tundo, Pure Appl. Chem., 73 (2001) 1117.
32 Y. Ono, Pure Appl. Chem., 68 (1996) 367.
33 K. Kumai, H. Miyashiro, Y. Kobayashi, K. Takei and R. Ishikawa, J. Power Sources, 81–82 (1999) 715.

Received: February 15, 2006
Accepted: March 10, 2006
OnlineFirst: June 27, 2007

DOI: 10.1007/s10973-006-7534-1