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Thermal stability of $LiPF_6$/EC + DEC electrolyte with charged electrodes for lithium ion batteries

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Abstract

The thermal stabilities of 1 M $LiPF_6$/EC + DEC and with electrodes were studied by calorimetry. The results show that both the electrolyte–$Li_{0.5}CoO_2$ and electrolyte–Li_xC_6 system have lower decomposition onset temperatures than either the separate electrolyte or electrodes. The electrolyte is oxidized by $Li_{0.5}CoO_2$, while its reaction with lithiated graphite occurs because the solid electrolyte interphase (SEI) breaks down at 57 °C. The 1 M $LiPF_6$/EC + DEC in air is less stable than in argon, but the reaction is similar.

Keywords: Lithium ion battery; Electrolyte; Electrode materials; Thermal stability; C80 calorimeter

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1. Introduction

Lithium ion batteries are widely used in many fields. Extensive applications of lithium ion batteries generate increasing safety concerns and many studies are focused on the safety of lithium ion batteries [1–8]. Many improvements in safety of lithium ion batteries, such as PTC [9], shutdown separator [9,10], electrode additives [11,12], flame retardants [13–18], etc. have been made, but there are still safety concerns with large scale applications such as electric vehicles [19]. Safety is related mainly to the thermal reactivity of the materials in the battery. When the temperature of a lithium ion battery increase because of abusive conditions (e.g., short circuit, overcharge, heating) self-heating may be initiated. Various exothermic and endothermic reactions involving both the solution and the electrodes can occur inside the battery. Possible processes contributing to self-heating include reactions between electrolyte and electrode materials and decomposition of the electrolyte solution. Because the electrolyte links to anode and cathode, its thermal stability is key for the safety of lithium ion batteries. Therefore, knowledge of the thermal behavior of the electrolyte, electrolyte-anode and electrolyte-cathode is essential for designing safer and higher performance batteries.

Ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) are the most widely used solvents and $LiPF_6$ is the dominant solute used in practical lithium ion batteries. The thermal stabilities of electrolytes and electrodes have been studied by differential scanning calorimetry (DSC) [20–24] and accelerating rate calorimetry (ARC) [24–26]. However, there often is generation of large pressures that cannot be contained with the typical hermetic DSC sample pans [27]. MacNeil [23] described welded Al sample vessel for DSC that ensures no escape of generated gases, but which complicates the operation. Furthermore, ARC is available to research self-heating substances, but is unfit to detect endothermic reactions. The high pressure stainless steel vessel used in the Setaram C80 calorimeter has good airtight characteristics, and operates at elevated temperatures [28], and therefore, was used to investigate the thermal stability of 1 M $LiPF_6$/EC + DEC and the electrolyte–electrode systems.

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2. Experimental

The organic solvents are commercially available products made by Zhangjiagang Guotai-Huarong Co., Ltd. The salt $LiPF_6$ was produced by Tianjin Jinniu Co., Ltd. Solutions of 1 M $LiPF_6$ in EC, DEC, and in EC + DEC (1:1 w/w) were prepared in argon filled glove box. The coin batteries were charged and discharged three times at 0.2 mA cm^{-2} with a Neware cycler. The high cutoff voltage and low cutoff voltage were set to 4.2 and 2.8 V, respectively, for $LiCoO_2$ half batteries. The batteries were finally charged to 4.2 V for the thermal experiments. For graphite half batteries, high cutoff voltage and low cutoff voltage were set to 3.0 and 0 V, respectively, and the batteries were finally discharged to 0 V for thermal experiments. All the batteries were disassembled in an argon filled glove box, and the delithiated $LiCoO_2$, i.e. $Li_{0.5}CoO_2$, and Li_xC_6 were rinsed in DMC twice to remove the electrolyte. In this study, a Setaram C80 calorimeter was used, the samples were sealed in an 8.5 ml high pressure vessel with dry argon or air condition, and then scanned from ambient to 300 °C at a 0.2 °C min^{-1} heating rate.

3. Results and discussion

3.1. Organic solvent thermal behavior

Fig. 1 shows the heat flow curves of EC, DEC and EC + DEC at 0.2 °C min^{-1} heating rate in argon. The pure EC has an exothermic process that starts near 164 °C, and peaks at 198 °C with −44 J g^{-1}. An endothermic process that begins at 154 °C in DEC continues to 242 °C, and then goes exothermic. The mixture of EC and DEC is more stable at elevated temperature. There is no heat flow below 192 °C, and slight exothermicitis above that.

3.2. $LiPF_6$ effect on the organic solvents thermal behavior

$LiPF_6$ is an unstable substance even if with high purity, endothermic processes are observed above 193 °C followed by a sharp endothermic peak at 196 °C with 22 J g^{-1} in Fig. 2. This sharp endothermic peak appears to be the melting of $LiPF_6$ as its melting point is 200 °C. A second endothermic peak at 282 °C with endotherm of 400 J g^{-1}, appears to be the complete decomposition to LiF and PF_5 [24,29].

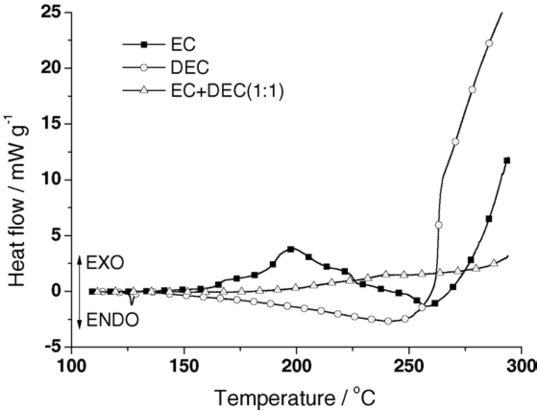


Fig. 1. Heat flow curves of EC, DEC and EC + DEC at 0.2 °C min^{-1} in argon.

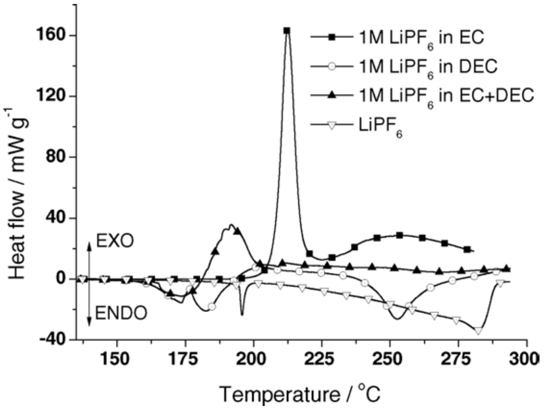
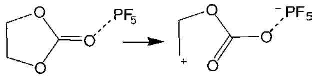
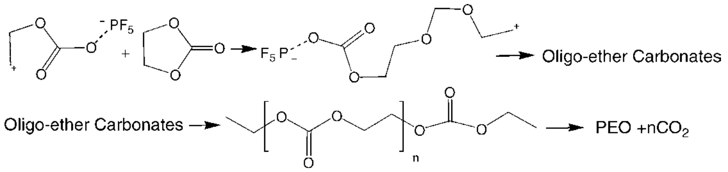


Fig. 2. Heat flow curves of $LiPF_6$, 1 M $LiPF_6$ in EC, DEC, and EC + DEC at 0.2 °C min^{-1} in argon.

$LiPF_6$ in solvents behaves remarkably different. In Fig. 2, 1 M $LiPF_6$ in EC shows an exothermic peak at 212 °C with a heat of reaction −355 J g^{-1} from 192 to 226 °C. It is thought that $LiPF_6$ acts as a Lewis acid with EC to cleave the ring and generate transesterification products, Eq. (1) [30,31]. The following broad exothermic process from 225 to 280 °C with a heat of reaction −393 J g^{-1} may be due to a polymerization reaction that generates polyethylene oxide (PEO) polymers and CO_2 [30,31], Eq. (2)



(1)



(2)

The 1 M $LiPF_6$ in DEC shows two endothermic processes with peaks at 183 and 253 °C. The first endothermic process is from 148 to 193 °C with the heat of 112 J g^{-1}. With the temperature rising, an exothermic process is observed, and the peak is at 202 °C with the heat of reaction −63 J g^{-1}.

The second endothermic process appears above 238 °C with $112\,\mathrm{J\,g^{-1}}$. DEC react with fluoride ion acting as a strong base in aprotic solvent (Eqs. (3) and (4)), which significantly lower the stability of DEC solutions [25]. Nuclear magnetic resonance (NMR) [25] identified the thermal decomposition products are CH_3CH_2F, FCH_2CH_2Y (Y is OH, F, etc.), CO_2, etc. From the results, the possible reactions can be proposed as Eqs. (5)–(7) [20,25]

$$C_2H_5OCOOC_2H_5 + PF_5 \rightarrow C_2H_5OCOOPF_4 + HF + C_2H_4 \quad (3)$$

$$C_2H_4 + HF \rightarrow C_2H_5F \quad (4)$$

$$C_2H_5OCOOPF_4 \rightarrow PF_3O + CO_2 + C_2H_4 + HF \quad (5)$$

$$C_2H_5OCOOPF_4 \rightarrow PF_3O + CO_2 + C_2H_5F \quad (6)$$

$$C_2H_5OCOOPF_4 + HF \rightarrow PF_4OH + CO_2 + C_2H_5F \quad (7)$$

The 1 M $LiPF_6$/EC + DEC electrolyte shows successive endothermic and exothermic processes. The endothermic onset temperature is almost the same as with 1 M $LiPF_6$ in DEC, near 140 °C. It can be speculated that the DEC reacts as Eq. (3). With temperature rising, it reaches to exothermic peak at 192 °C with heat generation of $-155\,\mathrm{J\,g^{-1}}$, and the peak is 20 °C lower than in 1 M $LiPF_6$/EC. After the temperature exceeds about 225 °C, the combined reactions of EC and DEC appear. $LiPF_6$ may be reacting with EC and DEC separately, but the exothermic peak is lower than in 1 M $LiPF_6$/EC solutions.

3.3. Effect of heating rate on the thermal behavior of electrolyte

The thermal stability also was affected by the heating rate, which can be seen from Fig. 3. The trends are similar, however, the onset temperature varies. The more rapid the heating rate the later the onset temperature.

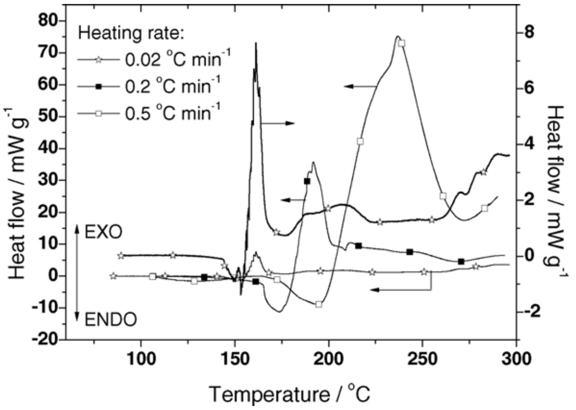


Fig. 3. Heat flow curves of 1 M $LiPF_6$ in EC + DEC electrolyte at 0.02, 0.2 and 0.5 °C $\mathrm{min^{-1}}$ in argon.

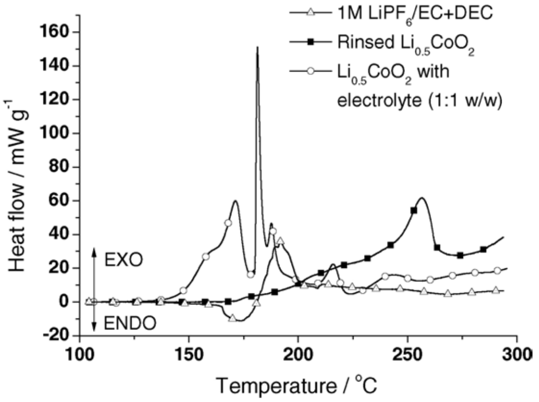


Fig. 4. Heat flow curves of 1 M $LiPF_6$ in EC + DEC, rinsed $Li_{0.5}CoO_2$ and their co-existing system at 0.2 °C $\mathrm{min^{-1}}$ in argon.

3.4. Thermal behavior of electrolyte co-existing with delithiated $LiCoO_2$

The delithiated $LiCoO_2$ is an unstable material that reacts with the electrolyte as shown in Fig. 4. The rinsed $Li_{0.5}CoO_2$ is stable below 170 °C, and then undergoes an exothermic reaction peaking at 256 °C. With the addition of electrolyte, it becomes less stable, the onset temperature is 130 °C with four exothermic peaks at 171, 181, 188 and 216 °C with a total heat of reaction $-728\,\mathrm{J\,g^{-1}}$ (based on the total sample mass). MacNeil and Dahn [32,33] reported that delithiated $Li_{0.5}CoO_2$ decomposes above 200 °C and releases O_2, Eq. (8):

$$Li_{0.5}CoO_2 \rightarrow \frac{1}{2}LiCoO_2 + \frac{1}{6}Co_3O_4 + \frac{1}{6}O_2 \quad (8)$$

In this study, this onset of the decomposition reaction is 170 °C, which may be related to the heating rate as heat flow detection limit. In the presence of electrolyte, the reaction of $Li_{0.5}CoO_2$ with electrolyte begins at 130 °C, much lower than the decomposition temperature of $Li_{0.5}CoO_2$ and electrolyte alone. The electrolyte reaction with $Li_{0.5}CoO_2$ may be caused by the oxidation of the solvent CoO was detected by MacNeil [33] by XRD. Above 170 °C, $Li_{0.5}CoO_2$ decomposes as Eq. (9), and the released O_2 will react with EC and DEC to produce CO_2 and H_2O.

These reactions account for exothermic peaks in Fig. 4. Electrolyte and $Li_{0.5}CoO_2$ co-existing are more reactive than the single compounds, which greatly decreases the thermal stability.

3.5. Thermal behavior of electrolyte co-existing with lithiated graphite

The thermal stability of graphite anodes in an electrolyte is controlled by a solid electrolyte interphase (SEI) formed on the lithiated graphite anode. Fig. 5 shows the thermal stability of lithiated graphite, electrolyte, and the co-existing system. $Li_{0.73}C_6$ has a broad exotherm between 68 and 165 °C, and

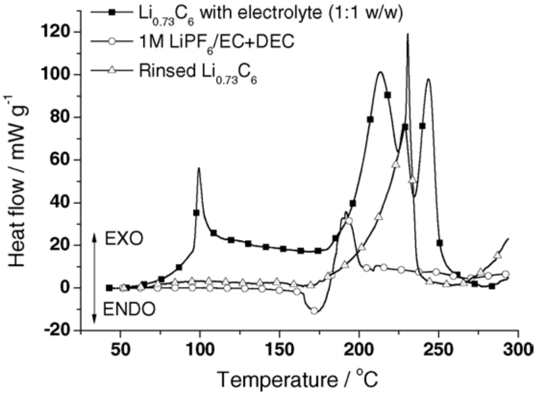


Fig. 5. Heat flow curves of 1 M $LiPF_6$ in EC + DEC, rinsed $Li_{0.73}C_6$ and their co-existing system at 0.2 °C min^{-1} in argon.

the following exothermic process onset temperature is 173 °C and reaches to the sharp peak at 231 °C with heat generation of $-604\,J\,g^{-1}$. In the presence of electrolyte, four exothermic peaks at 99, 214, 228 and 243 °C were detected. The reaction begins at 57 °C with heat generation of $-393\,J\,g^{-1}$ (based on the quantity of electrolyte). The low onset temperature and large heat generation are the key causes of thermal runaway in lithium ion batteries. The first exothermic reaction is the breakdown of SEI as judged from the previous literatures [34,35]. SEI is comprised of stable compounds (LiF, Li_2CO_3, and other inorganic compounds) and metastable components (lithium-alkyl carbonates, lithium semicarbonate) [35]. All these compounds may participate in the SEI decomposition reaction. However, the most possible reaction is [35]

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4\uparrow + CO_2\uparrow + 0.5O_2 \qquad (9)$$

After the SEI breakdown, the salts and the electrolyte can permeate the Li_2CO_3 and LiF film to reach the lithiated graphite surface. The intercalated Li can react with electrolyte, Eq. (10). Other reactions are also possible

$$2Li + C_3H_4O_3 \rightarrow Li_2CO_3 + C_2H_4\uparrow \qquad (10)$$

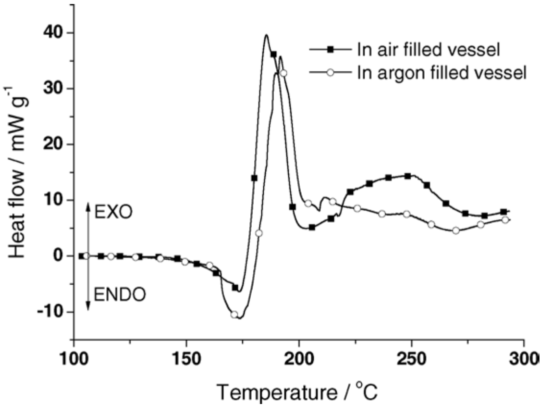


Fig. 6. Heat flow curves of 1 M $LiPF_6$ in EC + DEC electrolyte at 0.2 °C min^{-1} in air and argon.

3.6. *Thermal behavior of electrolyte under air*

The heat flow curve of 1 M $LiPF_6$/EC + DEC shows an endothermic process in air, which begins near 145 °C and peaks at 173 °C in Fig. 6. Then, it goes to an exothermic stage near 177 °C, which peaks at 185 °C. A broad exotherm follows till the end with $-298\,J\,g^{-1}$. The exothermic peak temperature is lowered and produces more heat, which indicates that the small quantity of oxygen and trace moisture accelerates the reactions.

4. Conclusions

EC and DEC alone are less stable than their mixture. When $LiPF_6$ is added to the organic solvent, the onset temperatures of DEC and EC + DEC decomposition are lowered, but 1 M $LiPF_6$ in EC has a higher onset temperature with more heat generation. In 1 M $LiPF_6$/EC + DEC electrolyte, $LiPF_6$ reacts with EC and DEC separately. In the electrolyte–electrode system, both the electrolyte–$Li_{0.5}CoO_2$ and electrolyte–Li_xC_6 system have lower decomposition onset temperature and more heat generation than either the separate electrolyte or electrode. The more rapid the heating rate, the higher the onset temperature for decomposition of the electrolyte. Air accelerates the reaction process with lower onset temperature.

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References

[1] P. Biensan, B. Simon, J.P. Peres, A.D. Guibert, M. Broussely, J.M. Bodet, F. Perton, J. Power Sources 81–82 (1999) 906–912.
[2] R.A. Leising, M.J. Palazzo, E.S. Takeuchi, K.J. Takeuchi, J. Electrochem. Soc. 148 (8) (2001) A838–A844.
[3] R.A. Leising, M.J. Palazzo, E.S. Takeuchi, K.J. Takeuchi, J. Power Sources 97–98 (2001) 681–683.
[4] S. Tobishima, K. Takei, Y. Sakurai, J. Yamaki, J. Power Sources 90 (2000) 188–195.
[5] M.D. Farrington, J. Power Sources 96 (2001) 260–265.
[6] R. Spotnitz, J. Franklin, J. Power Sources 113 (2003) 81–100.
[7] K.H. Lee, E.H. Song, J.Y. Lee, B.H. Jung, H.S. Lim, J. Power Sources 132 (2004) 201–205.
[8] T. Yamauchi, K. Mizushima, Y. Satoh, S. Yamada, J. Power Sources 136 (2004) 99–107.
[9] G. Venugopal, J. Power Sources 101 (2001) 231–237.
[10] G. Venugopal, J. Moore, J. Howard, S. Pendalwar, J. Power Sources 77 (1999) 34–41.
[11] H.J. Kweon, J.J. Park, J.W. Seo, G.B. Kim, B.H. Jung, H.S. Lim, J. Power Sources 126 (2004) 156–162.

[12] H.Y. Lee, J.K. Baek, S.M. Lee, H.K. Park, K.Y. Lee, M.H. Kim, J. Power Sources 128 (2004) 61–66.
[13] C.W. Lee, R. Venkatachalapathy, J. Prakash, Electrochem. Solid-State Lett. 3 (2) (2000) 63–65.
[14] K. Xu, M.S. Ding, S.S. Zhang, J.L. Allen, T.R. Jow, J. Electrochem. Soc. 149 (5) (2002) A622–A626.
[15] S.S. Zhang, K. Xu, T.R. Jow, J. Power Sources 113 (2003) 166–172.
[16] Y.E. Hyung, D.R. Vissers, K. Amine, J. Power Sources 119–121 (2003) 383–387.
[17] B.G. Dixon, R.S. Morris, S. Dallek, J. Power Sources 138 (2004) 274–276.
[18] S.I. Gonzales, W.T. Li, B.L. Lucht, J. Power Sources 135 (2004) 291–296.
[19] G.G. Botte, R.E. White, Z.M. Zhang, J. Power Sources 97–98 (2001) 570–575.
[20] T. Kawamura, A. Kimura, M. Egashira, S. Okada, J.I. Yamaki, J. Power Sources 104 (2002) 260–264.
[21] N. Katayama, T. Kawamura, Y. Baba, J. Yamaki, J. Power Sources 109 (2002) 321–326.
[22] B. Ravdel, K.M. Abraham, R. Gitzendanner, J. DiCarlo, B. Lucht, C. Campion, J. Power Sources 119–121 (2003) 805–810.
[23] D.D. MacNeila, R. Dahn, J. Electrochem. Soc. 150 (1) (2003) A21–A28.
[24] J.S. Gnanaraj, E. Zinigrad, L. Asraf, H.E. Gottlieb, M. Sprecher, M. Schmidt, W. Geissler, D. Aurbach, J. Electrochem. Soc. 150 (11) (2003) A1533–A1537.
[25] J.S. Gnanaraj, E. Zinigrad, L. Asraf, H.E. Gottlieb, M. Sprecher, D. Aurbach, M. Schmidt, J. Power Sources 119–121 (2003) 794–798.
[26] J. Jiang, J.R. Dahn, Electrochem. Commun. 6 (2004) 39–43.
[27] H. Maleki, G. Deng, A. Anani, J. Howard, J. Electrochem. Soc. 146 (9) (1999) 3224.
[28] J.H. Sun, X.R. Li, K. Hasegawa, G.X. Liao, J. Therm. Anal. Cal. 76 (3) (2004) 883–893.
[29] K. Tasaki, K. Kanda, S. Nakamura, M. Ue, J. Electrochem. Soc. 150 (12) (2003) A1628–A1636.
[30] S.E. Sloop, J.B. Kerr, K. Kinoshita, J. Power Sources 119–121 (2003) 330–337.
[31] M. Moshkovich, M. Cojocaru, H.E. Gottlieb, D. Aurbach, J. Electrochem. Soc. 497 (2001) 84–96.
[32] D.D. MacNeil, J.R. Dahn, J. Electrochem. Soc. 149 (7) (2002) A912–A919.
[33] D.D. MacNeil, J.R. Dahn, J. Electrochem. Soc. 148 (11) (2001) A1205–A1210.
[34] J. Yamaki, H. Takatsuji, T. Kawamura, M. Egashira, Solid State Ionics 148 (2002) 241–245.
[35] H. Yang, H. Bang, K. Amine, J. Prakash, J. Electrochem. Soc. 152 (1) (2005) A73–A79.