Thermal stability of propylene carbonate and ethylene carbonate–propylene carbonate-based electrolytes for use in Li cells

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Abstract

The thermal stability of mixed-solvent electrolytes used in lithium cells was investigated by differential scanning calorimetry (DSC) through the use of airtight containers. The electrolytes used were propylene carbonate (PC) and ethylene carbonate (EC) + PC, in which was dissolved 1 M LiPF$_6$, 1 M LiBF$_4$, 1 M LiClO$_4$, 1 M LiSO$_3$CF$_3$, 1 M LiN(SO$_2$CF$_3$)$_2$, or 1.23 M LiN(SO$_2$CF$_3$)(SO$_2$C$_4$F$_9$). The influence of lithium metal or the Li$_{0.5}$CoO$_2$ addition on the thermal behavior of these electrolytes was also investigated. The peak temperature of PC-based electrolytes increased following the order of LiPF$_6$ < LiClO$_4$ < LiBF$_4$ < LiN(SO$_2$CF$_3$)$_2$ < LiSO$_3$CF$_3$ < LiN(SO$_2$CF$_3$)(SO$_2$C$_4$F$_9$). The order of peak temperature of EC–PC-based electrolytes shows a similar tendency to that of EC–PC-based electrolytes, with the exception of the LiN(SO$_2$CF$_3$)$_2$ electrolyte. The EC–PC-based electrolytes with Li metal show a more stable profile compared with the DSC curves of the PC-based electrolytes with the Li metal. The solid electrolyte interphase (SEI) covers the surface of the Li metal and prevents further reduction of the electrolytes. EC may form a better SEI compared with PC. The PC-based electrolytes of LiSO$_3$CF$_3$, LiN(SO$_2$CF$_3$)$_2$ and LiN(SO$_2$CF$_3$)(SO$_2$C$_4$F$_9$) with the coexistence of Li$_{0.49}$CoO$_2$ show a broad peak at around 200 °C, which may be caused by the reaction of the Li$_{0.49}$CoO$_2$ surface and electrolytes. The PC-based electrolytes of LiPF$_6$, LiClO$_4$ and LiBF$_4$ with Li$_{0.49}$CoO$_2$ show exothermic peaks at higher temperatures than 230 °C. The peak temperatures of the EC–PC-based electrolytes with the coexistence of Li$_{0.49}$CoO$_2$ are nearly the same temperature as the EC–PC-based electrolytes. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Li-ion cells are widely used as power sources for portable electric devices. Recently, the study of the utilization of high-performance Li-ion cells as power sources of electric vehicles (EV) and other large-sized equipment has been undertaken by many corporations and laboratories. However, large-sized Li-ion cells are not practical to use, primarily due to safety considerations. Organic compounds are used as electrolytes of Li-ion cells, and these compounds are flammable. Therefore, the generation of heat by chemical decomposition and the chemical reactions in the cells are important factors to be considered. It is generally considered that the "thermal runaway" of Li cells occurs if the heat output exceeds the thermal diffusion [1,2]. Therefore, it is difficult to design large cells that can pass a safety-test criteria. The safety testing of Li-ion cells has been reported

by some laboratories [3–6]. In the past 10 years, the thermal stability or the thermal behavior of Li-ion cells has been investigated energetically by DSC or accelerating rate calorimetry (ARC) [7–11]. The thermal behavior of the cathode material of the Li-ion batteries, primarily lithium nickel oxide [12–17], lithium cobalt oxide [12,13,18], and lithium manganese oxide [12,13], has been measured by DSC. The thermal behavior of the anode materials, including graphite [11–13,19,20], various kinds of carbon [21], and Li metal [8] has been investigated with regards to both particle size [22] and the SEI [7,8,23–25] by both DSC and ARC. In addition, the thermal stability of the electrolytes of Li-ion batteries has been investigated in relationship to new, boron-based solutes [26] and various organic electrolytes [27].

It is not easy to measure the thermal stability of electrolytes, because of their low boiling points. Although it would be quite interesting to evaluate the stability in a closed sample case such as a cell case, there have been few previous reports of such investigations [28,29]. Botte et al. reported the thermal stability of LiPF$_6$/EC + ethylmethylcarbonate

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(EMC) using stainless steel hermetically sealed pans for DSC measurements [28]. We investigated the thermal stability of mixed solvent electrolytes used for practical Li-ion cells in a previous paper [30]. The electrolytes used were EC + diethylecarbonate (DEC), EC + dimethylecarbonate (DMC), PC + DEC, and PC + DMC in which 1 M $LiPF_6$ or 1 M $LiClO_4$ was dissolved, as well as the influence of the Li metal and water addition on the thermal behavior of these electrolytes under airtight conditions.

In the present study, we investigated the dependence of thermal stability on the Li salt type. The electrolytes used were PC and EC + PC, in which 1 M $LiPF_6$, 1 M LiBF4, 1 M $LiClO_4$, 1 M $LiSO_3CF_3$, 1 M $LiN(SO_2CF_3)_2$, or 1.23 M $LiN(SO_2CF_3)(SO_2C_4F_9)$ was dissolved. The influence of the lithium metal and $Li_{0.5}CoO_2$ addition on the thermal behavior of these electrolytes was also investigated.

2. Experimental

A total of 1 M $LiPF_6$/PC, 1 M LiBF4/PC, 1 M $LiClO_4$/PC and 1 M $LiClO_4$/EC + PC (1:1 in volume) were obtained from Tomiyama Chemical. Other electrolytes 1 M $LiSO_3CF_3$/PC, 1 M $LiN(SO_2CF_3)_2$/PC, 1.23 M $LiN(SO_2CF_3)(SO_2C_4F_9)$/PC, 1 M $LiPF_6$/EC + PC (1:1 in volume), 1 M LiBF4/EC + PC (1:1 in volume), 1 M $LiSO_3CF_3$/EC + PC (1:1 in volume), 1 M $LiN(SO_2CF_3)_2$/ EC + PC (1:1 in volume), and 1.23 M $LiN(SO_2CF_3)$-$(SO_2C_4F_9)$/EC + PC (1:1 in volume) were prepared using PC (Tomiyama Chemical), EC + PC (1:1 in volume) (Tomiyama Chemical), $LiPF_6$ (Stella Chemifa Corp.), LiBF4 (Morita Chemical Industries Co., Ltd.), $LiSO_3CF_3$ (Morita Chemical Industries Co., Ltd.), $LiN(SO_2CF_3)_2$ (3 M Corp.), and $LiN(SO_2CF_3)(SO_2C_4F_9)$ (Central Glass Co., Ltd.). The water content of the electrolytes measured by a Karl Fischer aquameter (Aquacounter AQ-7, Hiranuma Co.) was <70 ppm.

The thermal behavior of the electrolytes were measured by thermogravimetry–differential scanning calorimetry (TG–DSC) (Rigaku, Thermo plus). The sample for the DSC measurement was packed in a stainless steel case, which was then crimp-sealed in a glove box filled with argon. The heating rate of DSC was 5 °C min^{-1}. It was confirmed by the TG data that leakage from the case did not occur. The rupture of the sample case occurred for several samples. The DSC data shown in the paper are up to the temperature of the rupture.

Lithium metal was obtained from Honjo Metal. $LiCoO_2$ was prepared by firing a mixture of Li_2CO_3 and Co_3O_4 at 850 °C for 24 h following firing at 500 °C for 5 h in air [31]. Chemical delithiation of $LiCoO_2$ was carried out by stirring a suspension of 5 g of $LiCoO_2$ in 250 ml of 0.5 M H_2SO_4 for 24 h [31,32]. The product was filtered and washed several times with acetone, then dried at 80 °C in a vacuum. The Li content of Li_xCoO_2 (x) was analyzed to be 0.49 by atomic absorption spectroscopy (HITACHI, Z-5000).
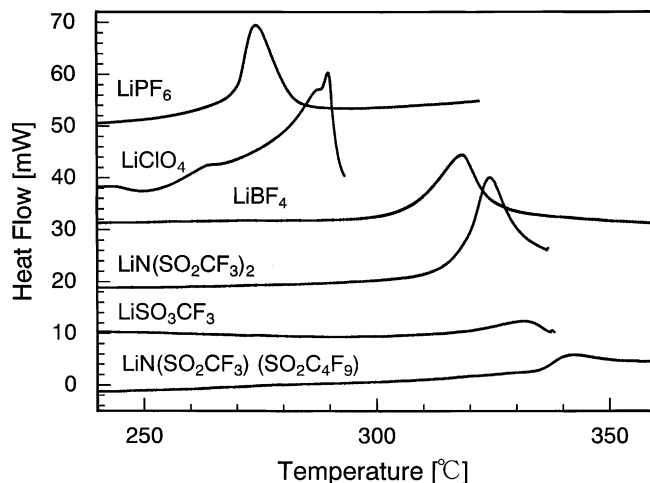

Fig. 1. DSC curves of the PC-based electrolytes of $LiPF_6$, $LiClO_4$, LiBF4, $LiN(SO_2CF_3)_2$, $LiSO_3CF_3$, and $LiN(SO_2CF_3)(SO_2C_4F_9)$.

3. Results and discussion

3.1. Thermal stability of electrolytes

Figs. 1 and 2 show the DSC curves of the PC-based and EC–PC-based electrolytes, respectively. The amount of electrolyte used for the measurement is 2 µl. Fig. 3 summarizes the peak temperature of these electrolytes. The DSC measurement of $LiN(SO_2CF_3)(SO_2C_4F_9)$/EC + PC was not successful, because the cap of the sample case opens by a high internal pressure. The peak temperature of LiN-$(SO_2CF_3)(SO_2C_4F_9)$/EC + PC is estimated to be >345 °C. The peak temperature of the PC-based electrolytes increased following the order of $LiPF_6 < LiClO_4 < LiBF_4 < LiN(SO_2$-$CF_3)_2 < LiSO_3CF_3 < LiN(SO_2CF_3)(SO_2C_4F_9)$. The order of peak temperature of the EC–PC-based electrolytes showed a similar tendency to that of the EC–PC-based electrolytes, with the exception of the $LiN(SO_2CF_3)_2$ electrolyte. The exothermic peaks were not observed for PC or EC + PC without the Li salt. Therefore, the exothermic
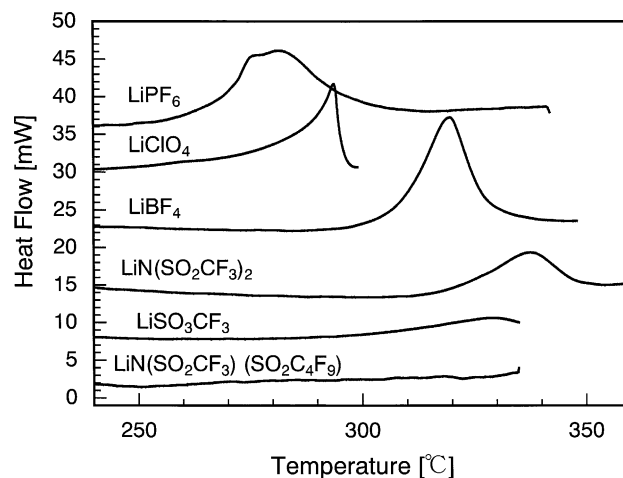

Fig. 2. DSC curves of the EC–PC-based electrolytes of $LiPF_6$, $LiClO_4$, LiBF4, $LiN(SO_2CF_3)_2$, $LiSO_3CF_3$, and $LiN(SO_2CF_3)(SO_2C_4F_9)$.

Fig. 3. Peak temperatures of electrolytes.

Fig. 5. DSC curves of the PC-based electrolytes of $LiPF_6$, $LiClO_4$, $LiBF_4$, $LiN(SO_2CF_3)_2$, $LiSO_3CF_3$, and $LiN(SO_2CF_3)(SO_2C_4F_9)$ with coexistence of the Li metal.
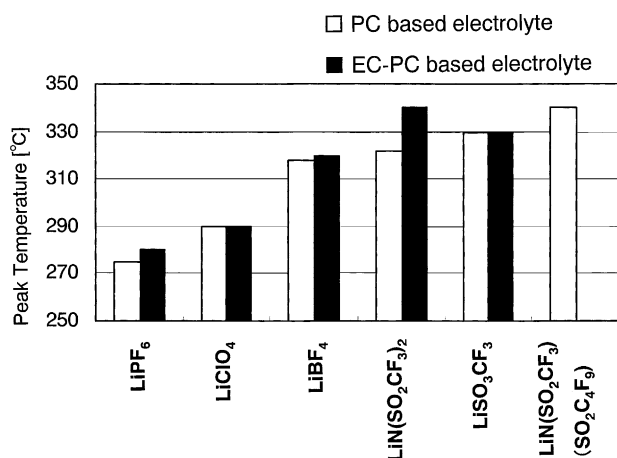
reactions presented by the peaks occurred due to the coexistence of Li salts. The salts with $-SO_2C_nF_{2n+1}$ function showed a better thermal stability. Solid $LiPF_6$ decomposes to PF_5 and LiF at around 250 °C. Sloop et al. showed experimentally that the reaction products of PF_5 and EC/DMC are the same as the thermal decomposition products of the $LiPF_6$/EC + DMC electrolyte [33]. This experiment suggests that $LiPF_6$, which is not dissociated in electrolytes, may produce PF_5 and decompose the electrolyte. Solid $LiBF_4$ also decomposes to BF_3 and LiF at around 320 °C, at a higher temperature than that of $LiPF_6$. BF_3 may also decompose the electrolyte. For this reason, the $LiBF_4$ electrolyte probably showed a higher peak temperature.

The amount of heat generation based on the electrolyte weight is summarized in Fig. 4. The PC-based and EC–PC-based electrolytes showed a similar tendency. The $LiClO_4$ electrolytes showed a very large heat generation. The amount of heat generation of the $LiSO_3CF_3$ and $LiN(SO_2CF_3)(SO_2C_4F_9)$ electrolytes was very small. The amount of heat generation of the PC-based or EC–PC-based electrolytes increased following the order of $LiN(SO_2CF_3)(SO_2C_4F_9) \approx LiSO_3CF_3 < LiN(SO_2CF_3)_2 < LiBF_4 \approx LiPF_6 < LiClO_4$.

3.2. Thermal stability of electrolytes with Li metal

Figs. 5 and 6 show the DSC curves of the PC-based and EC–PC-based electrolytes with the co-existence of the Li metal, respectively. The amount of electrolyte used for the measurement was 2 μl. The Li metal is about 1.3 mg. Lithium metal melts at 180 °C, and endothermic peaks appeared at this temperature in all of the profiles. The electrolytes did not react with the Li metal, even if the Li metal melted at 180 °C. However, $LiPF_6$/PC showed a small heat generation until the main peak at 240 °C. The PC-based electrolytes, except $LiBF_4$/PC, have a main peak at around 240 °C. This temperature is lower than the exothermic peak temperature of the corresponding electrolyte without the Li metal (Fig. 1). The EC–PC-based electrolytes showed a more stable profile compared with the DSC curves of the
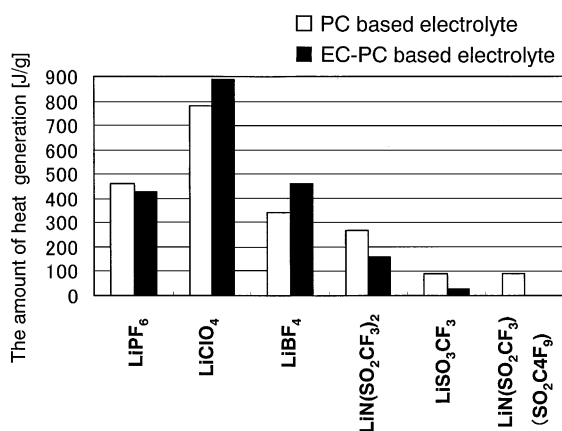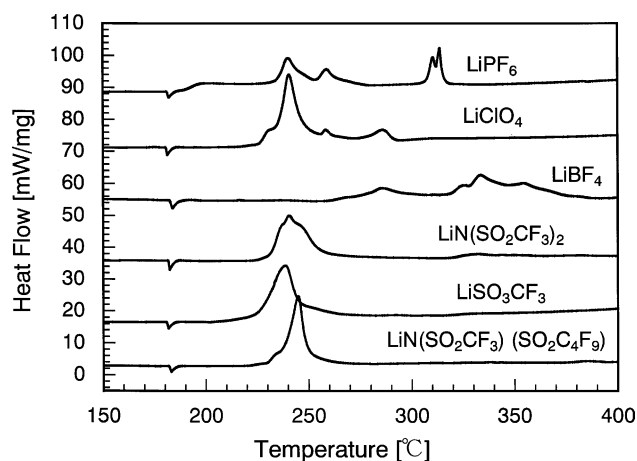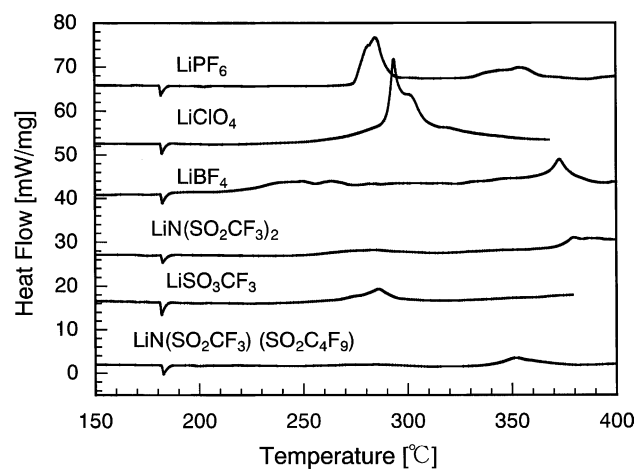

Fig. 4. Total amount of heat generation of electrolytes.

Fig. 6. DSC curves of EC–PC-based electrolytes of $LiPF_6$, $LiClO_4$, $LiBF_4$, $LiN(SO_2CF_3)_2$, $LiSO_3CF_3$, and $LiN(SO_2CF_3)(SO_2C_4F_9)$ with coexistence of the Li metal.

Fig. 7. Peak temperatures of electrolytes with coexistence of the Li metal.

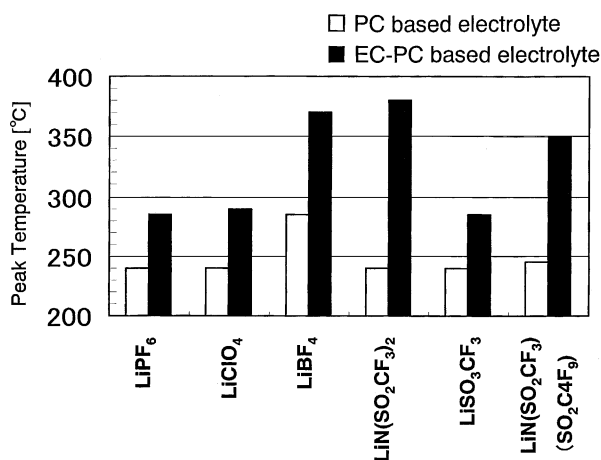Fig. 8. Total amount of heat generation of electrolytes with coexistence of the Li metal.

PC-based electrolytes. The main peak temperatures are >280 °C. However, $LiBF_4/EC + PC$ showed a small heat generation starting from 210 °C to the main peak at 370 °C. The solid electrolyte interphase (SEI) covered the surface of the Li metal, and prevented further reduction of electrolytes. EC may form a better SEI compared with PC. The peak temperatures of $LiPF_6/EC + PC$ with the Li metal was nearly the same temperature of $LiPF_6/EC + PC$ without the Li metal. This result suggests the possibility that the exothermic peak temperatures of $LiPF_6/EC + PC$ with the Li metal were caused by the electrolyte decomposition itself, followed by some reactions with the Li metal. There is also a similar relationship for $LiClO_4/EC + PC$. Fig. 7 summarizes the peak temperature of these electrolytes. The peak temperature of the PC-based electrolytes increased following the order of $LiPF_6 \approx LiClO_4 \approx LiN(SO_2CF_3)_2$ $\approx LiSO_3CF_3 \approx LiN(SO_2CF_3)(SO_2C_4F_9) < LiBF_4$. For the EC–PC-based electrolytes, the peak temperature increased following the order of $LiPF_6 \approx LiSO_3CF_3 \approx LiClO_4 <$ $LiN(SO_2CF_3)(SO_2C_4F_9) < LiN(SO_2CF_3)_2 \approx LiBF_4$. The amount of heat generation is summarized in Fig. 8. The amount of heat generation is based on the total weight of the electrolyte and the Li metal. The heat generation was 5–10 times larger compared with that of the corresponding electrolyte without the Li metal (Fig. 4). The coexistence of EC decreased the total heat generation of all the electrolytes, with the exception of the $LiClO_4$ electrolyte. $LiSO_3CF_3/$ $EC + PC$ and $LiN(SO_2CF_3)_2/EC + PC$ in particular showed very small heat generations.

It was shown that SEI is effective even if Li melts. SEI may capture liquid Li and protects the reaction. It is not easy to believe the effect of SEI. However, we would like to introduce another example of the SEI effect. We found 1 M $LiPF_6/CF_2HCOOCH_3$ is very stable to Li metal [29]. The survived lithium metal percentage in 1 M $LiPF_6/$ $CF_2HCOOCH_3$ was estimated by endothermic heat of Li melting and exothermic heat of Li freezing after rising temperature to 300 °C using DSC [34]. It was found that
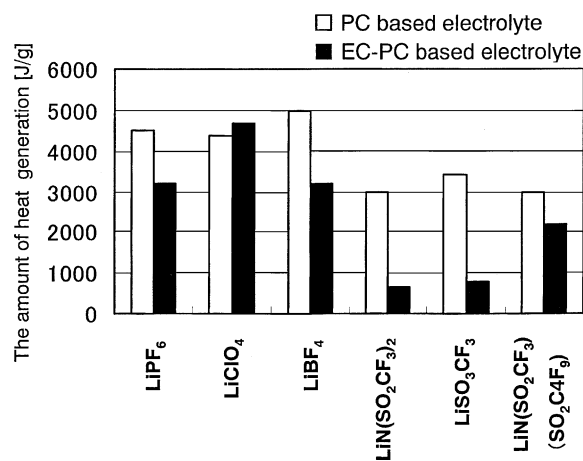
95% of Li did not react with the electrolyte after heating to 300 °C.

3.3. Thermal stability of electrolytes with $Li_{0.49}CoO_2$

Figs. 9 and 10 show the DSC curves of PC-based and EC–PC-based electrolytes with the co-existence of $Li_{0.49}CoO_2$, respectively. The amount of electrolyte used for the measurement was 1 ml. A heat generation was observed for PC or $EC + PC$ without Li salts at around 200 °C. $LiSO_3CF_3$, $LiN(SO_2CF_3)_2$ and $LiN(SO_2CF_3)(SO_2C_4F_9)$ electrolytes showed a similar peak at around 200 °C. It is reported that highly delithiated lithium cobaltate Li_xCoO_2 ($x = 0.4$) decomposes exothermally in connection with oxygen evolution at around 200 °C [35]. The evolved oxygen oxidizes electrolytes. The heat generation around 200 °C is probably caused by the reactions of solvents with the evolved oxygen. We have investigated the heat generation of 1 M $LiPF_6/$ $EC + DMC$ and $Li_{0.49}CoO_2$ more precisely [36]. As a result, we found that the peak starting at 190 °C probably reflected
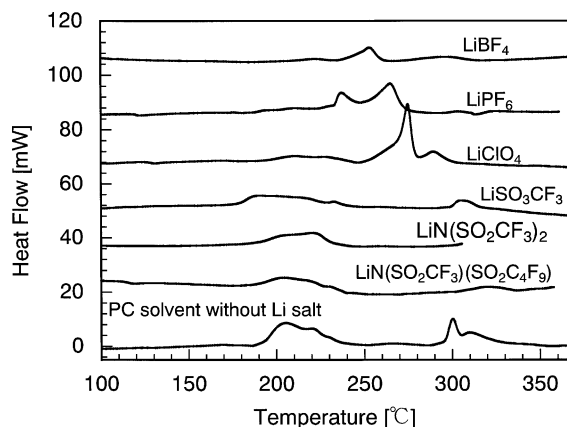

Fig. 9. DSC curves of PC-based electrolytes of $LiPF_6$, $LiClO_4$, $LiBF_4$, $LiN(SO_2CF_3)_2$, $LiSO_3CF_3$, and $LiN(SO_2CF_3)(SO_2C_4F_9)$ with coexistence of $Li_{0.49}CoO_2$.
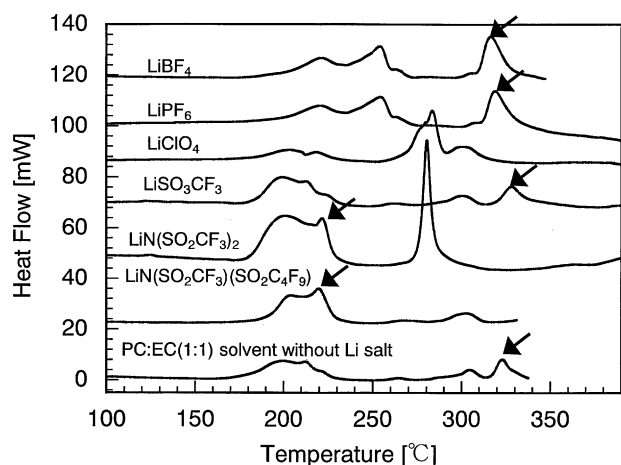
Fig. 10. DSC curves of EC–PC-based electrolytes of $LiPF_6$, $LiClO_4$, $LiBF_4$, $LiN(SO_2CF_3)_2$, $LiSO_3CF_3$, and $LiN(SO_2CF_3)(SO_2C_4F_9)$ with coexistence of $Li_{0.49}CoO_2$.

the decomposition of the solvent due to the active surface of $Li_{0.49}CoO_2$, and the peak starting at 230 °C was electrolyte oxidation caused by released oxygen from $Li_{0.49}CoO_2$. The PC-based electrolytes of $LiPF_6$, $LiClO_4$ and $LiBF_4$ showed exothermic peaks at a higher temperature than 230 °C. $LiPF_6$, $LiClO_4$ and $LiBF_4$ may contribute to protect the reaction starting at 190 °C, making some surface film on the surface of $Li_{0.49}CoO_2$. There was not that much difference between the PC-based and EC–PC-based electrolytes. However, the EC–PC-based electrolytes of $LiPF_6$ and $LiBF_4$ showed a different peak at around 220 °C. The protection of the reaction starting at 190 °C is not sufficient in these electrolytes. The different peaks are indicated as arrows in Fig. 10.

4. Conclusions

Based on the results of this study, we conclude that:

1. *Thermal stability of electrolytes*: The peak temperature of PC-based electrolytes increased following the order of $LiPF_6 < LiClO_4 < LiBF_4 < LiN(SO_2CF_3)_2 < LiSO_3CF_3 < LiN(SO_2CF_3)(SO_2C_4F_9)$. The order of the peak temperature of the EC–PC-based electrolytes showed a similar tendency to that of the PC-based electrolytes, with the exception of the $LiN(SO_2CF_3)_2$ electrolyte.
2. *Thermal stability of electrolytes with coexistence of the Li metal*: The EC–PC-based electrolytes show a more stable profile compared with the DSC curves of the PC-based electrolytes. The peak temperature of the PC-based electrolytes increased following the order of $LiPF_6 \approx LiClO_4 \approx LiN(SO_2CF_3)_2 \approx LiSO_3CF_3 \approx LiN(SO_2CF_3)(SO_2C_4F_9) < LiBF_4$. With the EC–PC-based electrolytes, the peak temperature increased following the order of $LiPF_6 \approx LiSO_3CF_3 \approx LiClO_4 < LiN(SO_2CF_3)(SO_2C_4F_9) < LiN(SO_2CF_3)_2 \approx LiBF_4$.

3. *Thermal stability of electrolytes with coexistence of $Li_{0.49}CoO_2$*: The PC-based electrolytes of $LiSO_3CF_3$, $LiN(SO_2CF_3)_2$ and $LiN(SO_2CF_3)(SO_2C_4F_9)$ show a broad peak at around 200 °C, which may be caused by the reaction of the $Li_{0.49}CoO_2$ surface and the electrolytes. The PC-based electrolytes of $LiPF_6$, $LiClO_4$ and $LiBF_4$ show exothermic peaks at higher temperatures than 230 °C. The peak temperatures of the EC–PC-based electrolytes are nearly the same temperatures as the PC-based electrolytes. However, if we consider this precisely, the EC–PC-based electrolytes of $LiPF_6$ and $LiBF_4$ showed a different peak at the lower temperature of 220 °C.

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