



## Thermal Stability of Electrolytes with Mixtures of LiPF<sub>6</sub> and LiBF<sub>4</sub> Used in Lithium-Ion Cells

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Thermal stability studies of electrolytes with mixtures of LiPF<sub>6</sub> and LiBF<sub>4</sub> were carried out using differential scanning calorimetry. The solvent was a mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate in the volume ratio of 3:3:1, respectively. We expected the occurrence of two independent exothermic peaks associated with LiPF<sub>6</sub> at the lower temperature and lithium LiBF<sub>4</sub> at the higher temperature, due to decomposition reactions resulting in the Lewis acids PF<sub>5</sub> and BF<sub>3</sub>. Instead, the mixed salt electrolyte exhibited a single exothermic peak. We deduced that the HF produced by the reaction of LiPF<sub>6</sub> with solvent was the reason for the existence of one exothermic reaction peak. The HF may react with LiBF<sub>4</sub> to give HBF<sub>4</sub>, which is very unstable and decomposes easily to HF and BF<sub>3</sub> at a lower temperature than the decomposition temperature of LiBF<sub>4</sub> itself. By comparison, a thermal study of a mixed salt electrolyte including LiPF<sub>6</sub> and LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> showed that the exothermic reaction of LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> with solvents is also influenced by HF produced in the reaction of LiPF<sub>6</sub> with solvents but that the strength of the influence is small compared with its effect on an electrolyte mixture including LiBF<sub>4</sub>.

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The lithium-ion battery is an attractive alternative to other batteries in view of its several merits, including high cell voltage, high energy density, light weight, etc. Recently, demand for Li-ion batteries has increased exponentially because of their common application as a power source for electronic portable devices, in addition to their potential for electric vehicles and other high-power equipment. In spite of the above merits and applications, however, lithium batteries often suffer from serious safety problems due to the flammable organic compounds used as electrolytes. It is well known that the electrodes in Li-ion batteries undergo exothermic reactions with electrolyte<sup>1,2</sup> when exposed to elevated temperatures. If the heat output during this process exceeds the thermal diffusion, then thermal runaway in Li-ion battery occurs.<sup>3,4</sup> Therefore, the heat generated by chemical decomposition and chemical reactions in the Li-ion battery is an important factor that must be considered in making a safer Li-ion battery.

Several researchers have reported on safety tests of Li-ion batteries,<sup>5-7</sup> and the thermal behavior of Li-ion batteries has been investigated using differential scanning calorimeter (DSC)<sup>8-11</sup> and accelerating rate calorimeter (ARC).<sup>12,13</sup> However, most of the thermal studies have focused on electrolytes involving only one kind of Li salt,<sup>8,10,11</sup> as well as electrode materials.<sup>9,14-18</sup> Further, in electrolytes with LiPF<sub>6</sub>, it is usually believed that the exothermic reaction of the electrolyte is due to the existence of a strong Lewis acid (PF<sub>5</sub>) produced from the LiPF<sub>6</sub> that is not ionized to free Li<sup>+</sup> and free PF<sub>6</sub><sup>-</sup>.<sup>19</sup> Therefore, it is of interest to carry out a systematic study on the thermal stability of an electrolyte containing two kinds of Li salts (LiPF<sub>6</sub>, LiBF<sub>4</sub>) using DSC. The electrolyte solvent used is a ternary solvent of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC).<sup>20-23</sup> We sought to measure heat generated during electrolyte decomposition and elucidate the individual contributions of LiPF<sub>6</sub> and LiBF<sub>4</sub> in Li salt mixtures. Finally, we were interested in ascertaining the reaction mechanism of exothermic reactions that take place in electrolytes containing Li salt mixtures on the basis of the above exothermic reaction.

### Experimental

The electrolytes were 1 M LiPF<sub>6</sub>, 0.67 M LiPF<sub>6</sub> + 0.33 M LiBF<sub>4</sub>, 0.5 M LiPF<sub>6</sub> + 0.5 M LiBF<sub>4</sub>, 0.33 M LiPF<sub>6</sub> + 0.67 M LiBF<sub>4</sub>, 1 M LiBF<sub>4</sub>, and 1 M LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>, each with EC:DMC:DEC = 3:3:1 volume ratio. 1 M LiPF<sub>6</sub>-EC, 1 M LiPF<sub>6</sub>-DMC, 1 M LiPF<sub>6</sub>-DEC, 1 M LiBF<sub>4</sub>-EC, 1 M LiBF<sub>4</sub>-DMC, and 1 M LiBF<sub>4</sub>-DEC were obtained from Tomiyama Chemical Co., Japan. The water content of these solutions was less than 20 ppm. A 4 μL portion of the solution was placed into a 20 μL stainless steel sample pan, which was then crimp-sealed with a stainless steel lid. All these processes were carried out in an argon-filled glove box. The thermal stability of the electrolytes contained in the airtight pans was measured by a thermogravimetry-differential scanning calorimeter (TG-DSC) instrument (Rigaku, Thermo plus, Japan). At the same time, TG measurement was performed to ascertain that there was no leak of the crimp-sealed pan. The DSC heating rate was 5°C/min.

### Results and Discussion

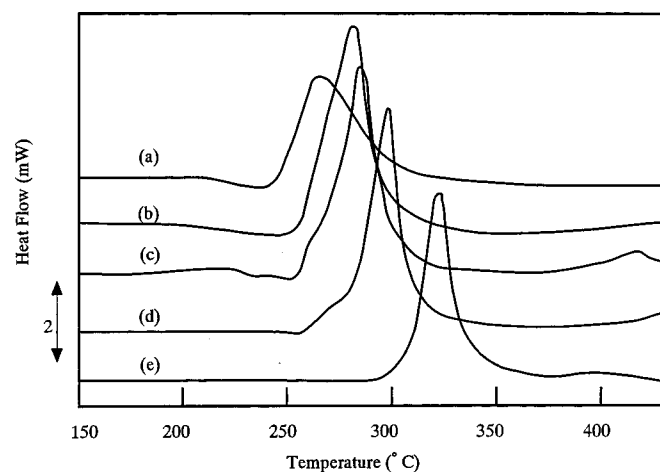
The DSC profiles of the 1 M LiPF<sub>6</sub>, 1 M LiBF<sub>4</sub>, and 1 M lithium salt mixture (molar ratios of LiPF<sub>6</sub> to LiBF<sub>4</sub> were 0.67:0.33, 0.5:0.5, and 0.33:0.67) in the 3:3:1 mixture of EC, DMC, and DEC are presented in Fig. 1. It was observed that the exothermic reaction peak temperatures of the electrolyte solutions are located around 265 and 320°C for 1 M LiPF<sub>6</sub> and 1 M LiBF<sub>4</sub>, respectively (Fig. 1a and b). In lithium salt mixtures, there is also only one exothermic reaction peak; as the concentration of LiPF<sub>6</sub> salt increases, the exothermic reaction peak temperature moves closer to the exothermic peak temperature of 1 M LiPF<sub>6</sub>. Sloop *et al.* has suggested that LiPF<sub>6</sub>, which is not ionized in electrolytes, produces a strong Lewis acid, PF<sub>5</sub>, thereby attacking the lone pair of electrons in the oxygen of solvent molecules.<sup>19</sup> LiBF<sub>4</sub> is similar to LiPF<sub>6</sub> and therefore BF<sub>3</sub>, a strong Lewis acid produced from LiBF<sub>4</sub>, could decompose the solvents. If no interactions exist between LiPF<sub>6</sub> and LiBF<sub>4</sub> when mixed, it would follow that the main exothermic reaction peak of the electrolyte mixtures would be split in two. However, as shown in Fig. 1, the mixtures showed no evidence of split exothermic reaction peaks that might be associated with the individual contributions of LiPF<sub>6</sub> and LiBF<sub>4</sub>.

There were shoulders at a lower temperature side of the peaks for (c) (0.5 M LiPF<sub>6</sub> + 0.5 M LiBF<sub>4</sub> electrolyte) and (d) (0.33 M LiPF<sub>6</sub> + 0.67 M LiBF<sub>4</sub> electrolyte) in Fig. 1. The shoulders

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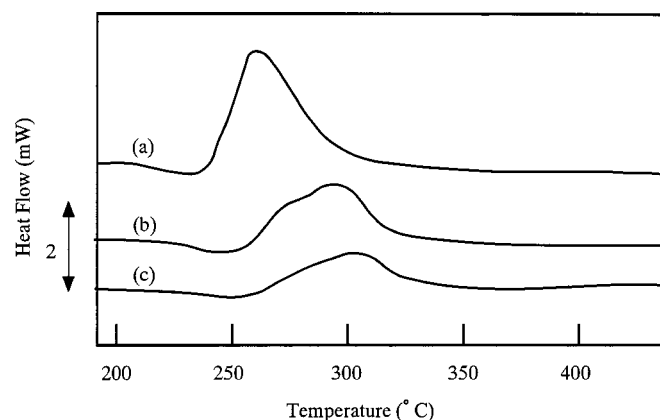
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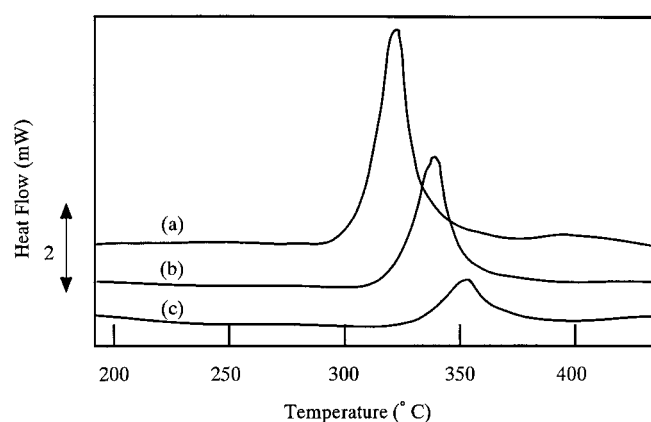
**Figure 1.** DSC profiles of  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ , and  $\text{LiPF}_6 + \text{LiBF}_4$  in EC + DMC + DEC (3:3:1) solvents; (a) 1 M  $\text{LiPF}_6$ , (b) 0.67 M  $\text{LiPF}_6 + 0.33$  M  $\text{LiBF}_4$ , (c) 0.5 M  $\text{LiPF}_6 + 0.5$  M  $\text{LiBF}_4$ , (d) 0.33 M  $\text{LiPF}_6 + 0.67$  M  $\text{LiBF}_4$ , and (e) 1 M  $\text{LiBF}_4$ .

seem to be caused by a two-step reaction of the exothermic reaction. The first step is a decomposition caused by  $\text{LiPF}_6$ . The second is a decomposition by some product of the first step. At the second step,  $\text{LiBF}_4$  decomposes at a lower temperature than that without  $\text{LiPF}_6$ . Figures 2 and 3 show the DSC profiles of unmixed  $\text{LiPF}_6$  and  $\text{LiBF}_4$  electrolytes at 1, 0.5, and 0.25 M. The shoulder in Fig. 1 is caused by the first step reaction. For example, 0.5 M  $\text{LiPF}_6 + 0.5$  M  $\text{LiBF}_4$  electrolyte has a shoulder at around 260°C (Fig. 1c), which is caused by the decomposition of 0.5 M  $\text{LiPF}_6$  as shown in Fig. 2b. When the concentrations of some decomposition products of the first step increase,  $\text{LiBF}_4$  also begins to decompose. The second peak temperature is around 280°C, which is lower than the peak temperature (340°C) of 0.5 M  $\text{LiBF}_4$  electrolyte as shown in Fig. 3b.

However, we still considered the possibility that the absence of split peaks was due to the deficiency of the solvent: it could be that all the solvent reacted with  $\text{PF}_5$  before the reaction with  $\text{BF}_3$  could take place. To check this hypothesis, we decided to decrease the concentration of Li salts. Figure 4 shows the DSC profiles of mixed  $\text{LiPF}_6 + \text{LiBF}_4$  electrolytes at (a) 0.5 M  $\text{LiPF}_6 + 0.5$  M  $\text{LiBF}_4$  (b) 0.25 M  $\text{LiPF}_6 + 0.25$  M  $\text{LiBF}_4$ , and (c) 0.165 M  $\text{LiPF}_6 + 0.165$  M  $\text{LiBF}_4$ . The exothermic peak temperatures shifted to a higher temperature as the concentration decreased. Still, as seen in Fig. 4, the main exothermic reaction peak was not



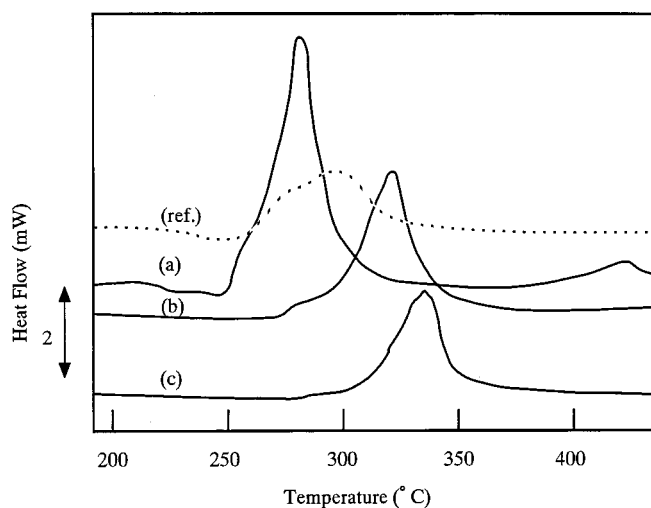
**Figure 2.** DSC profiles of  $\text{LiPF}_6/\text{EC} + \text{DMC} + \text{DEC}$  (3:3:1); (a) 1 M  $\text{LiPF}_6$ , (b) 0.5 M  $\text{LiPF}_6$ , and (c) 0.33 M  $\text{LiPF}_6$ .



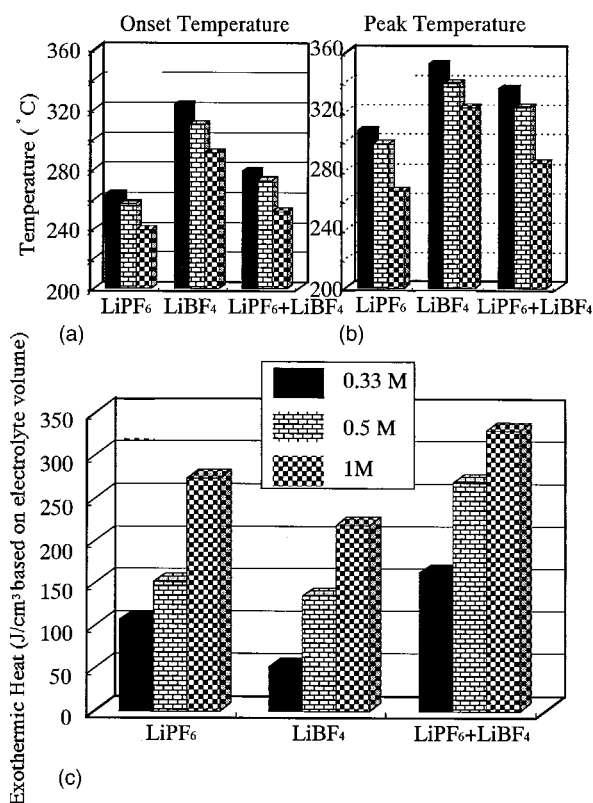
**Figure 3.** DSC profiles of  $\text{LiBF}_4/\text{EC} + \text{DMC} + \text{DEC}$  (3:3:1); (a) 1 M  $\text{LiBF}_4$ , (b) 0.5 M  $\text{LiBF}_4$ , and (c) 0.33 M  $\text{LiBF}_4$ .

clearly split despite the lower volume of  $\text{LiPF}_6$ . Rather, a decrease in heat was observed to result from the decrease of salt concentration, suggesting that deficiency of solvent is not the cause of the peak behavior. Figure 4 (ref.) shows the DSC profile of 0.5 M  $\text{LiPF}_6$  electrolyte. Compared to Fig. 4a, the 0.5 M  $\text{LiPF}_6 + 0.5$  M  $\text{LiBF}_4$  electrolyte, the 0.5 M  $\text{LiPF}_6$  electrolyte shows a smaller amount of heat generation. This result clearly indicates that  $\text{LiBF}_4$  also contributes in the reaction of the 0.5 M  $\text{LiPF}_6 + 0.5$  M  $\text{LiBF}_4$  electrolyte. We can infer the following based on these results: (i) the order for the onset and main peak temperature of used Li salts was  $\text{LiPF}_6 < \text{LiPF}_6 + \text{LiBF}_4 < \text{LiBF}_4$ ; (ii) the increase in exothermic heat quantity follows the order  $\text{LiBF}_4 < \text{LiPF}_6 < \text{LiPF}_6 + \text{LiBF}_4$ ; and (iii) as demonstrated by Botte *et al.*,<sup>8</sup> the lower the concentration of Li salt, the higher the onset temperature and main peak temperature. These results are summarized in Fig. 5.

We tried two additional experiments to confirm that a single main exothermic reaction peak is present for electrolyte containing  $\text{LiPF}_6 + \text{LiBF}_4$ . The first experiment was to decrease the scan rate of DSC from 5 to 1°C/min to attempt to separate the two reactions if they are indeed separate. The electrolyte used was 0.33 M  $\text{LiPF}_6 + 0.67$  M  $\text{LiBF}_4$  in EC:DMC:DEC (3:3:1). The concentration of  $\text{LiPF}_6$  was selected to be 0.33 M to decrease the influences of  $\text{LiPF}_6$ , which decomposes solvents at a lower temperature than



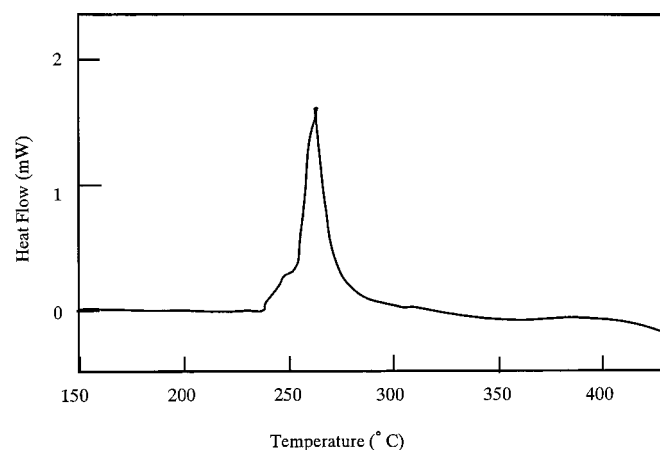
**Figure 4.** DSC profiles of  $\text{LiPF}_6 + \text{LiBF}_4/\text{EC} + \text{DMC} + \text{DEC}$  (3:3:1); (a) 0.5 M  $\text{LiPF}_6 + 0.5$  M  $\text{LiBF}_4$ , (b) 0.25 M  $\text{LiPF}_6 + 0.25$  M  $\text{LiBF}_4$ , and (c) 0.165 M  $\text{LiPF}_6 + 0.165$  M  $\text{LiBF}_4$  (ref.) 0.5 M  $\text{LiPF}_6$ .



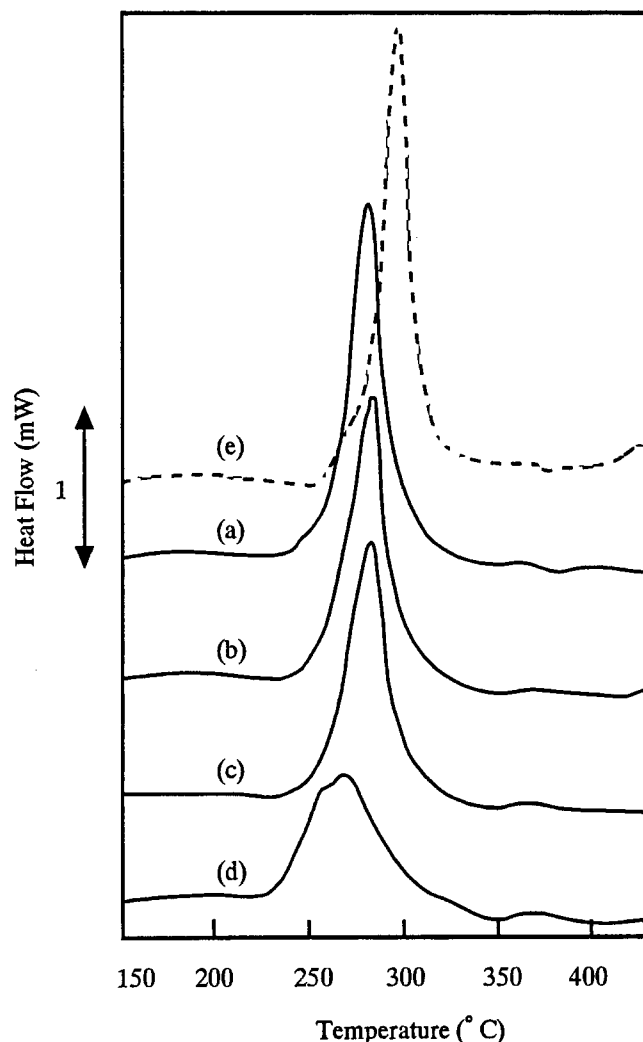
**Figure 5.** Comparison of (a) onset (b) peak, and (c) exothermic heat reaction of electrolytes in EC/DMC/DEC with LiPF<sub>6</sub>, LiBF<sub>4</sub>, and LiPF<sub>6</sub> + LiBF<sub>4</sub>. The concentrations of LiPF<sub>6</sub> + LiBF<sub>4</sub> at 0.33 M, 0.5 M, and 1 M were 0.165 M, 0.25 M:0.25 M, and 0.5 M:0.5 M, respectively.

LiBF<sub>4</sub>. As shown in Fig. 6, only a single peak was observed even though the scan rate was decreased. The total exothermic heat at 1°C/min was almost the same as that at 5°C/min.

The second experiment was to preheat the electrolyte (0.33 M LiPF<sub>6</sub> + 0.67 M LiBF<sub>4</sub> in EC:DMC:DEC (3:3:1)). The electrolyte was heated to 260, 268, and 272°C using DSC and subsequently cooled to 50°C followed by a final DSC measuring up to 430°C. The scan rate was 5°C/min. This experiment was designed to separate the reaction with LiPF<sub>6</sub> and LiBF<sub>4</sub>. The temperatures were selected so as not to induce any reaction of LiBF<sub>4</sub> with the solvent.



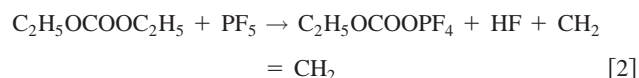
**Figure 6.** DSC profiles for 0.33 M LiPF<sub>6</sub> + 0.67 M LiBF<sub>4</sub> in EC/DMC/DEC (3:3:1) solvents at scan rates of 1°C/min.



**Figure 7.** DSC profiles for 0.33 M LiPF<sub>6</sub> + 0.67 M LiBF<sub>4</sub> in an EC/DMC/DEC (3:3:1) solvent mixture at scan rates of 5°C/min. The electrolyte was heated to 430°C after heating to (a) 260°C, (b) 268°C, (c) 272°C, (d) 275°C, and (e) no heating.

Figure 7 shows the resulting DSC profile of the experiment: the main exothermic peaks after the preheating shifted to a lower temperature. From Fig. 3, the peak of 0.67 M LiBF<sub>4</sub> electrolyte is found to be from 320 to 340°C. Therefore, the reactions with LiPF<sub>6</sub> and LiBF<sub>4</sub> cannot be separated from each other by preheating. Some reaction product created by the reaction with LiPF<sub>6</sub> must shift the reaction temperature with LiBF<sub>4</sub> to a lower temperature.

It was proposed by Kawamura *et al.*<sup>10</sup> that the decomposition of DEC solvent with LiPF<sub>6</sub> as electrolyte takes place as follows



Similarly, we can expect that HF could be produced from the reactions of either EC or DMC with PF<sub>5</sub>. Further, HF produced from the above reactions can also influence LiBF<sub>4</sub> in the following manner

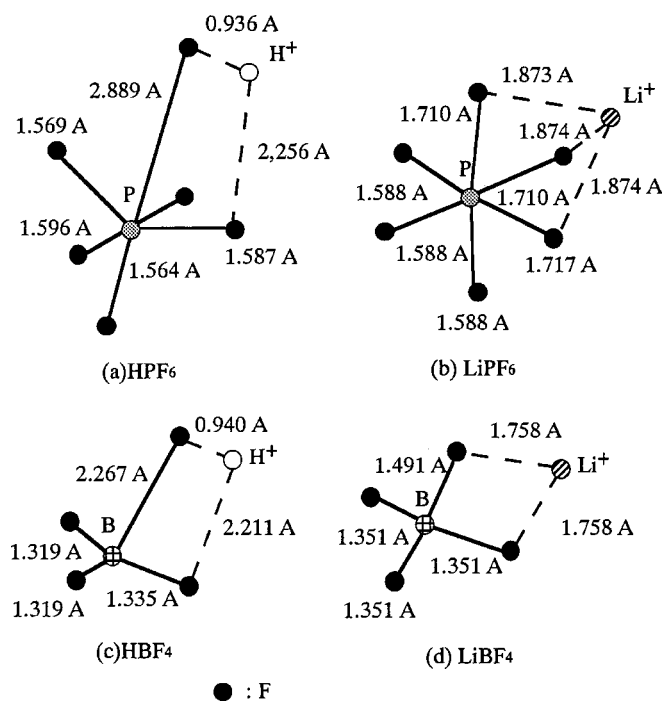
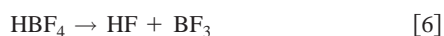


Figure 8. Optimized structures of  $\text{HPF}_6$ ,  $\text{LiPF}_6$ ,  $\text{HBF}_4$ , and  $\text{LiBF}_4$  by B3LYP/6-31G\* calculation.



One possible explanation for the observed unique behavior of Li salt mixtures may be ascribed to the role of HF produced from the reaction of  $\text{LiPF}_6$  with solvent. The mechanism of HF-catalyzed decomposition of  $\text{LiBF}_4$  can be understood by calculating the optimized structures of  $\text{HPF}_6$ ,  $\text{HBF}_4$ , and their lithium salts. The calculation was undertaken without considering any interaction with other molecules.  $\text{LiPF}_6$  and  $\text{LiBF}_4$  make contact ion-pairs in electrolyte with the influence of solvents. Therefore, the reliability of our calculation is limited. However, we think that our calculation results still have some meaning to predict the stability of the molecules, and would like to introduce our result. Figure 8 depicts the calculated interatomic distances for (a)  $\text{LiPF}_6$ , (b)  $\text{HPF}_6$ , (c)  $\text{LiBF}_4$ , and (d)  $\text{HBF}_4$  obtained by B3LYP/6-31G\* calculation. The coordination number of  $\text{H}^+$  or  $\text{Li}^+$  to the F atom of  $\text{PF}_6$  is changed from 1 to 3, and the most stable case was shown here. It is clearly seen from Fig. 8a and b that the interatomic distance between H coordinated with F and P for  $\text{HPF}_6$  is longer than that between Li and P for  $\text{LiPF}_6$ , *i.e.*, 2.889 and 1.717 Å, respectively. Thus we can say that the replacement of lithium by hydrogen decreases the stability of  $\text{PF}_6$  anion by increasing the interatomic distances of P and F atoms, thereby initiating the formation of HF as  $\text{HF} + \text{PF}_5$ . The case with  $\text{HBF}_4$  and  $\text{LiBF}_4$ , shown in Fig. 8c and d, is similar. Therefore, the  $\text{HBF}_4$  product in Reaction 5 is very unstable, and  $\text{HBF}_4$  can further decompose to other products, *i.e.*, HF and  $\text{BF}_3$  as shown in Reaction 6. If HF exists in the  $\text{LiBF}_4$  electrolyte,  $\text{BF}_3$  is produced from  $\text{HBF}_4$  at a lower temperature. Therefore, the reaction with  $\text{LiPF}_6$  and  $\text{LiBF}_4$  cannot be separated in the  $\text{LiPF}_6 + \text{LiBF}_4$  electrolytes. HF produced from Reaction 6 reacts with  $\text{LiBF}_4$  in Reaction 5 and finally it is observed that the cycling of Reactions 5 and 6 accelerates electrolyte decomposition.

The effect of mixing  $\text{LiPF}_6$  and  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  in the solvents was also investigated using the DSC-TG technique. Because the  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  does not decompose to form a Lewis acid ( $\text{PF}_5$  and

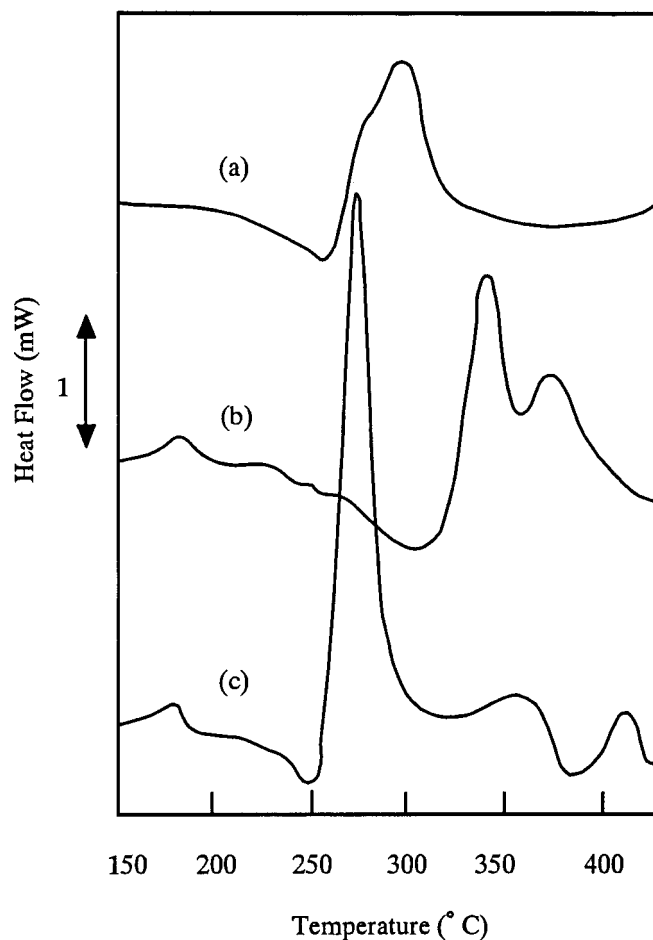


Figure 9. DSC profiles of  $\text{LiPF}_6 + \text{LiN}(\text{SO}_2\text{CF}_3)_2$  electrolytes in mixed EC/DMC/DEC (3:3:1) solvent; (a) 0.5 M  $\text{LiPF}_6$ , (b) 0.5 M  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ , and (c) 0.5 M  $\text{LiPF}_6 + 0.5 \text{ M LiN}(\text{SO}_2\text{CF}_3)_2$ .

$\text{BF}_3$ ), HF-catalyzed decomposition will not occur; therefore, it is interesting to investigate its behavior in contrast to  $\text{LiBF}_4$ . An electrolyte comprised of 0.5 M  $\text{LiPF}_6$  and 0.5 M  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  in EC, DMC, and DEC (3:3:1) depicts three characteristic peaks located at 270, 350, and 410°C (Fig. 9c). The main peak at 270°C is related to the reaction with  $\text{LiPF}_6$  because the 0.5 M  $\text{LiPF}_6$  electrolyte shows an exothermic peak at a similar temperature (Fig. 9a). The amount of the heat generation is larger for the 0.5 M  $\text{LiPF}_6 + 0.5 \text{ M LiN}(\text{SO}_2\text{CF}_3)_2$  electrolyte, which suggests that  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  also contributes to the main peak reaction of  $\text{LiPF}_6 + \text{LiN}(\text{SO}_2\text{CF}_3)_2$  electrolyte. However, the remaining two small peaks are related to the reaction of  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  because the  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  electrolyte shows two peaks at 330 and 360°C. This clearly suggests that the exothermic reaction of  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  with solvents is influenced by some products produced by the reaction of  $\text{LiPF}_6$  with solvents, but that the magnitude of the influence is smaller than with Li salt mixture containing  $\text{LiPF}_6$  and  $\text{LiBF}_4$ . This result supports the conclusion that the reaction product, which catalyzes the  $\text{LiBF}_4$  decomposition, is HF.

### Conclusions

We conclude that a single exothermic reaction peak is observed for a mixed  $\text{LiPF}_6 + \text{LiBF}_4$  electrolyte in a mixed EC/DMC/DEC (3:3:1) solvent. There were shoulders at a lower temperature side of the single exothermic reaction peak. The shoulders seem to be

caused by a two-step reaction of the exothermic reaction. The first step is a decomposition caused by  $\text{LiPF}_6$ . The second step is a decomposition by some product of the first step. At the second step,  $\text{LiBF}_4$  decomposes at a lower temperature than a  $\text{LiBF}_4$  electrolyte without  $\text{LiPF}_6$ . One candidate for the decomposition product of the first step which causes the second reaction is HF. However, further work must be done to identify the decomposition product

Mixing  $\text{LiPF}_6$  with  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  in the same EC/DMC/DEC (3:3:1) solvent mixture resulted in independent exothermic reaction peaks associated with either electrolyte. However,  $\text{LiPF}_6$  has a larger exothermic reaction heat in comparison to  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ . This confirms that the exothermic reaction of  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  with solvents is influenced similarly by some decomposition products of the first step but with a different result from the  $\text{LiPF}_6$  and  $\text{LiBF}_4$  mixture.

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