Thermal Stability of Electrolytes with Mixtures of LiPF₆ and LiBF₄ Used in Lithium-Ion Cells

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Thermal stability studies of electrolytes with mixtures of LiPF₆ and LiBF₄ were carried out using differential scanning calorimetry. The solvent was a mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate in a molar ratio of 3:3:1, respectively. We expected the occurrence of two independent exothermic peaks associated with LiPF₆ at the lower temperature and lithium LiBF₄ at the higher temperature, due to decomposition reactions resulting in the Lewis acids PF₅ and BF₃. Instead, the mixed salt electrolyte exhibited a single exothermic peak. We deduced that the HF produced by the reaction of LiPF₆ with solvent was the reason for the existence of one exothermic reaction peak. The HF may react with LiBF₄ to give HF and BF₃ at a lower temperature than the decomposition temperature of LiBF₄ by itself. By comparison, a thermal study of a mixed salt electrolyte including LiPF₆ and LiN(SO₂CF₂)₂ showed that the exothermic reaction of LiN(SO₂CF₂)₂ with solvents is also influenced by HF produced in the reaction of LiPF₆ with solvents but that the strength of the influence is small compared with its effect on an electrolyte mixture including LiBF₄.

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Experimental

The electrolytes were 1 M LiPF₆, 0.67 M LiPF₆ + 0.33 M LiBF₄, 0.5 M LiPF₆ + 0.5 M LiBF₄, 0.33 M LiPF₆ + 0.67 M LiBF₄, 1 M LiBF₄, and 1 M LiN(SO₂CF₂)₂, each with EC:DMC:DEC = 3:3:1 volume ratio. 1 M LiPF₆-EC, 1 M LiPF₆-DMC, 1 M LiPF₆-DEC, 1 M LiPF₆-EC, 1 M LiBF₄-DEC, and 1 M LiBF₄-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 LiPF₆, 1 M LiBF₄, and 1 M lithium salt mixture (molar ratios of LiPF₆ to LiBF₄ 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 LiPF₆ and 1 M LiBF₄, respectively (Fig. 1a and b). In lithium salt mixtures, there is also only one exothermic reaction peak; as the concentration of LiPF₆ salt increases, the exothermic reaction peak temperature moves closer to the exothermic peak temperature of 1 M LiPF₆. Sloop et al. has suggested that LiPF₆, which is not ionized in electrolytes, produces a strong Lewis acid, PF₅, thereby attacking the lone pair of electrons in the oxygen of solvent molecules. LiBF₄ is similar to LiPF₆ and therefore BF₃, a strong Lewis acid produced from LiBF₄, could decompose the solvents. If no interactions exist between LiPF₆ and LiBF₄ 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 LiPF₆ and LiBF₄.

There were shoulders at a lower temperature side of the peaks for (c) (0.5 M LiPF₆ + 0.5 M LiBF₄ electrolyte) and (d) (0.33 M LiPF₆ + 0.67 M LiBF₄ electrolyte) in Fig. 1. The shoulders

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

Figure 2. DSC profiles of LiPF$_6$ + LiBF$_4$ in EC + DMC + DEC (3:3:1): (a) 1 M LiPF$_6$, (b) 0.5 M LiPF$_6$, and (c) 0.33 M LiPF$_6$.

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

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

clearly split despite the lower volume of 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 LiPF$_6$ electrolyte. Compared to Fig. 4a, the 0.5 M LiPF$_6$ + 0.5 M LiBF$_4$ electrolyte, the 0.5 M LiPF$_6$ electrolyte shows a smaller amount of heat generation. This result clearly indicates that LiBF$_4$ also contributes in the reaction of the 0.5 M LiPF$_6$ + 0.5 M 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 LiPF$_6$ < LiPF$_6$ + LiBF$_4$ < LiBF$_4$; (ii) the increase in exothermic heat quantity follows the order LiBF$_4$ < LiPF$_6$ < LiPF$_6$ + LiBF$_4$; and (iii) as demonstrated by Botte et al., 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 LiPF$_6$ + 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 LiPF$_6$ + 0.67 M LiBF$_4$ in EC:DMC:DEC (3:3:1). The concentration of LiBF$_4$ was selected to be 0.33 M to decrease the influences of LiPF$_6$, which decomposes solvents at a lower temperature than...
LiBF₄. 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 LiPF₆ + 0.67 M LiBF₄ 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 LiPF₆ and LiBF₄. The temperatures were selected so as not to induce any reaction of LiBF₄ with the solvent. 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 LiBF₄ electrolyte is found to be from 320 to 340°C. Therefore, the reactions with LiPF₆ and LiBF₄ cannot be separated from each other by preheating. Some reaction product created by the reaction with LiPF₆ must shift the reaction temperature with LiBF₄ to a lower temperature.

Figure 5. Comparison of (a) onset (b) peak, and (c) exothermic heat reaction of electrolytes in EC/DMC/DEC with LiPF₆, LiBF₄, and LiPF₆ + LiBF₄. The concentrations of LiPF₆ + LiBF₄ at 0.33 M, 0.5 M, and 1 M were 0.165 M, 0.165 M, 0.25 M:0.25 M, and 0.5 M:0.5 M, respectively.

Figure 6. DSC profiles for 0.33 M LiPF₆ + 0.67 M LiBF₄ in EC/DMC/DEC solvent mixture at scan rates of 1°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. DSC profiles for 0.33 M LiPF₆ + 0.67 M LiBF₄ 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.

It was proposed by Kawamura et al.¹⁰ that the decomposition of DEC solvent with LiPF₆ as electrolyte takes place as follows

LiPF₆(s) → LiF(1) + PF₅(1)  \[1\]

C₂H₂OOCOC₂H₅ + PF₃ → C₂H₂OOCOPF₅ + HF + CH₃
  = CH₂ \[2\]

C₂H₂OOCOPF₅ → PF₅O + CO₂ + C₂H₄ + HF \[3\]

C₂H₂OOCOPF₅ + HF → PF₅OH + CO₂ + C₂H₄F \[4\]

Similarly, we can expect that HF could be produced from the reactions of either EC or DMC with PF₅. Further, HF produced from the above reactions can also influence LiBF₄ in the following manner.
Therefore, the reaction with LiPF₆ and LiN(SO₂CF₃)₂ in the solvents was also investigated using the DSC-TG technique. Because the LiN(SO₂CF₃)₂ does not decompose to form a Lewis acid (PF₅ and BF₃), HF-catalyzed decomposition will not occur; therefore, it is interesting to investigate its behavior in contrast to LiBF₄. An electrolyte comprised of 0.5 M LiPF₆ and 0.5 M LiN(SO₂CF₃)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 LiPF₆ because the 0.5 M LiPF₆ electrolyte shows an exothermic peak at a similar temperature (Fig. 9a). The amount of the heat generation is larger for the 0.5 M LiPF₆ + 0.5 M LiN(SO₂CF₃)₂ electrolyte, which suggests that LiN(SO₂CF₃)₂ also contributes to the main peak reaction of LiPF₆ + LiN(SO₂CF₃)₂ electrolyte. However, the remaining two small peaks are related to the reaction of LiN(SO₂CF₃)₂ because the LiN(SO₂CF₃)₂ electrolyte shows two peaks at 330 and 360°C. This clearly suggests that the exothermic reaction of LiN(SO₂CF₃)₂ with solvents is influenced by some products produced by the reaction of LiPF₆ with solvents, but that the magnitude of the influence is smaller than with Li salt mixture containing LiPF₆ and LiBF₄. This result supports the conclusion that the reaction product, which catalyzes the LiBF₄ decomposition, is HF. This result supports the conclusion that the reaction product, which catalyzes the LiBF₄ decomposition, is HF.

**Conclusions**

We conclude that a single exothermic reaction peak is observed for a mixed LiPF₆ + LiBF₄ 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 LiPF$_6$. The second step is a decomposition by some product of the first step. At the second step, LiBF$_4$ decomposes at a lower temperature than a LiBF$_4$ electrolyte without 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 LiPF$_6$ with LiN(SO$_2$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, LiPF$_6$ has a larger exothermic reaction heat in comparison to LiN(SO$_2$CF$_3$)$_2$. This confirms that the exothermic reaction of LiN(SO$_2$CF$_3$)$_2$ with solvents is influenced similarly by some decomposition products of the first step but with a different result from the LiPF$_6$ and LiBF$_4$ mixture.

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