

Thermal stability of alkyl carbonate mixed-solvent electrolytes for lithium ion cells

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Abstract

The thermal stability of some mixed-solvent electrolytes used in lithium cells was measured by differential scanning calorimetry (DSC) using airtight containers. The electrolytes used were ethylene carbonate (EC) + diethyl carbonate (DEC), EC + dimethyl carbonate (DMC), propylene carbonate (PC) + DEC, and PC + DMC in which was dissolved 1 M LiPF₆ or 1 M LiClO₄. The influence of water addition and lithium metal addition on the thermal behavior of these electrolytes was also investigated. The exothermic peak of LiPF₆ electrolytes containing DEC was found at 255 °C, and the peak temperature of the electrolytes containing DEC was 15–20 °C lower than that of LiPF₆ electrolytes containing DMC. This effect was also observed in the electrolytes including LiClO₄. DMC was found to be more reactive than DEC. The thermal behavior of various kinds of LiPF₆ electrolytes with lithium metal was measured by DSC. The exothermic reaction of 1 M LiPF₆/EC + DEC, 1 M LiPF₆/EC + DMC, and 1 M LiPF₆/PC + DMC with lithium metal began at the melting point of lithium metal because of the break down of the solid electrolyte interface (SEI). The temperature was approximately 180 °C, whereas the self-heating of 1 M LiPF₆/PC + DEC occurred before the melting point of lithium metal. The temperature at which the self-exothermal reaction began was 140 °C. Therefore, the lithium metal in this electrolyte was found to be thermally unstable. When water was added to the above electrolytes with lithium metal, the exothermic reaction began at less than 130 °C, probably due to a collapse of SEI in response to the HF that was a product of the reaction between LiPF₆ and the added water. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Li-ion cells are widely used as power sources for portable electric devices. Recently, studies of the utilization of high-performance Li-ion cells as power sources for electric vehicles (EV) and other large-sized equipment have been undertaken by many corporations and laboratories. However, large-sized Li-ion cells are not yet used in practice, 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 chemical reactions in the cells is an important factor to be considered. In general, Li-ion cells are less than 50 g in mass [1], as it is difficult to design large cells that pass safety-test criteria. Safety testing of Li-ion

cells has been reported by some laboratories [2–5]. In the past decade, the thermal stability or thermal behavior of Li-ion cells has been investigated energetically by DSC or accelerating rate calorimetry (ARC) [1,6–9]. The thermal behavior of cathode materials of Li-ion batteries, primarily lithium nickel oxide [10–15], lithium cobalt oxide [10,11,16], and lithium manganese oxide [10,11], has been measured by DSC. The thermal behavior of anode materials, including graphite [9–11,17,18], various kinds of carbon [19], and lithium metal [6], has been investigated with regard to both particle size [20] and solid electrolyte interface (SEI) [1,6,21–23] by both DSC and ARC. In addition, the thermal stability of electrolytes of Li-ion batteries has been investigated in relation to new boron-based solutes [24] and various organic electrolytes [25].

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 no reports of such investigations. Therefore, in the present study we

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used DSC to measure the thermal stability of alkyl carbonate mixed-solvent electrolytes as well as the influence of lithium metal and water addition on the thermal behavior of these electrolytes under air-tight conditions.

2. Experimental

An ethylene carbonate (EC) and diethyl carbonate (DEC) solution with a 1:1 volume ratio (Tomiya Co.) was used. The water content of this solution was less than 70 ppm. A 3 μ l portion of the solution was placed into a 20 μ l stainless steel sample pan that was then crimp-sealed with a stainless steel lid. These processes were carried out in an argon-filled dry box. The assembled sample pan was taken from the dry box, and the thermal stability was measured by a differential scanning calorimeter (Rigaku Thermo plus TG8110). The water content of the solution was measured by a Karl Fischer aquameter (Aquacounter AQ-7, Hiranuma Co.). Approximately, 10 mg Al_2O_3 was placed in a reference pan for the DSC measurement. A volume of 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$, 1 M $\text{LiPF}_6/\text{EC} + \text{dimethyl carbonate (DMC)}$, 1 M $\text{LiPF}_6/\text{propylene carbonate (PC)} + \text{DEC}$, and 1 M $\text{LiPF}_6/\text{PC} + \text{DMC}$ were obtained from Tomiyama Co. The water content of these electrolytes was under 100 ppm. The DSC measurement was performed for these electrolytes with/without water and/or lithium metal.

In addition, the thermal stability of 1 M $\text{LiClO}_4/\text{EC} + \text{DEC}$, 1 M $\text{LiClO}_4/\text{EC} + \text{DMC}$, 1 M $\text{LiClO}_4/\text{PC} + \text{DEC}$, 1 M $\text{LiClO}_4/\text{PC} + \text{DMC}$ (Tomiya Co.) with/without water (about 10,000 ppm) was also analyzed by DSC. The composition of all the mixed-solvents used resulted in a 1:1 volume ratio.

Initially, we measured the thermal stability of all the electrolyte solutions with/without addition by differential thermal analysis (DTA) [26]. The DTA and DSC results showed the same tendency. Therefore, the reliability of the data appears to be satisfactory.

3. Results and discussion

Fig. 1 shows the DSC curves of 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$, 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$, 1 M $\text{LiPF}_6/\text{PC} + \text{DEC}$, and 1 M $\text{LiPF}_6/\text{PC} + \text{DMC}$. Exothermic peaks were observed between 230 and 280 $^\circ\text{C}$ for the mixed-solvents with LiPF_6 , suggesting that LiPF_6 is related to an exothermic decomposition reaction. The peak temperature of the electrolytes containing DEC was 15–20 $^\circ\text{C}$ lower than that of the electrolytes containing DMC. Compared with DMC, DEC reacts easily with LiPF_6 . It is well known that LiPF_6 in electrolytes reacts with water by the following mechanism [27]:

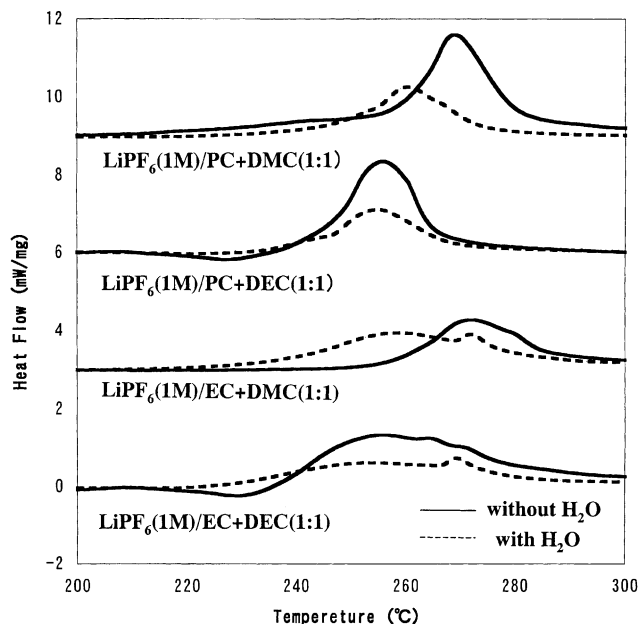
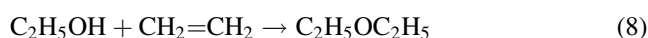
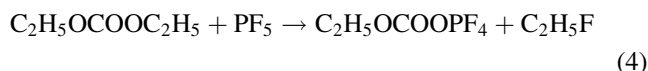
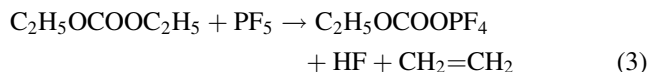


Fig. 1. DSC profiles of 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$ (1:1), 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1), 1 M $\text{LiPF}_6/\text{PC} + \text{DEC}$ (1:1), and 1 M $\text{LiPF}_6/\text{PC} + \text{DMC}$ (1:1) electrolytes with/without water.

LiPF_6 , which is not dissociated in electrolytes, produces a strong Lewis acid, PF_5 . PF_5 attacks the electron lone pair of oxygen of a water molecule and then decomposes. By analogy, PF_5 may attack the electron lone pair of oxygen of a solvent molecule and then decompose. Indeed, Steven E. Sloop et al. have experimentally shown that the reaction products of PF_5 with EC/DMC are the same as the thermal-decomposition products of $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolytes [28]. Mori et al. [25] have identified the thermal-decomposition products of $\text{LiPF}_6/\text{diisopropyl carbonate}$ as $(\text{CH}_3)_2\text{CHF}$, $\text{CH}_3\text{CH}=\text{CH}_2$, $(\text{CH}_3)_2\text{CHOH}$, CO_2 , and $(\text{CH}_3)_2\text{CHO}(\text{CHCH}_3)_2$. From these results, the following reactions can be proposed for LiPF_6/DEC electrolyte decomposition.



In LiPF_6/DMC , reactions like those of Eqs. (3) and (5) do not occur because DMC does not have an ethyl group. It is possible that these reactions lower the onset temperature of the exothermic reaction of LiPF_6/DEC in comparison with LiPF_6/DMC .

Table 1

Calorific values of 1 M LiPF₆/EC + DEC (1:1), 1 M LiPF₆/EC + DMC (1:1), 1 M LiPF₆/PC + DEC (1:1), and 1 M LiPF₆/PC + DMC (1:1) with/without water

LiPF ₆ (1 M)/EC + DEC (1:1)	LiPF ₆ (1 M)/EC + DMC (1:1)	LiPF ₆ (1 M)/PC + DEC (1:1)	LiPF ₆ (1 M)/PC + DMC (1:1)
500	370	530	380
200	230	270	230
40	62	51	61

Another possible reason is as follows. PF₅ is a strong Lewis acid. A Lewis acid attacks an electron-pair, and the larger electron density causes an immediate attack. In Eqs. (3) and (5), PF₅ attacks the carbonyl oxygen atom (oxygen atom in C=O) because of its large electron density. In this case, the larger the charge density of the oxygen atom, the more immediate the attack of PF₅. C₂H₅⁻ is a more electron-donative group than CH₃⁻, which is why DEC is more reactive with PF₅ than DMC. For the reasons stated above, DEC may decompose more easily than DMC.

DSC curves of the LiPF₆ electrolytes with water are also shown in Fig. 1. Smaller exothermic peaks were obtained for the electrolytes with added water than for those without water. The reason for the reduction in the exothermic peak was a decrease in LiPF₆ caused by the reaction between LiPF₆ and H₂O (Eq. (2)). Table 1 shows the calorific value of electrolytes and electrolytes with water (about 10,000 ppm) and the percentage of calorific values after water addition in comparison with the values before water addition. The calorific values of 1 M LiPF₆/EC + DEC with water and 1 M LiPF₆/PC + DEC with water are 40 and 51% of those of the electrolytes without water. For 1 M LiPF₆/EC + DMC with water and 1 M LiPF₆/EC + DEC with water, the calorific values are approximately 60% of those of the electrolytes without water. In addition, the heat-generation curves have a tendency to shift to a lower temperature with the addition of water, which is likely caused by the reaction of solvents with HF (that is the reaction product of LiPF₆ with water). The calorific value 370 J/g of 1 M LiPF₆/EC + DMC was the smallest of all the electrolytes without water addition. When water was not added, the calorific values of electrolytes containing DMC were smaller than those of electrolytes containing DEC. This result did not change even if considering the difference in molecular weight between DMC and DEC. When water was added to these electrolytes, the calorific values became almost the same.

Table 2

Calorific values of 1 M LiClO₄/EC + DEC (1:1), 1 M LiClO₄/EC + DMC (1:1), 1 M LiClO₄/PC + DEC (1:1), and 1 M LiClO₄/PC + DMC (1:1) with/without water

	LiClO ₄ (1 M)/EC + DEC (1:1)	LiClO ₄ (1 M)/EC + DMC (1:1)	LiClO ₄ (1 M)/PC + DEC (1:1)	LiClO ₄ (1 M)/PC + DMC (1:1)
Calorific value (without water) (J/g)	1040	820	1250	940
Calorific value (with water) (J/g)	950	830	1031	764

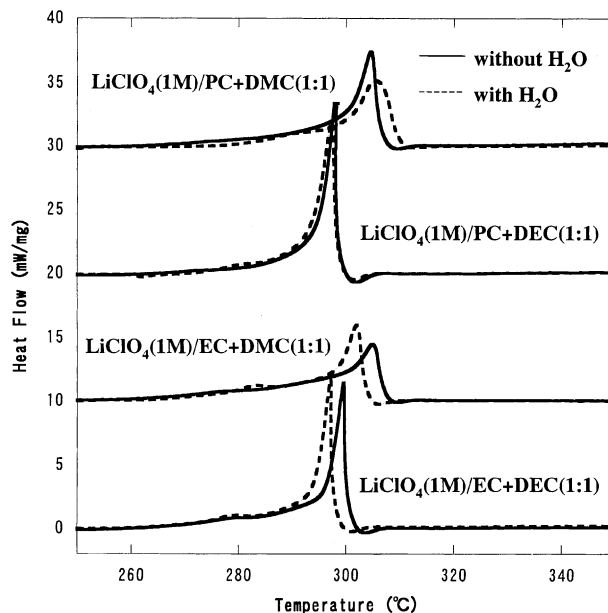


Fig. 2. DSC profiles of 1 M LiClO₄/EC + DEC (1:1), 1 M LiClO₄/EC + DMC (1:1), 1 M LiClO₄/PC + DEC (1:1), and 1 M LiClO₄/PC + DMC (1:1) electrolytes with/without water.

Fig. 2 shows the DSC curve of 1 M LiClO₄/EC + DEC, 1 M LiClO₄/EC + DMC, 1 M LiClO₄/PC + DEC, and 1 M LiClO₄/PC + DMC with/without water (approximately 10,000 ppm). The peak temperature of electrolytes containing DEC was 10 °C lower than that of electrolytes containing DMC. This result is similar to that for electrolytes containing LiPF₆. DEC is more reactive than DMC in both cases. There is no great difference in the DSC curves between only electrolytes and electrolytes with water because LiClO₄ does not react with H₂O. Table 2 shows the calorific values of electrolytes containing LiClO₄ with/without water (approximately 10,000 ppm). The calorific values of electrolytes containing DEC were larger than those of electrolytes containing DMC. This difference can't be ignored, however, even if the difference in the molecular weights of the electrolytes is considered. This tendency (DEC electrolytes > DMC electrolytes in calorific values) can also be seen in LiPF₆ electrolytes. The smallest heat value in electrolytes without water, 820 J/g, was obtained for 1 M LiClO₄/EC + DMC. The value was two-thirds of the largest value (1 M LiClO₄/PC + DEC). The calorific value of LiClO₄ electrolytes was twice or three times that of the LiPF₆ electrolytes.

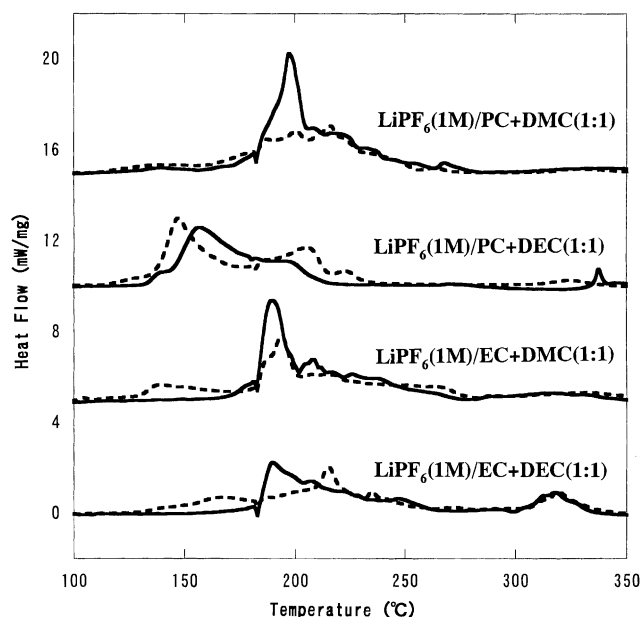
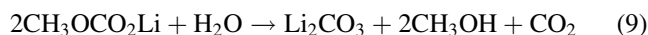


Fig. 3. DSC profiles of 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$ (1:1), 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1), 1 M $\text{LiPF}_6/\text{PC} + \text{DEC}$ (1:1), and 1 M $\text{LiPF}_6/\text{PC} + \text{DMC}$ (1:1) electrolytes with lithium metal and with both lithium metal and water. The solid line is electrolytes with lithium metal, and the dotted line is electrolytes with lithium metal and water.

Fig. 3 shows the DSC curve of LiPF_6 electrolytes with lithium metal, and with both lithium metal and water. Lithium metal in electrolytes forms a SEI, becoming thermally stable up to its melting point. Lithium metal in 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$, 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$, and 1 M $\text{LiPF}_6/\text{PC} + \text{DMC}$ was found to be thermally stable up to 180 °C, which is its melting point. However, the self-heat of the sample with 1 M $\text{LiPF}_6/\text{PC} + \text{DEC}$ with lithium metal was generated at 140 °C. The calorific value of this sample peaked immediately after the beginning of heat-generation. Hence, this heat-generation was caused not by the formation of a new SEI like lithiated graphite [1]. The SEI of this sample seemed to disappear entirely at 140 °C. Aurbach et al. have reported that lithium metal dissolves in DEC without SEI formation, with the reaction product dissolving in solvent [29]. In accordance with this result, we found that SEI on lithium in 1 M $\text{LiPF}_6/\text{PC} + \text{DEC}$ (1:1) is very thermally unstable and that the SEI breaks down at 140 °C. However, 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$ (1:1) was observed to be more stable, forming a seemingly more stable SEI than that of $\text{PC} + \text{DEC}$. It is reasonable to conclude that EC is the most stable electrolyte with lithium metal, as EC-based electrolytes show the best Li-cycling efficiency [30]; in addition, EC appears to work well for a graphite anode [31,32]. The heat-generation is initiated before the melting point of Li, indicating that the SEI is not perfect even if Li does not melt.

When water was added to LiPF_6 electrolytes with lithium metal, the self-heating onset temperature decreased, dropping to between 110 and 120 °C for all electrolytes. Aurbach et al. have proposed a mechanism by which $\text{CH}_3\text{OCO}_2\text{Li}$ in

SEI changes in response to the reaction with water [27] as follows:



Kanamura et al. have shown that LiF is the primary component of SEI when HF is added to electrolytes [33]. Based on these reports, it is expected that the main components in SEI would change to Li_2CO_3 and to a LiF-rich composite with the addition of water. Usually such inorganic materials act as a good protection film in SEI. However, our results show that the decomposition temperature decreases with the addition of water. We believe that $\text{CH}_3\text{OCO}_2\text{Li}$ is an important material with regard to the thermal stability of Li. In other words, when cracks and pinholes of inorganic materials in SEI are filled with $\text{CH}_3\text{OCO}_2\text{Li}$, $\text{CH}_3\text{OCO}_2\text{Li}$ prevents the direct contact of electrolytes with lithium metal.

4. Conclusions

The thermal stability of mixed-solvent electrolytes for Li-ion cells was measured by DSC. The exothermic peak temperatures of electrolytes containing DEC were lower than those of electrolytes containing DMC. DEC reacts easily with LiPF_6 and LiClO_4 in comparison with DMC. Heat-generation of 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$ with lithium metal occurs at 140 °C, which is considerably lower than the melting point of lithium metal. Stable SEI is not formed on lithium metal in 1 M $\text{LiPF}_6/\text{PC} + \text{DEC}$. When water was added to LiPF_6 electrolytes with lithium metal, the exothermic reaction began at less than 130 °C as a result of direct contact between lithium metal and electrolytes.

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