

Thermal studies of fluorinated ester as a novel candidate for electrolyte solvent of lithium metal anode rechargeable cells

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Abstract

The thermal stability of fluorinated ester electrolytes with and without lithium metal and the positive electrode material at the charged state were investigated, in terms of application for electrolytes in lithium metal anode cells. The fluorinated ester electrolytes are solutions dissolving LiPF₆ in carboxylic acid esters whose original carboxylic acids are partially fluorinated. The corresponding non-fluorinated ester electrolytes were also studied for comparison. According to differential scanning calorimetry (DSC) measurement, fluorinated ester electrolytes exhibited significant thermal stability when coexisting with lithium metal or Li_{0.5}CoO₂. LiPF₆/methyl difluoroacetate showed the best stabilization effect, which shifted the exothermic peak of the electrolyte with lithium metal or Li_{0.5}CoO₂ to about 300°C. In addition, LiPF₆/methyl difluoroacetate exhibited a good lithium anode cycling efficiency. We believe that LiPF₆/methyl difluoroacetate is a very promising electrolyte for use in realizing lithium metal anode secondary cells. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fluorinated ester electrolytes; Thermal stability; Lithium metal anode; Secondary cells

1. Introduction

Lithium rechargeable cells with lithium metal anodes have been studied for a long time, even before the invention of lithium ion cells, because the lithium metal anode has a very large theoretical capacity of 3860 mAh/g, with contrast to the value of 372 mAh/g for LiC₆ carbon anode. However, the lithium metal anode rechargeable cells do not see wide commercial use due to the poor thermal stability of the lithium metal anode. Several investigations [1–5] have focused on this limitation, and some of them have succeeded in enhancing our understanding of the behaviors of battery components at their stability limits.

The non-aqueous electrolytes used in lithium batteries consist of certain lithium salts and flammable organic solvents, and this makeup has been considered one of the reasons for the failure of these batteries in terms of safety. However, there has been no study investigating the degree to which flammable solvents influence the safety failure of batteries. We have previously estimated the thermal stability of the 1 M LiPF₆/[ethylene carbonate (EC) or propylene carbonate (PC)]/[diethyl carbonate (DEC) or dimethyl

carbonate (DMC)] used in conventional lithium batteries with and without lithium metal by means of thermal analysis using such techniques as differential scanning calorimetry (DSC) [6,7]. When coexisting with lithium metal, these electrolytes exhibited an exothermic peak at around 180°C, the melting point of lithium metal. We expect that this is one of the key reactions controlling the thermal stability of cell components, and that a depression of this exothermic reaction would be effective in improving cell safety.

Many of the fluorine-containing organic compounds are non-flammable themselves and have quite unique properties. Therefore, many partly fluorinated organic solvents have been studied as co-solvents of electrolytes to improve the flammability and low temperature performance of graphite anode and lithium ion cells [8–10]. A high cycling efficiency of lithium metal has been reported using CF₃SO₃Li/ethyltrifluoroacetate + methyl acetate (MA) [11]. In the present study, partially fluorinated carboxylic acid esters were used as the electrolyte solvent and LiPF₆ as the salt. Using the fluorinated ester electrolytes, we investigated the thermal stability of electrolytes with and without lithium metal and the positive electrode material at the charged state, in terms of application for electrolytes in lithium metal anode cells.

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Table 1
Solvents

Non-fluorinated solvent		Fluorinated solvent	
Sample number	Solvent	Sample number	Solvent
1	CH ₃ COOCH ₃ (MA)	1'	CHF ₂ COOCH ₃ (MFA)
2	CH ₃ COOCH ₂ CH ₃ (EA)	2'	CHF ₂ COOCH ₂ CH ₃ (EFA)
3	CH ₃ CH ₂ COOCH ₃	3'	CF ₃ CF ₂ COOCH ₃
4	CH ₃ CH ₂ COOCH ₂ CH ₃	4'	CF ₃ CF ₂ COOCH ₂ CH ₃
5	H(CH ₃) ₂ CCOOCH ₃	5'	F(CF ₃) ₂ CCOOCH ₃
6	H(CH ₂) ₃ COOCH ₃	6'	F(CF ₂) ₃ COOCH ₃
7	H(CH ₂) ₃ COOCH ₂ CH ₃	7'	F(CF ₂) ₃ COOCH ₂ CH ₃
8	H(CH ₂) ₄ COOCH ₂ CH ₃	8'	H(CF ₂) ₄ COOCH ₂ CH ₃
9	H(CH ₂) ₇ COOCH ₂ CH ₃	9'	F(CF ₂) ₇ COOCH ₂ CH ₃

2. Experimental

Table 1 summarizes the fluorinated esters used in this study which were supplied by Daikin Fine Chemical Co. Ltd. (Japan). LiPF₆ salt (Stella Chemifa Corporation, Japan) could be dissolved in esters 1' (MFA: methyl difluoroacetate) and 2' (EFA: ethyl difluoroacetate) to a salt concentration of 1 M. However, LiPF₆ salt could be dissolved to a salt concentration of less than 0.2 M in the other fluorinated esters. Therefore, in the present study, we used the solutions of 1' and 2' fluorinated esters with 0.2 M of LiPF₆, and the other fluorinated esters were saturated with LiPF₆. For purpose of comparison, we prepared the solutions of corresponding esters (Wako Chemical Co., Japan) with 0.2 M of LiPF₆. We also performed similar measurements using the conventional electrolyte solution used in lithium batteries, 1 M LiPF₆/EC + DMC 1:1 in volume (Tomiya Chemical Co., Japan).

The thermal stability of fluorinated esters was monitored by a TG-DSC apparatus (Rigaku Thermo plus TG8110, Rigaku, Japan). Each sample (5 μl for liquid) for TG-DSC measurement was packed in a stainless steel case, which was then crimp-sealed in a glove box filled with argon. In some cases, a piece (several milligrams) of lithium metal or charged LiCoO₂ pellet was additionally sealed in the stainless steel case. It was confirmed that leakage from the case did not occur by the TG data, which was measured at the same time as the DSC measurement. A LiCoO₂ pellet was prepared by mixing LiCoO₂ (70 wt.%), acetylene black (25 wt.%) and polytetrafluoroethylene binder (5 wt.%), packed in a coin cell with lithium metal anode and 1 M LiPF₆/EC + DMC electrolyte, and then charged to Li_{0.5}CoO₂ in a constant current mode. The cycling efficiency of the lithium metal electrode with 1 M LiPF₆/esters and 1 M LiPF₆/fluorinated esters (1' and 2') was estimated by a cycle test using a coin cell. Initially, lithium metal was placed only on one side in the cell. Lithium was deposited electrochemically onto the other stainless steel face at the constant current density of 0.1 mA/cm² for 2 h, and then stripped from the face reversibly until the cell voltage

reached 1.5 V. This deposition/strip cycle was performed 70 times.

3. Results and discussion

3.1. Thermal stability of LiPF₆/fluorinated esters electrolytes

Fig. 1 shows the DSC profiles of MA (1) and MFA (1') containing 0.2 M of LiPF₆, and 1 M LiPF₆/EC + DMC. An exothermic peak appears at around 250–300°C in all profiles. This peak is not observed in the profile for the solvent itself. Therefore, the exothermic reaction represented by this peak occurs due to the coexistence of LiPF₆. We can estimate the thermal stability of LiPF₆ solution by the position of this peak. The peak temperatures of this exothermic reaction of all fluorinated esters and corresponding esters containing LiPF₆ are summarized in Fig. 2. It seems that the thermal stabilities of the LiPF₆/fluorinated esters were similar to those of the LiPF₆/corresponding esters except for the case of esters 3, 4, 5, and 7. It should be noted that the fluorinated esters contained a smaller amount of LiPF₆ than the corresponding esters, except in the case of 1 and 2. Fluorine substitution in the ester framework appears to have contributed little to the exothermic decomposition of esters with LiPF₆.

In LiPF₆ electrolytes, ionic dissociation is not high, and associated LiPF₆ is in equilibrium with LiF and PF₅. PF₅ is a strong Lewis acid, that reacts with a small amount of water in electrolytes following the reaction PF₅+H₂O → PF₃O+2HF [12]. Based on analogy with this reaction, organic solvents may have reacted with PF₅ at a high temperature. The thermal decomposition of LiPF₆ electrolytes is probably caused by PF₅ in the electrolytes. It has been reported that the direct reaction of PF₅ with EC/EMC is similar to the thermal decomposition of LiPF₆ in EC/EMC [13]. PF₅ may attack the carbonyl oxygen of non-fluorinated solvents. The reaction mechanism and the stabilities of PF₅-solvent complexes are not changed significantly by the fluorination of

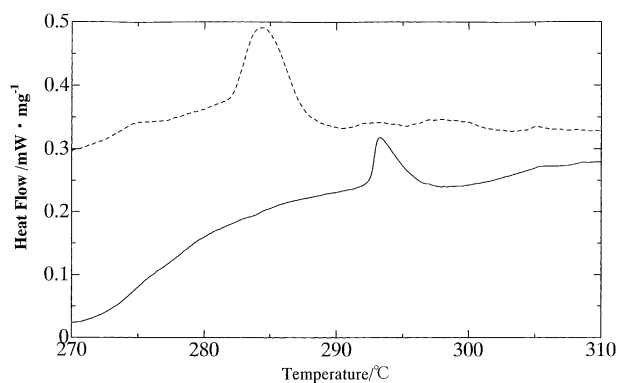


Fig. 1. DSC profiles of electrolytes (solid curve: 0.2 M LiPF₆/MFA; dotted curve: 0.2 M LiPF₆/MA).

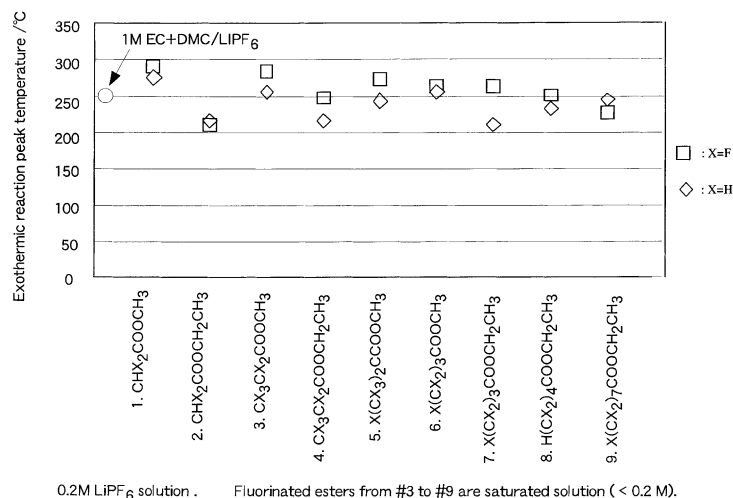


Fig. 2. Exothermic reaction peak temperature of electrolytes.

the esters, since the thermal stabilities of LiPF_6 /fluorinated esters were similar to those of the LiPF_6 /corresponding esters.

3.2. Thermal stability of LiPF_6 /fluorinated ester electrolytes with lithium metal

Fig. 3 shows the DSC profiles of MA and MFA containing 0.2 M of LiPF_6 with lithium metal. Lithium metal melts at 180°C and endothermic peaks appear at this temperature in both profiles. A large exothermic peak is observed at 220°C in the case of heating of the LiPF_6 /MA/lithium metal system. This indicates the reduction of LiPF_6 MA solution by lithium metal. However, there is not any exothermic reaction of the LiPF_6 /MFA/lithium metal system around this temperature. Nakajima et al. reported that “the fluoroesters are more easily reduced than EC/DEC by electrochemical reduction” [8]. This means that the fluoroester electrolytes are more reactive with Li metal than EC/DEC electrolyte. As a rule, reduction stability of partly fluorinated solvents is bad, because of the strong electron-withdrawing effect

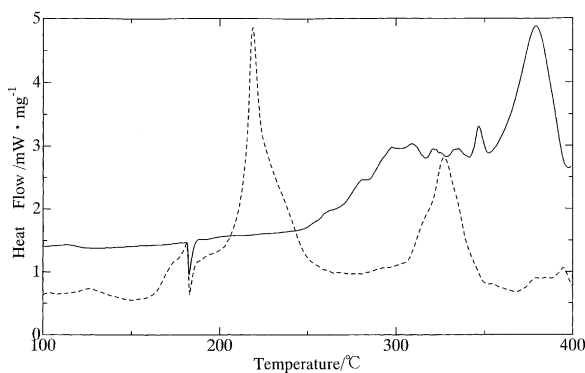


Fig. 3. DSC profiles of electrolytes with lithium metal (solid curve: 0.2 M LiPF_6 /MFA; dotted curve: 0.2 M LiPF_6 /MA).

of the fluorine atoms. Therefore, we have to consider the contribution of the solid electrolyte interphase (SEI) [14].

SEI covers the surface of lithium metal and prevents further reduction. In the case of heating the LiPF_6 /MA/lithium metal system, the SEI layer may be effective up to 200°C and the reduction rate may be so exceeded that SEI layer cannot protect the reduction at higher temperature. The effectiveness of the SEI layer can be estimated by the position of this exothermic peak; that is, the higher temperature of the exothermic peak may indicate that, in this case, the SEI layer was thick enough to prevent substantial reduction. When the LiPF_6 /MFA/lithium metal system was heated, no exothermic peak could be observed below 250°C and a broad peak appeared at around 290°C . This indicates that the LiPF_6 /MFA/lithium metal system may provide a thicker and more effective SEI layer on the lithium surface than the corresponding ester system.

However, we have to consider also the reactivity of the solvent itself with lithium metal. Many esters can also exist in enol form in addition to the keto form. The enol form reacts quickly with lithium metal [15]. The enol form of MFA may be unstable compared with that of MF, because of the strong electron-withdrawing effect of the fluorine atoms. Therefore, the content of enol MFA is very small. This is another possible reason of low reaction temperature of LiPF_6 /MA/lithium metal system.

Fig. 4 summarizes the peak temperatures of this exothermic reduction for the LiPF_6 /fluorinated esters/lithium metal systems and LiPF_6 /corresponding esters/lithium metal systems. Many of the fluorinated ester systems provide an exothermic peak temperature higher than the melting point of lithium metal, while the corresponding ester systems generate an exothermic reduction below the melting point of lithium metal. This indicates that non-fluorinated esters may react with lithium metal at low temperature because of their enol form, and fluorinated esters may help to produce a thick and effective SEI layer to prevent further

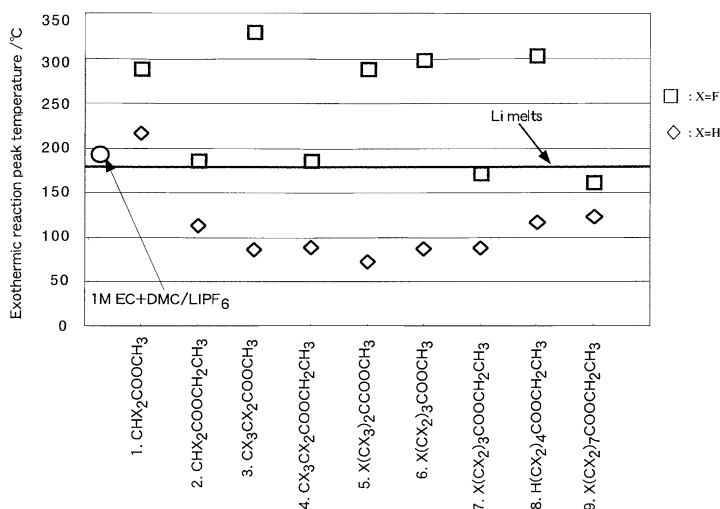


Fig. 4. Exothermic reaction peak temperature of electrolytes with lithium metal.

reduction of LiPF₆ solution even above the melting point of lithium metal.

It has been reported that methyl formate is reduced on the Li surface to form lithium formate, which is the major species in the SEI layer, and methane gas [16]. If we assume the reaction product of MA to be lithium acetate, lithium difluoroacetate may form a stronger SEI than lithium acetate. Another possibility is that lithium difluoroacetate may react with lithium metal to form LiF. It is likely that LiF is responsible for the production of an effective SEI layer to prevent further reduction of the LiPF₆ solution. In addition, we must consider the role of other inorganic species, such as Li₂O, Li₂CO₃ and LiOH. A study into this matter is currently underway in our laboratory.

3.3. Cycling efficiency of the deposition and dissolution of lithium in LiPF₆/fluorinated esters

Fluorinated esters probably produce an effective SEI layer to protect against the reaction with lithium metal. The SEI layer may be thick and strong. Based on this fact, we were anxious about a possibility of poor cycling efficiency of fluorinated ester electrolytes.

Fig. 5 summarizes the cycling efficiency of lithium deposition/dissolution using 1 M LiPF₆ electrolytes of MFA (1'), MA (1), EFA (2'), and ethyl acetate (EA) (2). An electrolyte based on MFA brought the highest efficiency of 84%. Among similar framework esters, fluorinated esters provided good electrolytes for an effective lithium deposition and dissolution process.

Our method used to evaluate lithium cycling efficiency is so-called “Li on stainless steel [1]”. This method is the simplest method. However, the evaluated efficiency is generally smaller compared with other method such as “Li on Li” or “Full cell” [1]. For example, the cycling efficiency of 1 M LiClO₄/ethylene carbonate (EC)/1,3-dioxolane (DOL) is 85% when we use “Li on Pt”, a similar method as “Li on

stainless steel”. However, the cycling efficiency of 1 M LiClO₄/EC/DOL is 95% when we use “Li on Li” [17]. From this consideration, we believe cycling efficiency of the MFA electrolyte is high enough. The cycling efficiency of LiPF₆/EC/1,2-dimethoxyethane (DME), LiPF₆/EC/1,2-

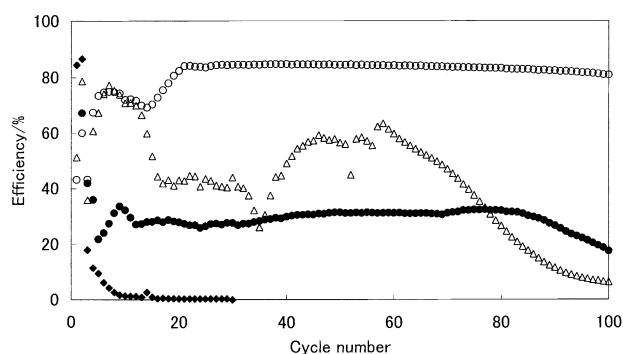


Fig. 5. Lithium cycling efficiency in electrolytes (○) 1 M LiPF₆/MFA; (△) 1 M LiPF₆/EFA; (●) 1 M LiPF₆/MA; (◆) 1 M LiPF₆/EA.

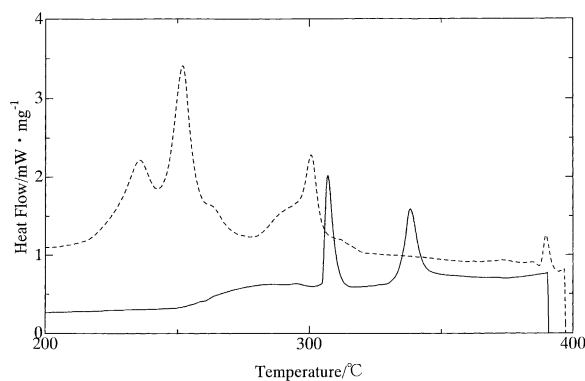


Fig. 6. DSC profiles of electrolytes with Li_{0.5}CoO₂ (solid curve: 0.2 M LiPF₆/MFA; dotted curve: 0.2 M LiPF₆/MA).

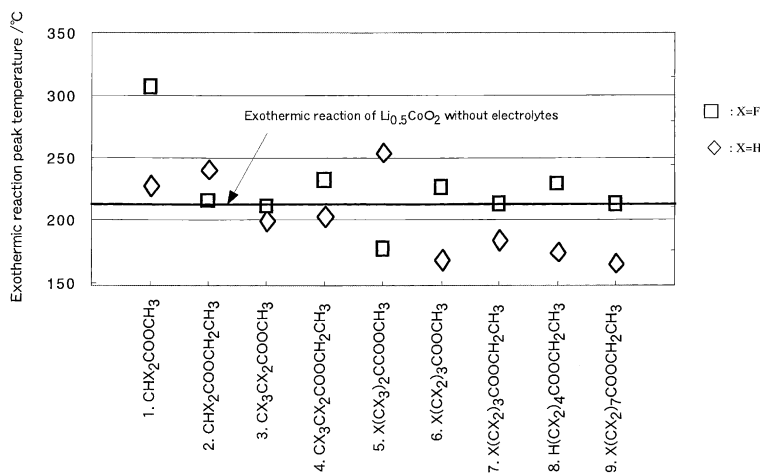


Fig. 7. Exothermic reaction peak temperature of electrolytes with $\text{Li}_{0.5}\text{CoO}_2$.

diethoxyethane (DEE), $\text{LiPF}_6/\text{EC}/\text{DMC}$, and $\text{LiPF}_6/\text{EC}/\text{DEC}$ are 93, 90, 98, and 82%, respectively, when we use “Full cell (spinel $\text{LiMn}_2\text{O}_4/\text{Li}$ cell)” [1].

The cycling capacity of the graphite anode in 1 M $\text{LiClO}_4/\text{EC} + \text{DEC} + \text{MFA}$ has been studied by Nakajima et al. [8]. They also found that MFA had a better capacity than other fluoroesters. They suggested that the reason for this enhanced capacity was the lower reduction potential of the MFA electrolyte (0.87 V versus Li) close to the reduction potential of EC, because MFA contains only two fluorine atoms. In another study, an electrolyte $\text{CF}_3\text{SO}_3\text{Li}/\text{ethyltrifluoroacetate} + \text{MA}$ showed a high cycling efficiency of lithium metal anode [11]. In this paper, we have focused on the performance of single solvent electrolytes. We will soon begin to study the performance of mixed solvent electrolytes containing MFA or other fluorinated esters.

3.4. Thermal stability of $\text{LiPF}_6/\text{fluorinated ester electrolytes with } \text{Li}_{0.5}\text{CoO}_2$

Fig. 6 shows the DSC profiles of MA (1) and MFA (1') containing 0.2 M of LiPF_6 with a piece of $\text{Li}_{0.5}\text{CoO}_2$ pellet. The $\text{LiPF}_6/\text{MA}/\text{Li}_{0.5}\text{CoO}_2$ system shows three exothermic peaks with a shoulder around 200–300°C. The peak positions are 230, 250 and 300°C. $\text{Li}_{0.45}\text{CoO}_2$ with 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ has been reported [18] to generate heat due to decomposition and reaction of the cathode and electrolyte at around 220 and 240°C. In the case of the LiPF_6/MA system, either of the two peaks around 230 and 250°C may represent this heat generation. The peak around 300°C was caused by the thermal decomposition of the LiPF_6/MA electrolyte itself (see Fig. 2). In contrast, no peak appears in this area and two sharp peaks appear at as high temperature as 300°C in the case of the LiPF_6/MFA system. Because the peak of Li_xCoO_2 without an electrolyte is much smaller than that in the case with an electrolyte [19], $\text{Li}_{0.5}\text{CoO}_2$ may decompose independently and does not react with LiPF_6/MFA at around this temperature. The peak around 300°C was caused by the

thermal decomposition of the LiPF_6/MFA electrolyte itself (see Fig. 2). The position of the exothermic peaks of the $\text{LiPF}_6/\text{various fluorinated esters and corresponding esters}/\text{Li}_{0.5}\text{CoO}_2$ systems are summarized in Fig. 7. With the exception of ester 2' and 5', all fluorinated esters tended to inhibit the reaction with $\text{Li}_{0.5}\text{CoO}_2$.

4. Conclusion

The DSC measurements indicated that electrolytes containing LiPF_6 salt and fluorinated ester solvents exhibited significant thermal stability toward lithium metal or $\text{Li}_{0.5}\text{CoO}_2$. LiPF_6/MFA showed the best stabilization effect, shifting the exothermic peak with lithium metal or $\text{Li}_{0.5}\text{CoO}_2$ to about 300°C. This effect may have been brought about by a strong SEI layer on lithium metal and inhibition of the reaction with $\text{Li}_{0.5}\text{CoO}_2$. LiPF_6/MFA exhibited a good lithium anode cycling efficiency, even if the electrolyte formed a strong SEI layer on lithium metal. The thermal stability of lithium metal anode secondary batteries will be improved by the use of LiPF_6/MFA electrolyte.

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