



LiPF₆/methyl difluoroacetate electrolyte with vinylene carbonate additive for Li-ion batteries

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ABSTRACT

A methyl difluoroacetate (MFA)-based LiPF₆ solution was applied as an electrolyte to improve the thermal stability of Li-ion batteries. The addition of vinylene carbonate (VC) improved the electrochemical characteristics of the electrolyte significantly, and satisfactory reversible capacity and cycling performance were obtained with a graphite negative electrode. The thermal stability of the electrolytes was investigated with DSC. Regardless of whether or not VC was used, the electrolyte exothermically decomposed at a temperature higher than 450 °C. The thermal behavior of a mixture of lithiated graphite and VC-added electrolyte was also studied in detail. The ratio between the electrolyte and the electrode was a dominant factor in the heat generation of the mixture. A sharp exothermic peak at about 330 °C was observed when the electrode was superabundant, but the heat value was much smaller than that obtained with 1 mol dm⁻³ LiPF₆/EC-DMC electrolyte under the same conditions. When the electrolyte was superabundant, a mild exothermic decomposition of the electrolyte became the dominant reaction in the mixture. X-ray photoelectron spectroscopic analysis was carried out on delithiated graphite electrodes to study the effect of VC additive on solid electrolyte interphase (SEI) modification. VC-added MFA-based electrolyte was considered to be a good candidate for developing safer Li-ion batteries.

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1. Introduction

Li-ion batteries are widely used as power sources for various portable electronic devices because they offer a long cycle life, high energy density, and high voltage performance. Recently, laboratories and corporations have been employing high-performance Li-ion batteries as practical power sources for electric vehicles, for which large-scale batteries are necessary. However, the thermal dissipation rate is much lower in large-scale batteries than in normal batteries due to the reduction of specific surface areas. Therefore, the potential safety risk becomes a serious problem with the scaling-up of batteries, especially when the batteries are used severely or abused. Thus, materials with better thermal stability are needed for the design of safer batteries and to broaden the application field of Li-ion batteries to large-scale devices.

The safety issues of Li-ion batteries are closely related to the thermal stability of constituent materials [1,2]. Now commercial electrolytes for Li-ion batteries normally consist of certain lithium salts and mixed organic solvents. The presence of flammable

organic solvents had been considered an important cause of the safety failure of batteries [3–7]. However, recently it was reported that even nonflammable organic electrolytes could induce fire hazards [8]. Therefore, an ideal solvent for battery electrolytes should have good stability against high temperature regardless of its flammability. As organic compounds containing fluorine species have high thermal stability and quite unique properties, some fluorinated organic solvents have been studied as potential solvents or cosolvents of electrolytes [9–12]. Our group has reported that, among several kinds of partially fluorinated carboxylic acid esters, methyl difluoroacetate (CHF₂COOCH₃, MFA) showed the best electrochemical properties and thermal stability as an electrolyte solvent when LiPF₆ was applied as the salt [11]. MFA-based electrolyte also showed better thermal stability than ethylene carbonate/dimethyl carbonate (EC/DMC)-based electrolyte. Moreover, when mixed with a lithiated carbon electrode, 1 mol dm⁻³ LiPF₆/MFA electrolyte generated much less heat than 1 mol dm⁻³ LiPF₆/EC-DMC electrolyte [13]. Unfortunately, our subsequent studies could not reproduce the good electrochemical performance of the 1 mol dm⁻³ LiPF₆/MFA electrolyte, although the purity of MFA solvent had been confirmed repeatedly by GC-MS. In contrast, rapid capacity fading during cycling was obtained. As partially fluorinated carboxylic acid ester had been reported to be rather unstable against the

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reduction on the negative electrode [10], it was suspected the passivation film formed with the LiPF₆/MFA electrolyte had an insufficient protective effect, which induced a continuous reduction of MFA solvent during Li-ion intercalation. Therefore, a solid electrolyte interphase (SEI) with a good passivation effect is necessary when MFA is applied as a bulk electrolyte solvent.

Vinylene carbonate (VC) might be the most famous one among various SEI modification additives for battery electrolyte and has been widely applied in Li-ion battery research and development [14]. Due to its high reduction potential of 1.4 V [15] vs. Li⁺/Li, VC can be reduced and forms an effective passivation film on the negative electrode surface before the bulk electrolyte components are involved. In this study, VC was added into 1 mol dm⁻³ LiPF₆/MFA electrolyte as an additive. The effects of VC on electrochemical characteristics of the electrolyte were studied by comparing the charge/discharge behavior of batteries with or without VC. At the same time, the influence of VC on electrolyte thermal stability was investigated using a thermogravimetry-differential scanning calorimeter (TG-DSC). X-ray photoelectron spectroscopy (XPS) studies were also carried out to analyze the VC contribution on the SEI component.

2. Experimental

MFA solvent (Daikin Industries) was used as received in the present study. 3 vol.%VC (Mitsubishi Chemical) was added into the MFA solvent when additive is needed for the electrolyte. LiPF₆ salt was purchased from Stella Chemifa. 1 mol dm⁻³ LiPF₆ electrolyte was prepared by dissolving LiPF₆ salt in the MFA solvent or VC-added MFA solvent. For comparison, commercially available 1 mol dm⁻³ LiPF₆/EC-DMC (1:1 (v/v), Tomiyama Chemicals) was also used. To protect from oxygen and moisture, all samples were prepared in an Ar-filled glove-box with a dew point below -70 °C.

Two-electrode half-cells (R2032) were used to evaluate the electrochemical properties of the electrolytes. Each cell consisted of a graphite working electrode, a polypropylene separator (Celgard 3501), and a lithium foil as a counter electrode. The graphite electrode was prepared by spreading a slurry of 95 wt.% natural graphite (LF-18D, Chuetsu Graphite) and 5 wt.% poly(vinylidene fluoride) (PVdF)-binder (KF#9100, Kureha Chemical) dissolved in N-methyl-2-pyrrolidinone (NMP) onto a 0.1-mm-thick porous Cu-foil current collector. Circular electrodes (15-mm diameter) with a thickness of 38–42 μm and typical loading of 6 mg cm⁻² active material were dried at 120 °C for 12 h in a vacuum oven. All electrochemical tests were carried out at 25 °C in a constant temperature oven. The electrochemical cell was cycled between 20 and 2000 mV at a constant current density of 0.4 mA cm⁻² accompanied by 8 h of constant voltage charging at 20 mV during each cycle. A relaxation period of 10 min at the end of each discharge/charge course was performed. To get a delithiated graphite electrode, the cycling procedure was interrupted at a 2000 mV cut-off voltage. To get a lithiated graphite electrode, the cycling procedure was interrupted at a 20 mV cut-off voltage. All potentials reported in this work were referenced to the Li/Li⁺ redox couple.

For thermal analysis and XPS analysis, the pre-cycled graphite/Li half-cell was disassembled in the Ar-filled glove box. The graphite electrode was rinsed and soaked in MFA solvent for 4 h and vacuum-dried at room temperature for 12 h. Most of the low-molecular-weight components were dissolved away from the electrode in the rinsing step and evacuated during vacuum drying.

The thermal characteristics of electrolytes were analyzed by a Thermo Plus TG-DSC 8230L system (Rigaku). On the one hand, the thermal stability of the MFA-based electrolyte itself was investi-

gated. 2 μl electrolyte was crimp-sealed in a stainless steel pan in the Ar-filled glove-box. The sealed pan was removed from the glove box and heated from room temperature to 550 °C at a heating rate of 5 °C min⁻¹ in air, with alumina as a reference material. During measurement, the TG signal was monitored simultaneously to confirm that the pan was hermetic. On the other hand, the thermal behavior of electrolyte coexisting with lithiated graphite was also studied. In the Ar-filled glove-box, a certain amount of fully lithiated graphite electrode was removed from the Cu current collector after washing and drying, and then packed into a DSC pan. After that, a certain amount of electrolyte was loaded into the pan and the pan was crimp-sealed as soon as possible. The following DSC measurement was the same as described above.

The surface composition of fully delithiated graphite electrode was investigated by XPS analysis. The test electrode was sealed under an argon atmosphere using a vessel for transfer into the XPS sample chamber without being exposed to air. Li 1s, F 1s, and O 1s spectra were obtained by repeated scans.

3. Results and discussion

Fig. 1 shows the discharge/charge curves of half-cells with 1 mol dm⁻³ LiPF₆/MFA electrolyte (Fig. 1a) and 1 mol dm⁻³ LiPF₆/MFA + 3%VC electrolyte (Fig. 1b) over the initial two cycles. For comparison, the cycling profiles of 1 mol dm⁻³ LiPF₆/EC-DMC electrolyte are presented in Fig. 1c. For the 1 mol dm⁻³ LiPF₆/MFA electrolyte, the cell gave a first discharge of 426 mAh g⁻¹ and its first charge capacity was 295 mAh g⁻¹ (shown in Fig. 1a). A coulombic efficiency of 69% was obtained. However, in the second cycle, the discharge capacity decreased rapidly to 240 mAh g⁻¹, although the coulombic efficiency increased to 95%. This result was different from that of our previous report [13]. There was a slight difference between the cycling conditions of these two works, but it was not sufficient to explain the much more rapid capacity fading in the present work. By now no clear hypothesis can be submitted to explain the difference, because the experimental conditions in the present work were well controlled, including solvent purity, coin cell structure, atmosphere in the glove-box, and so on. It was doubted that some trace impurities in MFA accelerated its reduction during cycling and induced the continuous consumption of solvent during Li-ion intercalation (as shown in Fig. 2).

Comparison between Fig. 1a and c reveals that there was no Li-ion intercalation plateau in the second discharge curve of the 1 mol dm⁻³ LiPF₆/MFA electrolyte. This indicated that Li ion transfer from the MFA electrolyte into the graphite electrode was obstructed or at least concealed by the MFA reduction decomposition reaction. Therefore, a SEI modification additive, such as VC, was needed here for the LiPF₆/MFA electrolyte.

As shown in Fig. 1b, the electrochemical properties of SEI were improved significantly after 3% VC was added into the electrolyte. From the first cycle, a lower irreversible capacity of 98 mAh g⁻¹ was obtained with the 1 mol dm⁻³ LiPF₆/MFA + VC electrolyte compared with 130 mAh g⁻¹ of the 1 mol dm⁻³ LiPF₆/MFA electrolyte. As the first discharge capacity was 454 mAh g⁻¹, a high charge capacity of 356 mAh g⁻¹ was obtained with the 1 mol dm⁻³ LiPF₆/MFA + VC electrolyte after the first cycle. In the second cycle, similar to what was observed in the second discharge curve of the 1 mol dm⁻³ LiPF₆/EC-DMC electrolyte, several Li-ion intercalation plateaus were presented in the discharge curve. This indicated effective Li intercalation into graphite through SEI. Accordingly, a high charge capacity of 355 mAh g⁻¹ and coulombic efficiency of 97% were observed for the second cycle with 1 mol dm⁻³ LiPF₆/MFA + VC electrolyte. This result, including reversible capacity and cycling efficiency, was comparable to that of the 1 mol dm⁻³ LiPF₆/EC-DMC electrolyte.

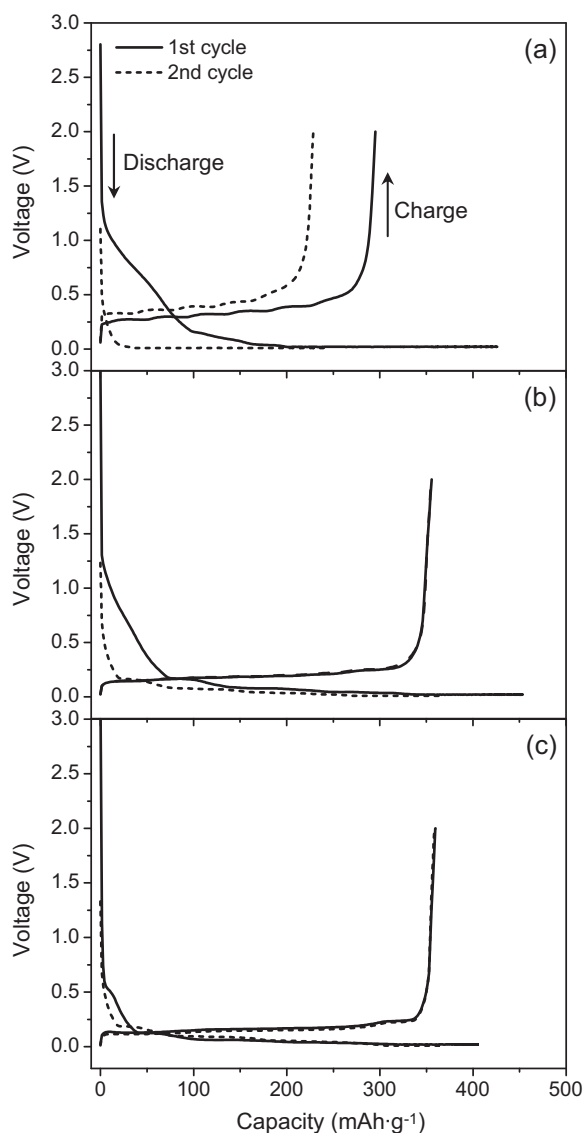


Fig. 1. The initial two discharge/charge profiles of graphite electrodes in (a) 1 mol dm^{-3} LiPF_6/MFA electrolyte, (b) 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + 3\% \text{VC}$ electrolyte, and (c) 1 mol dm^{-3} $\text{LiPF}_6/\text{EC-DMC}$ electrolyte.

By comparing the first discharge curves of three electrolytes in detail, the effect of VC on SEI modification in MFA-based electrolyte was clarified. The potential of the first turning point of each discharge curve indicated the reduction activity of each electrolyte. For both MFA-based electrolytes, the potentials were higher than 1.2 V, which was consistent with Nakajima's report [10]. For 1 mol dm^{-3} $\text{LiPF}_6/\text{EC-DMC}$ electrolyte, the potential was about 0.7 V, which was 0.5 V lower than that of MFA-based electrolytes. Obviously, the MFA-based electrolytes had much higher reduction activity than the EC-DMC electrolyte. On the other hand, it was noticed that the reduction potential of 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + \text{VC}$ was a little higher than that of 1 mol dm^{-3} LiPF_6/MFA . This indicated that the VC additive was electrochemically reduced earlier than MFA during cycling, which might be the key point of the SEI modification effect of VC. Due to the reduction and polymerization of VC [16], a passivation film formed on the graphite surface, so the MFA reduction on the graphite was suppressed. This effect was clear at lower potential, as the VC additive significantly changed the electrochemical behavior of the MFA-based electrolyte at lower potential. For the 1 mol dm^{-3} LiPF_6/MFA electrolyte, no obvious plateau was obtained except that a glasis started from 0.3 V, which indicated

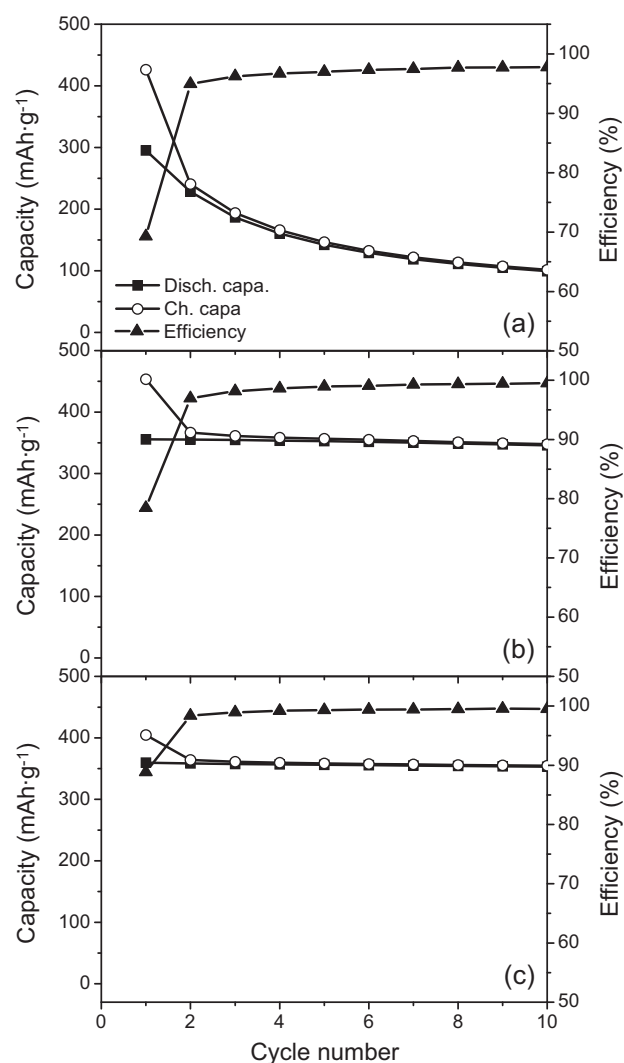


Fig. 2. Cycling performance of graphite electrodes in (a) 1 mol dm^{-3} LiPF_6/MFA electrolyte, (b) 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + 3\% \text{VC}$ electrolyte, and (c) 1 mol dm^{-3} $\text{LiPF}_6/\text{EC-DMC}$ electrolyte.

an unremitting reductive reaction of the electrolyte together with the Li ion intercalation. For the 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + \text{VC}$ electrolyte, two obvious plateaus, at 0.3 and 0.08 V, were obtained even in the first discharge curve, which was somewhat similar to the first discharge curve of the 1 mol dm^{-3} $\text{LiPF}_6/\text{EC-DMC}$ electrolyte. This clearly showed the modification effect of VC on SEI formation in MFA-based electrolyte, so the excessive reduction of electrolyte was depressed effectively and the Li ion intercalation became dominant with the decrease in potential.

Fig. 2 shows the cycling performance of graphite/Li half-cells with the test electrolytes. Under the cycling conditions described, the 1 mol dm^{-3} $\text{LiPF}_6/\text{EC-DMC}$ electrolyte showed perfect cycling performance. A large discharge/charge capacity of $355/353 \text{ mAh g}^{-1}$ was obtained after 10 cycles. Unfortunately, for the 1 mol dm^{-3} LiPF_6/MFA electrolyte, capacity fading was remarkable. After 10 cycles, the charge capacity decreased from 295 to only 100 mAh g^{-1} although the coulombic efficiency was 98%. But when the VC additive was applied, a high discharge/charge capacity of $348/346 \text{ mAh g}^{-1}$ was maintained after 10 cycles, and a coulombic efficiency of >99% was calculated accordingly. This result was really comparable to that of the EC-DMC electrolyte.

As MFA-based electrolytes were introduced as a kind of thermally stable electrolyte, the thermal stability of the electrolyte

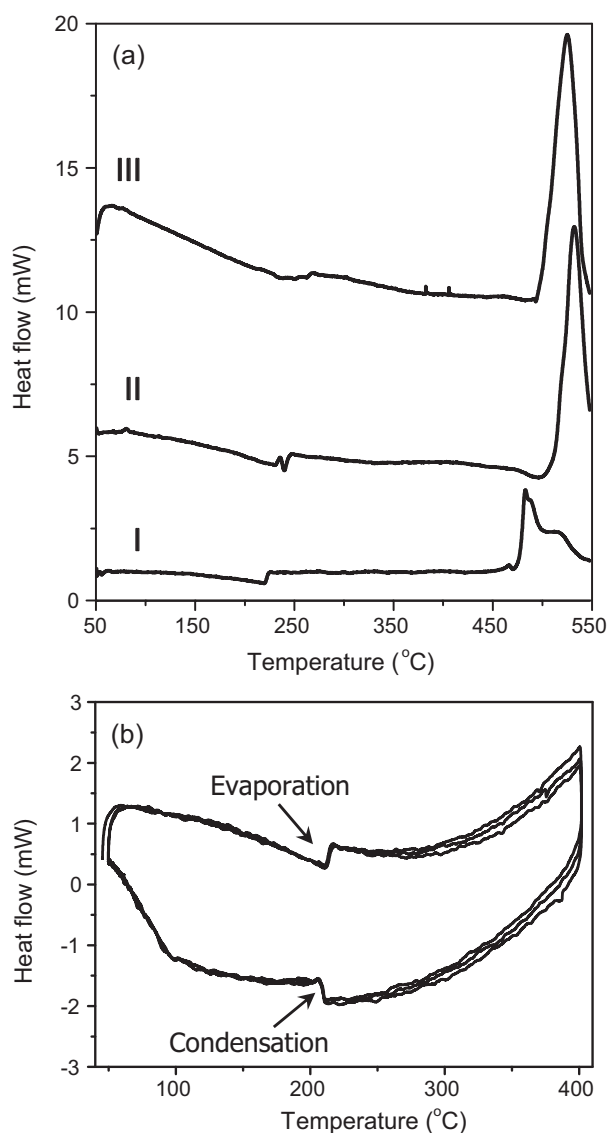


Fig. 3. (a) DSC curves of (I) MFA solvent, (II) 1 mol dm⁻³ LiPF₆/MFA electrolyte, (III) 1 mol dm⁻³ LiPF₆/MFA+3%VC electrolyte and (b) cooling and reheating DSC curve of MFA solvent.

should receive much attention when organic additives are added into the electrolyte. Therefore, DSC measurements were carried out in the present work to study the thermal behavior of the electrolyte at elevated temperatures. Fig. 3a shows the DSC curves of 2 μ l MFA solvent, the 1 mol dm⁻³ LiPF₆/MFA electrolyte, and the 1 mol dm⁻³ LiPF₆/MFA+VC electrolyte. Both solvent and electrolytes showed good thermal stability up to 450 °C, which was about 200 °C higher than that of 1 mol dm⁻³ LiPF₆/EC-DMC electrolyte [17,18]. By reheating the MFA solvent to 300 °C, it became clear that a mild endothermic heat that peaked at about 220 °C was attributable to the evaporation of MFA solvent (see Fig. 3b). This mild endothermic peak was followed by a small, sharp endothermic peak caused by thermal dissociation of LiPF₆ salt when the electrolyte was heated up. When the temperature was higher than 450 °C, both the solvent and electrolytes showed exothermic decomposition heat. It was reasonable to understand that the heat generation from the electrolyte was much greater than that from the solvent. But it was valuable to find that the VC additive did not show any negative effect on the thermal stability of the MFA-based electrolyte, except for a slight decrease in the onset temperature of the electrolyte thermal decomposition.

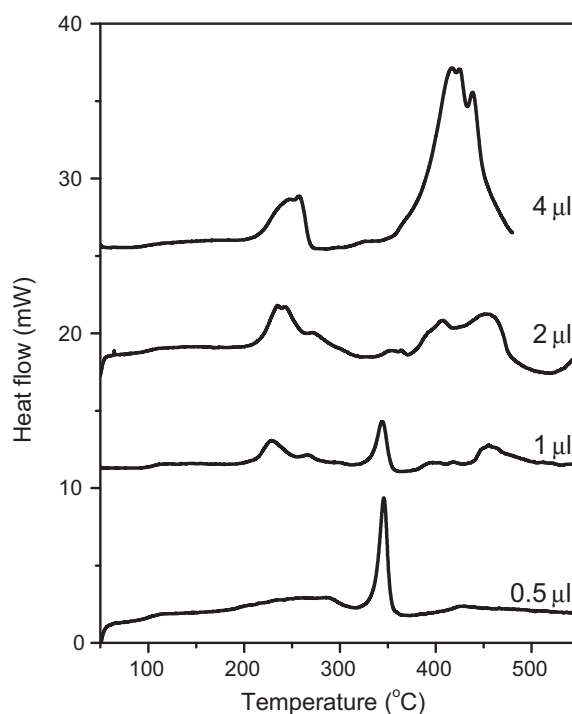


Fig. 4. DSC curves of 1 mg fully lithiated graphite electrode powder mixed with 0.5, 1, 2, and 4 μ l 1 mol dm⁻³ LiPF₆/MFA + 3%VC electrolyte.

From application viewpoint, heat generation caused by the reaction between the lithiated negative electrode and the electrolyte was crucial for the safety of Li-ion batteries. Therefore, the thermal behavior of the lithiated graphite mixed with the 1 mol dm⁻³ LiPF₆/MFA+VC electrolyte was investigated in detail. A given amount of electrode powder and electrolyte were sealed together in a DSC pan. With the temperature ramping up, the TG signal was also monitored besides the DSC signal to make sure the pan did not leak.

Fig. 4 shows the variations in DSC curves to the amount of coexisting 1 mol dm⁻³ LiPF₆/MFA+VC electrolyte while the lithiated graphite electrode was fixed at 1 mg. When the amount of electrolyte was 0.5 μ l only, a mild exothermic plateau from 180 to 280 °C was detected, followed by a sharp exothermic peak at about 350 °C. However, when the amount of electrolyte increased to 1 μ l, the exothermic peak at 350 °C did not increase, but decreased rapidly. At the same time, a mild exothermic heat at about 230 °C was found. Besides that, several peaks appeared in the range from 370 to 500 °C, although they were not significant. With a further increase in electrolyte from 1 to 2 and 4 μ l, the exothermic peak at 350 °C disappeared completely while the exothermic peak at 230 °C increased and shifted to a higher temperature gradually. At the same time, the exothermic peaks in the range from 370 to 500 °C grew rapidly until they became dominant. Obviously, the dominant reactions in the system varied with the ratio between the electrode and electrolyte, which induced different thermal behavior of the mixtures. Because no exothermal peak at a temperature lower than 300 °C was found when the 1 mol dm⁻³ LiPF₆/MFA+VC electrolyte and lithiated graphite [17] were heated separately, the exothermic peak at 230 °C and the mild exothermic plateau from 180 to 280 °C should be attributable to reactions between electrolyte and lithiated graphite, although the reactions might be somewhat different due to the ratio between the reactants. It was previously reported that a secondary SEI formed on the surface of lithiated graphite when it was heated up together with the 1 mol dm⁻³ LiPF₆/EC-DMC electrolyte [17–19]. A similar mechanism might be able to

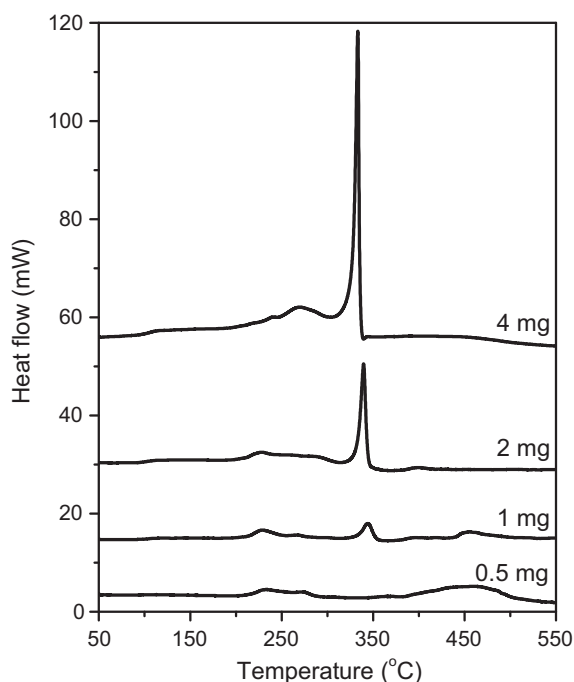


Fig. 5. DSC curves of $1 \mu\text{l}$ 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + 3\% \text{VC}$ electrolyte mixed with 0.5, 1, 2, and 4 mg lithiated graphite electrode powder.

explain the phenomena here. With the increase in temperature during DSC measurement, the reduction reaction of MFA solvent on the surface of lithiated graphite was accelerated. Therefore, a secondary SEI formed gradually on the surface of the negative electrode and caused exothermic heat from 180 to 280 °C. After that, when the lithiated graphite was sufficient, the residual intercalated Li ions reacted with SEI (including secondary SEI) and electrolyte, and then caused a sharp exothermic heat at about 350 °C. But when the electrolyte was excessive, the residual electrolyte was thermally decomposed at a higher temperature. However, because the formation of secondary SEI consumed solvent only, the LiPF_6 salt in residual electrolyte was concentrated. That was the reason why the thermal decomposition temperature of the residual electrolyte shifted to a lower temperature (370–500 °C) than that of the 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + \text{VC}$ electrolyte. Certainly, the exothermic decomposition of SEI (including secondary SEI) was supposed to have happened simultaneously in this temperature range.

Fig. 5 shows the DSC curves of a mixture of the $1 \mu\text{l}$ 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + \text{VC}$ electrolyte with a given amount of lithiated

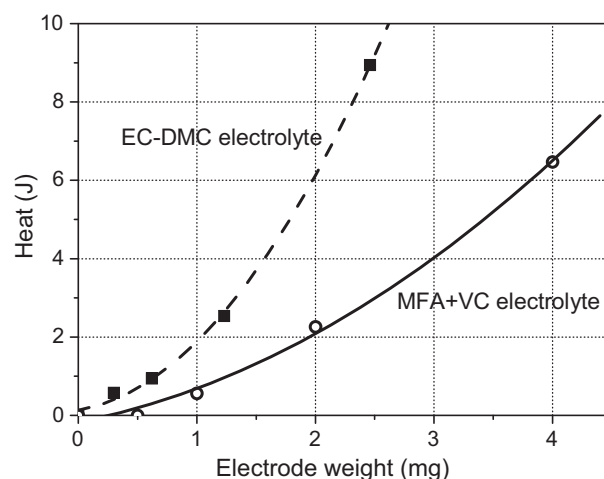


Fig. 6. Comparison of the heat generation from the mixtures of lithiated graphite and different electrolytes.

graphite electrode. The most important feature of the figure is the drastic exothermic heat at about 330 °C when 4 mg lithiated graphite was mixed with $1 \mu\text{l}$ electrolyte. However, when the coexisting electrode was decreased to 2 mg or less, this peak shifted to a higher temperature and faded rapidly. According to the conclusion from Fig. 4, it was reasonable to attribute the exothermic heat at about 350 °C to the reaction between intercalated graphite and SEI (including secondary SEI) and electrolyte. However, although a sharp exothermic peak was observed, the heat value was much lower than the heat generated from the mixture of lithiated graphite and the 1 mol dm^{-3} $\text{LiPF}_6/\text{EC-DMC}$ electrolyte. Fig. 6 shows the heat value of the main peaks obtained from the mixture of a given amount of lithiated graphite and $1 \mu\text{l}$ electrolyte. For the 1 mol dm^{-3} $\text{LiPF}_6/\text{EC-DMC}$ electrolyte, because of the drastic heat generation, the maximal amount of lithiated graphite was controlled at 2.5 mg. From the two polynomial fitting lines it was easy to conclude that the 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + \text{VC}$ electrolyte had much better thermal stability than the 1 mol dm^{-3} $\text{LiPF}_6/\text{EC-DMC}$ electrolyte for practical application. In the present work, because a fully lithiated graphite electrode could not be obtained with the 1 mol dm^{-3} LiPF_6/MFA electrolyte, the comparison between 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + \text{VC}$ and 1 mol dm^{-3} LiPF_6/MFA mixed with lithiated graphite was not carried out.

In order to investigate the VC effect on the formation of SEI, XPS measurements were also carried out onto the dried electrodes. Fig. 7 shows the Li 1s, F 1s, and O 1s spectra of graphite electrodes in

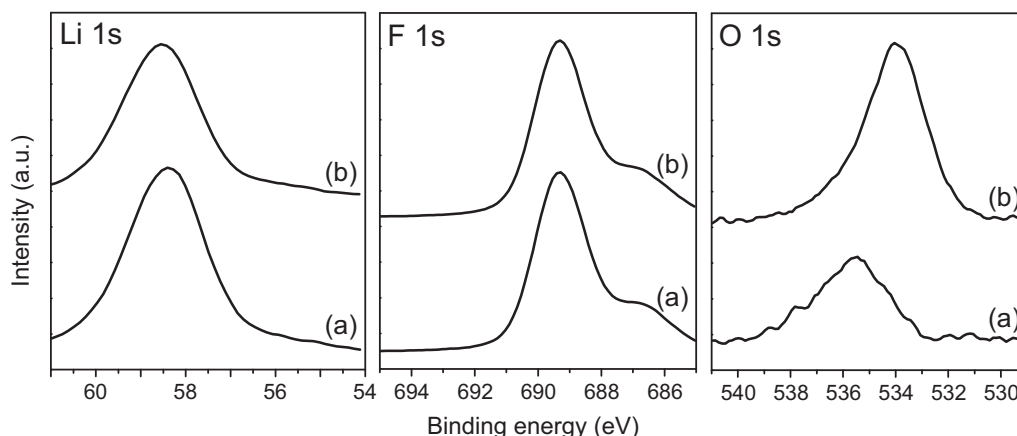


Fig. 7. XPS spectra of delithiated graphite electrodes cycled in (a) 1 mol dm^{-3} LiPF_6/MFA electrolyte and (b) 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + 3\% \text{VC}$ electrolyte.

the delithiated state obtained after the second cycle in 1 mol dm^{-3} LiPF_6/MFA or 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + \text{VC}$ electrolyte. According to our previous research [13], CHF_2COOLi was expected to be the main component of SEI formed on Li metal when 1 mol dm^{-3} LiPF_6/MFA was used as the electrolyte. Here, on the delithiated graphite, the same supposition could be made due to the similarity of the XPS spectra. When VC was added into the electrolyte, the XPS spectra of Li 1s and F 1s were similar to those obtained without added VC, but the intensity of the peaks was a little lower. At the same time, O 1s spectra showed clear dependence on the presence of VC additive, including higher density and lower binding energy of the peak. These phenomena indicated that the SEI formed in 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + \text{VC}$ electrode was more oxygen-rich than that formed in 1 mol dm^{-3} LiPF_6/MFA electrolyte. This might be attributable to the reduction reaction of VC during cycling. A detailed study will be carried out in the future to make this point clear.

4. Conclusion

To improve the thermal stability of Li-ion batteries, 1 mol dm^{-3} LiPF_6/MFA solution was applied as an electrolyte. However, large irreversible capacity and poor cycling efficiency were obtained with 1 mol dm^{-3} LiPF_6/MFA electrolyte, and these results were attributable to the poor passivation effect of the SEI formed solely with MFA solvent. When 3% VC was applied to the electrolyte as an SEI modification additive, the electrochemical characteristics of the electrolyte were improved significantly. With natural graphite as the negative electrode material, reversible capacities of 356 and 346 mAh g^{-1} were obtained after the first and the tenth cycles, respectively. The thermal stability of the electrolytes was investigated with DSC. At a DSC heating rate of 5°C min^{-1} , whether or not additive was used, the exothermic decomposition temperature of the electrolytes was more than 200°C higher than that of the 1 mol dm^{-3} $\text{LiPF}_6/\text{EC-DMC}$ electrolyte. Moreover, the thermal behavior of the 1 mol dm^{-3} $\text{LiPF}_6/\text{MFA} + 3\%\text{VC}$ electrolyte mixed

with the fully lithiated graphite electrode was studied in detail. The ratio between electrolyte and electrode was found to be a dominant factor in the heat generation of the mixture. A sharp exothermic peak at about 330°C was observed when the electrode was superabundant, but the heat value was much smaller than that obtained with 1 mol dm^{-3} $\text{LiPF}_6/\text{EC-DMC}$ electrolyte under the same conditions. When the electrolyte was superabundant, a mild exothermic decomposition of the electrolyte became the dominant reaction in the mixture. The effect of VC additive on SEI modification was also investigated by XPS. CHF_2COOLi was expected to be the main component of SEI even when VC was added to the MFA electrolyte. VC-added MFA-based electrolyte was considered to be a good candidate in the development of safer Li-ion batteries.

References

- [1] U. von Sacken, E. Nodwell, A. Sundher, J.R. Dahn, J. Power Sources 54 (1995) 240.
- [2] S. Tobishima, J. Yamaki, J. Power Sources 81–82 (1999) 882.
- [3] M.N. Richard, J.R. Dahn, J. Electrochem. Soc. 146 (1999) 2068.
- [4] M.N. Richard, J.R. Dahn, J. Electrochem. Soc. 146 (1999) 2078.
- [5] D.D. MacNeil, D. Larcher, J.R. Dahn, J. Electrochem. Soc. 146 (1999) 3596.
- [6] Q. Wang, J. Sun, X. Yao, C. Chen, J. Electrochem. Soc. 153 (2006) A329.
- [7] H. Yang, X. Shen, J. Power Sources 167 (2007) 515.
- [8] Y. Shigematsu, M. Ue, J. Yamaki, J. Electrochem. Soc. 156 (2009) A176.
- [9] J.O. Besenhard, W.K. Appel, L.H. Lie, G.H. Wroldnigg, K.-C. Moeller, M. Winter, Abstracts of the Second Hawaii Battery Conference, Hawaii Natural Energy Institute, The University of Hawaii, Hawaii, 4–7 (January), 1999, p. 181.
- [10] T. Nakajima, K. Dan, M. Koh, J. Fluorine Chem. 87 (1998) 221.
- [11] J. Yamaki, I. Yamazaki, M. Egashira, S. Okada, J. Power Sources 102 (2001) 288.
- [12] K. Sato, I. Yamazaki, S. Okada, J. Yamaki, Solid State Ionics 148 (2002) 463.
- [13] M. Ihara, B.T. Hang, K. Sato, M. Egashira, S. Okada, J. Yamaki, J. Electrochem. Soc. 150 (2003) A1476.
- [14] K. Xu, Chem. Rev. 104 (2004) 4303.
- [15] X. Zhang, R. Kostecki, T.J. Richardson, J.K. Pugh, P.N. Ross, J. Electrochem. Soc. 148 (2001) A1341.
- [16] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, Electrochim. Acta 47 (2002) 1423.
- [17] T. Doi, L. Zhao, M. Zhou, S. Okada, J. Yamaki, J. Power Sources 185 (2008) 1380.
- [18] L. Zhao, M. Zhou, T. Doi, S. Okada, J. Yamaki, Electrochim. Acta 55 (2009) 125.
- [19] J. Yamaki, H. Takatsuji, T. Kawamura, M. Egashira, Solid State Ionics 148 (2002) 241.