Electrochemical and thermal properties of graphite electrodes with imidazolium- and piperidinium-based ionic liquids

Irina A. Profatilova*, Nam-Soon Choi, Sae Weon Roh, Sung Soo Kim

Energy Laboratory, Corporate R&D Center, Samsung SDI Co. Ltd., 575 Shin-dong, Yeongtong-gu, Suwon-si, Gyeonggi-do, 443-731, Republic of Korea

ARTICLE INFO

ABSTRACT

The electrochemical and thermal properties of graphite electrodes with electrolytes containing 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) and *N*-methyl,*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (MPPpTFSI) ionic liquids are investigated. The ionic liquids undergo extensive reductive decomposition on a graphite electrode during the first charge. The effect of a fluoroethylene carbonate (FEC) additive on the reductive decomposition of the ionic liquids is examined by electrochemical, scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) analysis. Thermal reactions between a lithiated graphite electrode and an ionic liquid-containing electrolyte are investigated with differential scanning calorimetry (DSC). The introduction of an ionic liquid can effectively reduce the exothermic heat evolution from the thermal reactions between a lithiated graphite electrode and an electrolyte.

1. Introduction

The development of lithium-ion battery (LIB) technologies and their application in the field of large-scale power sources, such as electric vehicles (EVs) and hybrid EVs, require enhanced reliability and greater safety. The main components of LIBs should withstand to the inevitable heating of batteries during high current flow [1].

In recent decades, graphitized carbon has been used as negative (anode) electrode material. Apart from the high specific capacity and superior cycling properties of carbon-based anodes, the low thermal stability of lithiated graphite with an electrolyte should be noted [2]. Heating a lithiated carbon electrode and an electrolyte triggers the thermal decomposition of the solid electrolyte interphase (SEI) layer, the electrolyte, and the electrode binder [3–13]. One of the governing factors for the thermal decomposition of lithiated graphite anodes is the electrolyte, which usually consists of a carbonate solvent and a lithium salt. Carbonate solvents that contribute to the dissociation of lithium salts are volatile and potentially combustible [1] and can lead to the thermal runaway of batteries.

The unique properties of ionic liquids, such as negligible vapour pressure, low flammability, high thermal stability and high ionic conductivity, have stimulated interest in the use of these materials as a means for improving LIB safety [14–16]. The formation of an unstable SEI layer by the reductive decomposition of the ionic liquid on an anode surface, restricts the application of ionic liquids. Therefore, an appropriate SEI-forming additive is necessary to guarantee the electrochemical performances of ionic liquid-containing electrolytes. Novak and co-workers [17] reported that a vinylene carbonate (VC) additive was able to intercalate Li$^+$ ions into a graphite electrode in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) and methyltrioctylammonium bis(trifluoromethylsulfonyl)imide (MTOTFSI) with 1 M LiPF$_6$. It was also reported that ethylene carbonate (EC) and VC additives prevent the reductive decomposition of an ionic liquid on the graphite anode surface in an electrolyte composed of *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide (DEMETFSI) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) [18]. Despite these studies of various ionic liquids, there are no rigorous reports of the thermal behaviour of ionic liquid-containing electrolytes with lithiated graphite anodes.

In the present work, EMITFSI and *N*-methyl,*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (MPPpTFSI) ionic liquids are used as a co-solvent in EC/EMC 3/7 with 1.3 M LiPF$_6$ as an attempt to decrease the flammability of electrolytes and to increase the thermal properties of lithiated graphite electrodes. A report is given of the influence of a fluoroethylene carbonate additive on the electrochemical intercalation of lithium ions into graphene layers and the thermal decomposition behaviour of lithiated graphite electrodes at elevated temperatures.

* Corresponding author. Tel.: +82 31 210 7571; fax: +82 31 210 7555.
E-mail addresses: irishkapro@mail.ru, irina.profatilov@samsung.com
(I.A. Profatilova).

2. Experimental

To evaluate the electrochemical properties of graphite electrodes, a slurry was prepared by mixing 97 wt.% graphite as an active material with 3 wt.% polyvinylidene fluoride (PVdF) binder dissolved in anhydrous N-methyl-2-pyrrolidinone (NMP). The resulting slurry was cast on copper foil and the composite electrode was dried in a convection oven at 110 °C for 2 h. The electrode was pressed to a thickness of approximately 40 μm in order to obtain proper electronic conductivity.

The composition of each electrolyte solution is presented in Table 1. Ethylene carbonate (EC), ethyl methyl carbonate (EMC), fluoroethylene carbonate (FEC), and lithium hexafluorophosphate ($LiPF_6$) were provided by Cheil Industries. N-Methyl,N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (MPPpTFSI) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI) ionic liquids were provided by Toyo-Gosei. The associated chemical structures are shown in Fig. 1. Electrolytes were prepared by adding an ionic liquid to an EC/EMC (3/7, v/v) mixture, and 1.3 M $LiPF_6$ was dissolved in the resulting solution.

A coin-type half-cell with a graphite electrode and a Li metal electrode was assembled in an Ar-filled glove box with less than 1 ppm of oxygen and moisture. Cycling tests were galvanostatically performed at a 0.1 C rate using a computer-controlled battery measurement system (TOSCAT 3000 U).

After rinsing the electrodes in dimethyl carbonate (DMC) solvent, the surface morphology was examined by scanning electron microscopy (SEM, JEOL JSM-6700F). During the acquisition of the SEM images, an energy-dispersive X-ray spectrometer (EDX) was also used to characterize the chemical components in the region under the investigation.

The flammability of the electrolyte solutions was examined by means of the following method. A glass filter (1 cm × 4 cm) was soaked with an electrolyte for 1 min and then set horizontally on a stand. The flame of an alcohol lamp was brought close (10 cm) to the filter, and then removed after 5 s. The flammability of each electrolyte was tested three times.

Thermogravimetric analysis (TGA) of ionic liquids was carried out under a dry nitrogen atmosphere at a heating rate of 10 °C min^{-1} over range from 25 to 700 °C. To measure the thermal properties of lithiated graphite electrodes with electrolytes, coin half-cells were charged to a potential of 0.01 V vs. Li/Li$^+$ and then carefully opened in a dry room. The retrieved electrodes were rinsed in DMC solvent to remove residual electrolyte and dried under a vacuum. The resulting lithiated graphite electrode was sealed together with electrolyte in a hermetic stainless-steel pan (Perkin Elmer). All of the differential scanning calorimetry (DSC, DuPont TA Instrument 2000) measurements were carried out at a heating rate of 10 °C min^{-1} over a range of 50–380 °C. The amount of an entrapped electrolyte was 30 wt.% based on the lithiated graphite powder.
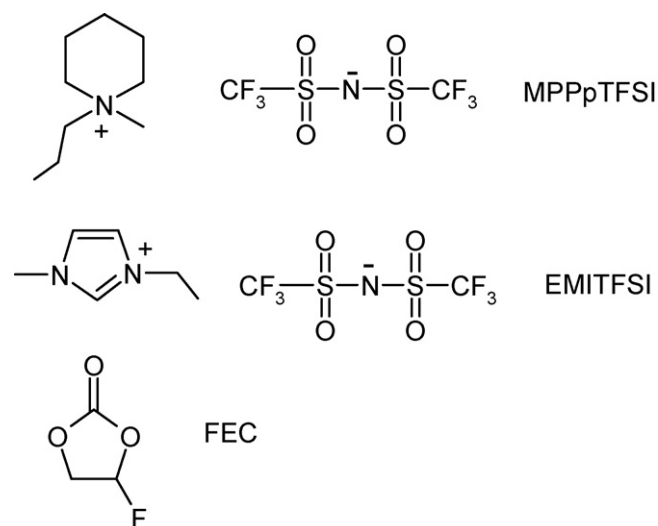

Fig. 1. Chemical structures of MPPpTFSI and EMITFSI ionic liquids, and FEC additive.

3. Results and discussion

3.1. Electrochemical properties of coin half-cells with ionic liquid-containing electrolytes

The first charge and discharge curves of the Li/graphite coin half-cells are given in Fig. 2. Even though fluoroethylene carbonate (FEC) was used as the SEI-forming agent in EC/EMC with 1.3 M $LiPF_6$, the analogous reversible capacity with the FEC-free electrolyte is shown in Table 1 and Fig. 2(a). The reversible capacity was distinctly improved from 317 to 343 mAh g^{-1} by incorporating the FEC additive into N-methyl,N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (MPPpTFSI)-containing electrolyte in Fig. 2(b). This indicates that FEC effectively restrains the electrochemical decomposition of the MPPpTFSI ionic liquid on the graphite surface. This point is clearly shown in the dQ/dV graph in Fig. 3(b). Use of the MPPpTFSI-containing electrolyte without FEC results in a high irreversible capacity and reveals a considerable reductive decomposition peak around 0.53 V vs. Li/Li$^+$ that disappears in the presence of FEC, as depicted in Fig. 3(b). As shown in Fig. 2(c), the potential plateau at 1.0 V ascribed to the electrochemical reduction of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) is quite long whereas the potential plateau close 0 V related to Li$^+$ ions intercalation is hardly observed in an EMI electrolyte solution. A discharge capacity of 11 mAh g^{-1} was obtained with a quite low coulombic efficiency of approximately 2%. By comparison, FEC drastically improved the discharge capacity from 11 to 332 mAh g^{-1} during the first cycle, as shown in Fig. 2(c) and Table 1. This indicates that FEC electrochemically decomposes before the occurrence of the electrolyte reduction

Table 1
Composition of electrolytes, specific charge/discharge capacities, and initial coulombic efficiency (ICE) of C/Li coin half-cells during the first cycle.

Electrolyte	EC/EMC[a]	EMITFSI (vol.%)	MPPpTFSI	LiPF$_6$ (M)	Charge capacity (mAh g^{-1})	Discharge capacity	ICE (%)
Ref	100	–	–	1.3	364	331	91
Ref–FEC[b]	100	–	–	1.3	361	337	93
MPPp	70	–	30	1.3	389	317	81
MPPp–FEC[b]	70	–	30	1.3	372	343	92
EMI	70	30	–	1.3	593	11	2
EMI–FEC[b]	70	30	–	1.3	401	332	83

[a] A volume ratio of EC and EMC = 30:70.
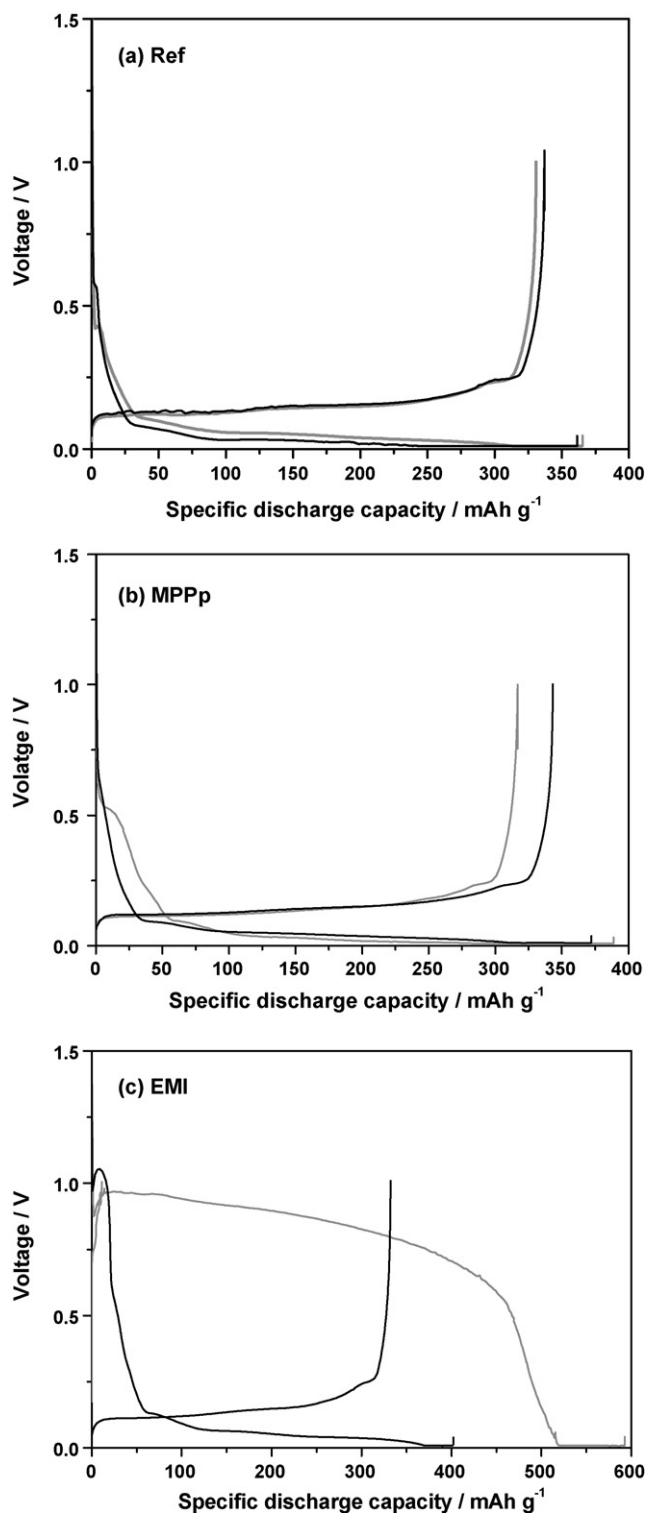
[b] 5 wt.% FEC based on each electrolyte added.

Fig. 2. Charge and discharge curves of Li/graphite coin half-cells during first cycle. Gray line: without FEC and black line: with FEC.

Fig. 3. dQ/dV graphs during first charge of coin half-cells.

and forms an effective SEI that prevents considerable decomposition of ionic liquids on the graphite surface [17].

To clarify the influence of FEC on the surface chemistry of graphite electrodes fully-charged in ionic liquid-containing electrolytes, SEM observations were carried out in combination with EDX analysis. There are no significant differences between the SEM images for fully-charged graphite anodes with or without FEC, as shown in Fig. 4(a)–(d). Fig. 4(e) clearly shows the graphite parti-
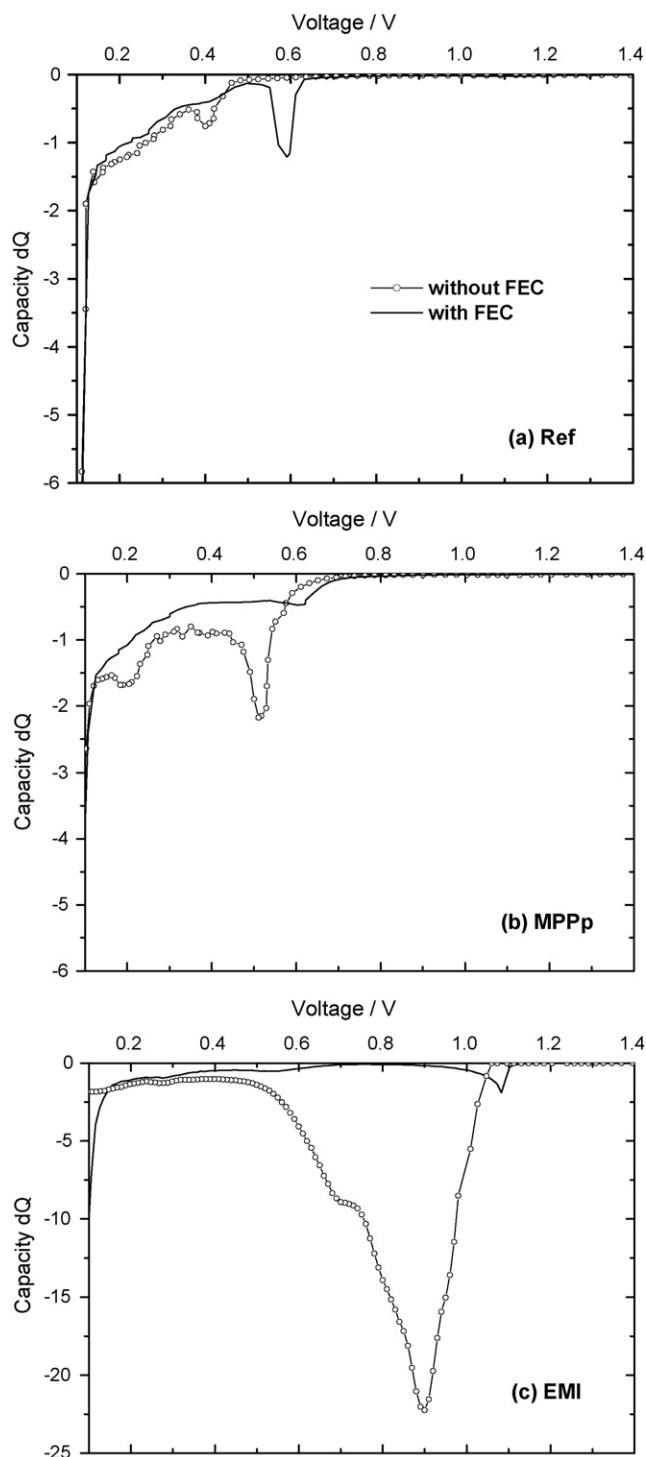
cles to be covered with a thick velvety layer, which is apparently formed during the reductive decomposition of the EMITFSI ionic liquid. The EDX analysis revealed that the chemical composition of the graphite electrode surface strongly depends on the electrolyte composition. The EDX spectrum of the graphite electrode charged in the Ref electrolyte (Table 1) produces peaks that correspond to carbon (C) and oxygen (O), while the peak assigned to fluorine (F) appears in the Ref–FEC electrolyte, as presented in Fig. 5(a) and (b). The F signal is likely due to the products formed during the reductive decomposition of FEC on the graphite surface. The
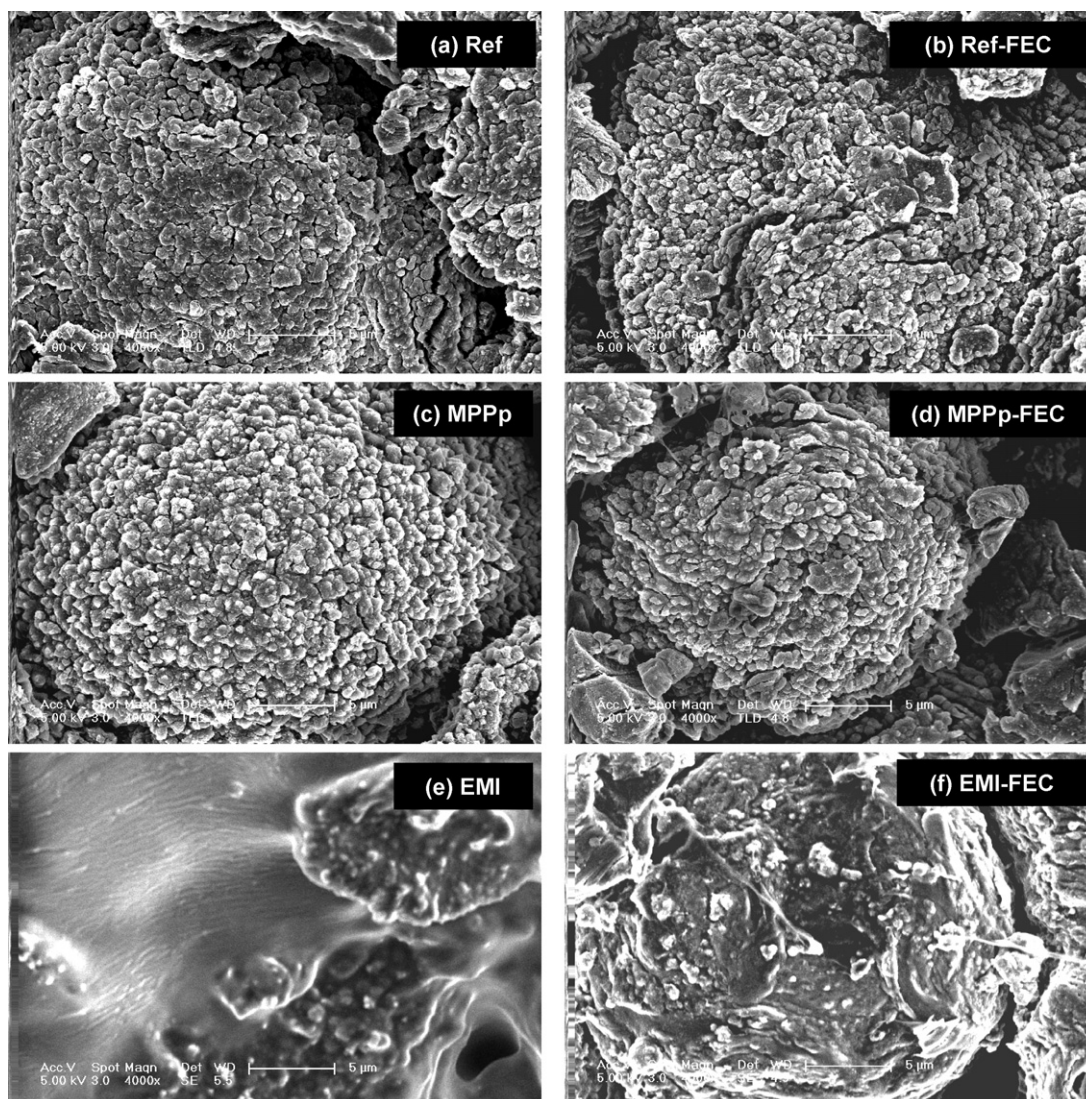
Fig. 4. SEM images of charged graphite electrodes.

EDX spectrum of a graphite electrode charged in the MPPp electrolyte shows peaks corresponding to sulfur (S), phosphorous (P) and F, as seen in Fig. 5(c). The S and P signals are attributed to compounds formed via the decomposition of the TFSI$^-$ and PF$_6^-$ anions and are not observed for a fully-charged graphite electrode with the MPPp–FEC electrolyte. This indicates that the FEC suppresses the electrochemical decomposition of the TFSI$^-$ and PF$_6^-$ anions. Indeed, the graphite electrode with the MPPp–FEC electrolyte exhibits much enhanced electrochemical reversibility during the first cycle in Fig. 2(b). Atomic amounts related to nitrogen (N), O, F, P, and S are detected in the EDX spectrum when using an EMI electrolyte, as shown in Fig. 5(e). This indicates that both the cationic and anionic moieties of the EMITFSI ionic liquid and the PF$_6^-$ anion electrochemically decompose on the graphite surface at around 1 V vs. Li/Li$^+$ during the first lithium intercalation. It is concluded the considerable decomposition of the EMITFSI ionic liquid causes irreparable damage to the graphite electrode in Figs. 2(c) and 5(e). Similarly, the S and P signals assigned to the decomposition compounds of the TFSI$^-$ and PF$_6^-$ anions vanish in the presence of FEC in the EMI electrolyte.

In summary, comparison of electrolytes with and without FEC clearly shows that FEC inhibits the electrochemical decomposition of MPPpTFSI, EMITFSI, and PF$_6^-$ and forms an electrochemically-stable SEI that facilitates the reversible electrochemical reaction. The study of the long-term electrochemical cycling properties of cells with ionic liquid-containing electrolytes is a focus of future work.

3.2. Flammability and thermal behavior of electrolyte solutions

To clarify the effect of ionic liquids on battery safety, flammability tests of electrolytes both with and without an ionic liquid were performed. The results are summarized in Table 2. The Ref

Table 2
Results of flammability testing of mixed electrolytes including onset temperature of first exothermic reaction between electrolyte and lithiated graphite anode obtained by DSC measurements, and total heat evolution over the range 50–380 °C.

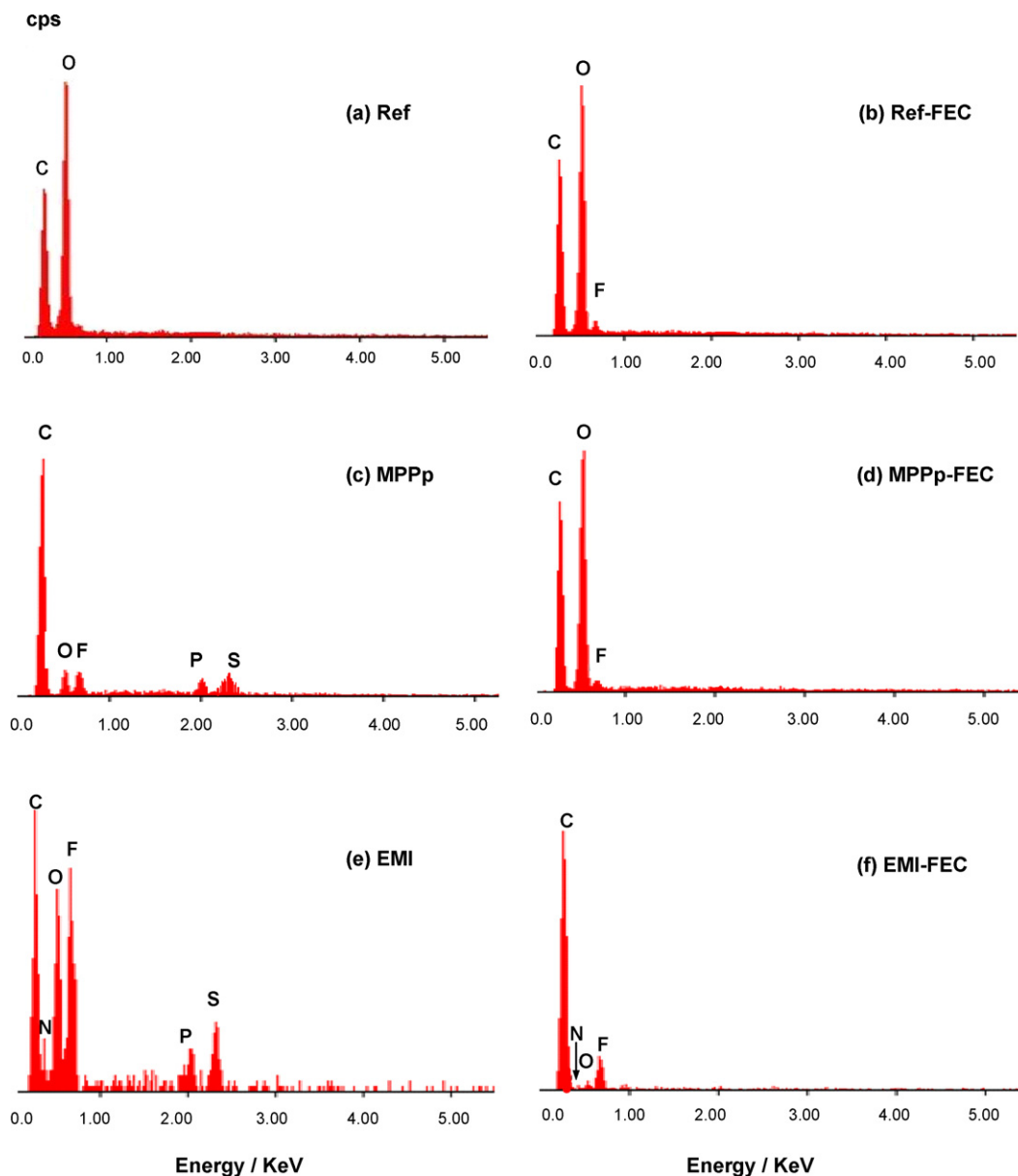| Electrolyte	Flammability, occurrence of flame	Onset temperature (°C)	Total heat evolution (J g^{-1})
Ref	3/3	97	551
Ref–FEC	3/3	107	695
MPPp	0/3	77	440
MPPp–FEC	0/3	96	383
EMI	0/3	72	105
EMI–FEC	0/3	101	348

cps

Fig. 5. EDX spectra of surface of charged graphite electrodes.

and Ref–FEC electrolytes without an ionic liquid are flammable and the burning time after ignition is approximately 7 s. By contrast, the MPPpTFSI and EMITFSI-containing electrolytes do not show any combustion after removing the flame source. This result is in good agreement with the report [19] that 1 M LiPF$_6$ dissolved in an EC/DMC/EMC mixture with a MPPpTFSI ionic liquid exhibits non-flammablity.

Differential scanning calorimetry (DSC) curves of the electrolytes and solvent mixtures sealed in a hermetic stainless pan are presented in Fig. 6. The thermal reactions between the hydrogen fluoride (HF) generated from LiPF$_6$ at about 64 °C and an evaporated EMC in a Ref electrolyte triggers the beginning of a broad exothermic peak at 80 °C, as shown in Fig. 6(a) [20]. It is probable that the broad exothermic peak between 80 and 250 °C is the result of the subsequent thermal reactions of PF$_5$ (g) produced from LiPF$_6$ decomposition and organic solvents. It is clear that no exothermic decomposition peaks below 250 °C are observed for the EC/EMC (3/7) without LiPF$_6$ salt in Fig. 6(d). The exothermic heat evolved above 250 °C is due to the thermal decompositions of the EC and EMC solvents in Fig. 6(a) and (d). The introduction of an ionic liq-
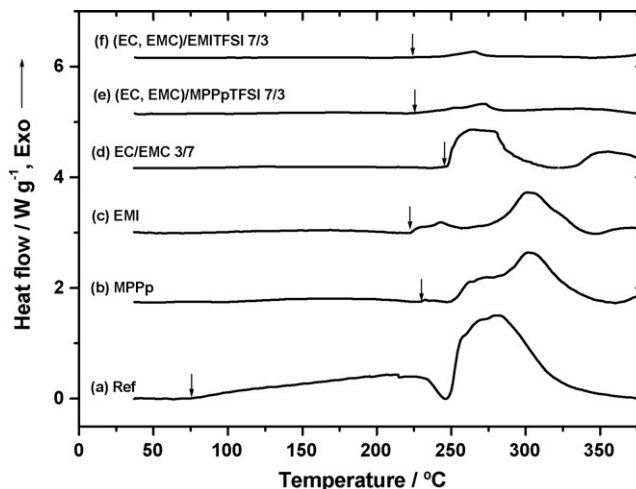

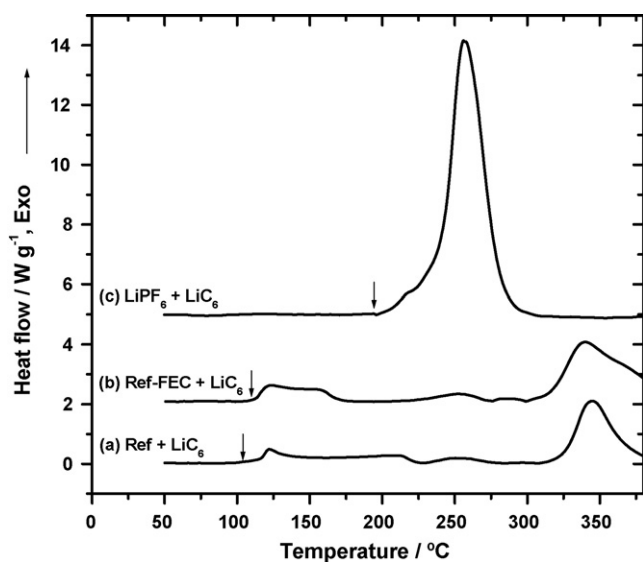**Fig. 6.** DSC thermograms of electrolyte solutions and solvent mixtures.

Fig. 7. DSC thermograms for fully-charged graphite electrodes with electrolytes or $LiPF_6$ salt.

Fig. 8. DSC heating curves for fully-charged and discharged graphite electrodes with and without MPPp-containing electrolytes.

uid to an electrolyte eliminated the first exothermic peaks with an onset temperature of 80 °C for the MPPp and EMI electrolytes, respectively, in Fig. 6(b) and (c). The total heat evolution of the MPPp and EMI electrolytes in the temperature range 30–380 °C was 242 and 154 J g^{-1}, respectively, while EC/EMC (3/7) with 1.3 M $LiPF_6$ generated a greater heat of 695 J g^{-1}. Salt-free mixtures of (EC, EMC)/MPPpTFSI and (EC, EMC)/EMITFSI led to much smaller exothermic peaks in Fig. 6(e) and (f). From this result, it is concluded that the $LiPF_6$ salt exerts a significant influence on exothermic reactions over 220 °C in the MPPp and EMI electrolytes. It should be mentioned that pure MPPpTFSI and EMITFSI ionic liquids do not give any exothermic peaks when heated in a hermetic DSC pan to 380 °C. The decomposition temperatures of MPPpTFSI and EMITFSI ionic liquids (5 wt.% weight loss) measured by thermogravimetry analysis are 398 and 388 °C, respectively. It is clear that ionic liquids are capable of reducing the electrolyte flammability and the exothermic heat produced by the thermal decompositions of $LiPF_6$ salt and the EC/EMC solvent mixture.

3.3. Thermal behaviour of lithiated graphite electrodes with electrolytes containing ionic liquids

The thermal reactions between a fully-charged graphite electrode and an electrolyte were measured using DSC. It is known that the thermal decomposition of a lithiated graphite anode with an electrolyte is determined by two principal factors: one is the thermal resistibility of SEI layer formed electrochemically on the graphite electrode surface, and the other is the amount of Li$^+$ ions intercalated into the graphene layers [3–5,13,21–23]. Fig. 7 depicts the DSC heating curves for lithiated graphite electrodes with the Ref and Ref–FEC electrolytes and with $LiPF_6$ salt obtained over the range of 50–380 °C. Exothermic reactions of the Ref electrolyte with a lithiated graphite have been described in detail using DSC and FT-IR spectroscopy in a previous study [20]. An exothermic peak with an onset at around 90 °C, shown in Fig. 7(a), was associated with the thermal decomposition of a SEI layer with an electrolyte. The two broad peaks between 180 and 300 °C resulted from the thermal reaction between the Ref electrolyte and lithiated graphite. Finally, a large exothermic peak at 350 °C was ascribed to the formation of a secondary SEI layer (lithium alkylcarbonates and Li_2CO_3) and the thermal decomposition reactions of a PVdF binder with lithiated graphite [20].
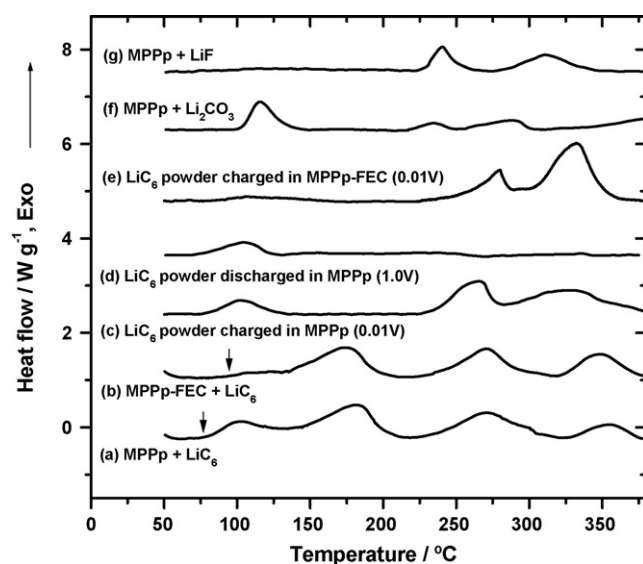
The MPPpTFSI ionic liquid considerably reduces the exothermic heat evolution from the thermal reactions between the lithiated graphite and the electrolyte, as shown in Figs. 7(a) and 8(a), and Table 2. By contrast, heating of the MPPp electrolyte with LiC_6, results in a low onset around 77 °C in Fig. 8(a). A series of DSC model experiments was carried out to clarify the origin of this exothermic peak in Fig. 8(c)–(g). The DSC measurements for lithiated and delithiated graphite powders without an electrolyte are presented in Fig. 8(c) and (d). Even after lithium deintercalation from the graphite electrode, an exothermic peak is observed at around 100 °C. This implies that a metastable SEI formed via the reductive decomposition of organic solvents, $LiPF_6$, and the MPPpTFSI ionic liquid in MPPp electrolyte, undergoes an exothermic decomposition with a low onset of 70 °C. This is consistent with the results of EDX analysis of the graphite surface obtained in MPPp electrolyte in Fig. 5(c). The presence of FEC in the MPPpTFSI-containing electrolyte shifts the onset of LiC_6 with an electrolyte to a relatively high temperature and considerably reduces the first exothermic peak when compared with MPPp, as shown in Fig. 8(a) and (b). The DSC heating curve for a graphite powder charged in MPPp exhibits an exothermic peak with the onset around 75 °C, whereas this exothermic peak disappears in MPPp–FEC in Fig. 8(c) and (e). It is considered that the SEI formed by the electrochemical reduction of FEC is thermally stable. From the EDX results for the graphite surface with oxygen and fluorine atoms in Fig. 5(d), it is concluded that the SEI is composed of Li_2CO_3, LiF, and lithium alkylcarbonates in the MPPp–FEC electrolyte [24,25].

An analogous influence of FEC on the thermal properties of SEI was observed for the EMI electrolyte with LiC_6. The SEI formed via the intensive decompositions of EMITFSI gave a low onset temperature of 72 °C in the EMI electrolyte with LiC_6 as shown in Fig. 9(a). The data clearly shows that this exothermic peak appears even in the absence of the electrolyte, see Fig. 9(c). The onset temperature of the first exothermic peak for fully-charged graphite with a EMI-containing electrolyte shifts from 72 to 101 °C in the presence of FEC, as depicted in Fig. 9(a) and (b). As stated in Section 3.1, FEC prevents the reductive decomposition of the EMITFSI ionic liquid and results in the reversible lithium intercalation into graphene layers. Moreover, a graphite powder fully-charged in EMI–FEC electrolyte displays no exothermic peak near 100 °C in Fig. 9(d). The exothermic peak around 115 °C in Fig. 9(b) is probably caused by thermal reactions between the electrolyte and Li_2CO_3, as shown
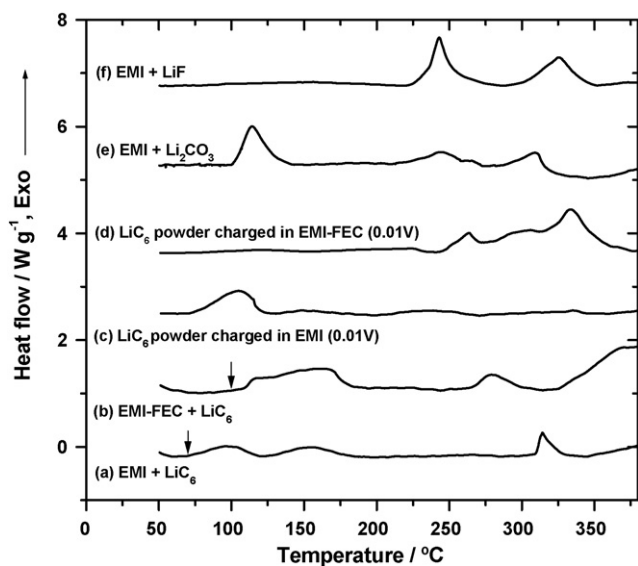
Fig. 9. DSC heating curves for fully-charged graphite electrodes with and without EMI-containing electrolytes.

in Fig. 9(e). It is clear that the reductive decomposition of FEC on the graphite surface produces a thermally-resistant SEI layer. A similar result was obtained in a study [23] where ethyltriacetoxysilane, 1,3-benzoldioxole, tetra(ethylene glycol)dimethylether and vinylene carbonate additives in ethylene carbonate (EC)/diethyl carbonate (DEC) with 1 M $LiBF_4$ improved the onset temperature of thermally-activated reactions between a graphite electrode and an electrolyte.

Heating of the MPPp electrolyte with LiC_6 produces three exothermic peaks over 130 °C that do not change after the introduction of FEC to the electrolyte solution. The broad exothermic peak at around 180 °C in Fig. 8(a) and (b) is probably associated with the thermal reaction between MPPp and intercalated lithium. This is conformed from the DSC result for the MPPp electrolyte with a Li metal in Fig. 10(a). $LiPF_6$ salt heated with a lithiated graphite powder shows intensive decompositions at 260 °C in Fig. 7(c), which can explain the nature of the thermal reaction at around 270 °C in Fig. 8(a) and (b). Finally, the exothermic peak with an onset of
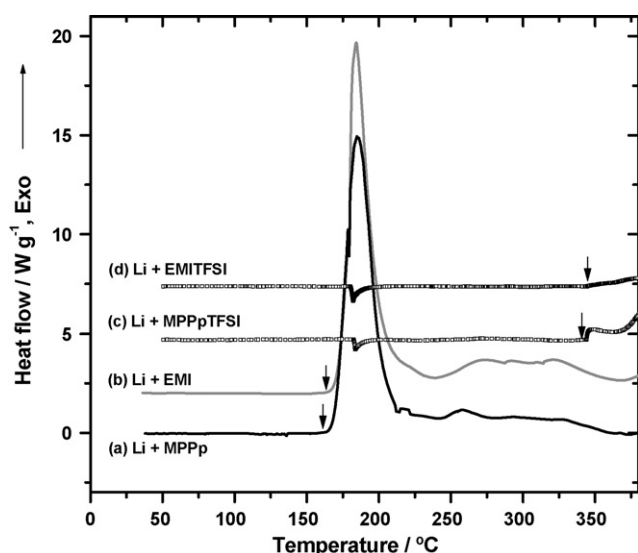

Fig. 10. DSC thermograms for Li metal with electrolytes or ionic liquids.

320 °C in Fig. 8(a) and (b) is probably caused by the thermal reaction between MPPpTFSI and Li metal, as shown in Fig. 10(c).

It is noticeable that the lowest heat over the range 50–380 °C is evolved during the heating of the EMI electrolyte with lithiated graphite, as shown in Table 2 and Fig. 9(a). This is probably due to the small number of lithium ions inserted into the graphene layers, as stated in Section 3.1 and Table 1. An exothermic heat evolved over 150 °C during the heating of a lithiated graphite powder with the EMI–FEC electrolyte can be attributed to the decomposition of the EMI–FEC electrolyte with Li metal by a comparison of Figs. 9(b) and 10(b). An exothermic peak with the maximum at around 280 °C is apparently due to the reaction between the $LiPF_6$ salt and the lithiated graphite in Fig. 9(b). The exothermic reaction between the EMITFSI ionic liquid and Li metal with an onset around 330 °C in Fig. 10(d) can explain the origin of the last broad exothermic peak in Fig. 9(b).

According to the work of Yamaki et al. [11], the thermal reactions of lithiated graphite particles covered with PVdF binder with an electrolyte begin at around 300 °C because the protection effect of the PVdF binder is not sufficient at elevated temperatures. It was suggested that the swelling of the PVdF binder with an electrolyte occurred during heating of the lithiated graphite. This is in good agreement with the present results. The ionic liquid effectively mitigates the thermal reactivity of the newly exposed lithiated graphite during swelling of the PVdF binder, which considerably reduces the intensity of the exothermic peaks near 330 °C, as shown in Figs. 8(a), (b) and 9(a), (b). It is concluded that the thermally-stable ionic liquids can appreciably hinder the exothermic decomposition reactions of lithiated graphite electrodes with volatile organic solvents that result otherwise in a large heat evolution.

4. Conclusions

The electrochemical properties of C/Li coin half-cells with ionic liquid-containing electrolytes are markedly improved by introducing a FEC additive. SEM and EDX analyses of the graphite electrodes reveal that the SEI layer formed in ionic liquid-containing electrolytes with the FEC additive is mostly composed of fluorine and oxygen atoms. Moreover, the SEI layer formed by the electrochemical reduction of FEC effectively restrains the electrochemical decomposition of $TFSI^-$ ionic liquids and PF_6^- anions. It is found that FEC can form an electrochemically and thermally stable SEI layer and thereby prevent the reductive decomposition of the ionic liquid on the graphite electrode. The EMITFSI or MPPpTFSI-containing electrolytes exhibit non-flammability unlike conventional carbonate-based electrolytes. DSC measurements confirm that the total exothermic heat evolution for lithiated graphite electrodes with ionic liquid-containing electrolytes is diminished over the range 50–380 °C when compared with EC/EMC with 1.3 M $LiPF_6$.

Acknowledgement

References

[1] P.G. Balakrishnan, R. Ramesh, T.P. Kumar, J. Power Sources 155 (2006) 401–414.
[2] R. Spotnitz, J. Franklin, J. Power Sources 113 (2003) 81–100.
[3] M. Richard, J. Dahn, J. Electrochem. Soc. 146 (1999) 2068–2077.
[4] A.D. Pasquier, F. Disma, T. Bowmer, A.S. Gozdz, G. Amatucci, J.-M. Tarascon, J. Electrochem. Soc. 145 (1998) 472–477.
[5] K. Edstrom, A.M. Andersson, A. Bishop, L. Fransson, J. Lindgren, A. Hussenius, J. Power Sources 97–98 (2001) 87–91.
[6] E.P. Roth, D.H. Doughty, J. Franklin, J. Power Sources 134 (2004) 222–234.
[7] J. Jiang, J. Dahn, Electrochim. Acta 49 (2004) 4599–4604.

[8] H. Yang, H. Bang, K. Amine, J. Prakash, J. Electrochem. Soc. 152 (2005) A73–A79.
[9] I. Watanabe, J.-I. Yamaki, J. Power Sources 153 (2006) 402–404.
[10] H. Yang, X.-D. Shen, J. Power Sources 167 (2007) 515–519.
[11] J.-I. Yamaki, H. Takatsuji, T. Kawamura, M. Egashira, Solid State Ionics 148 (2002) 241–245.
[12] P. Biensan, B. Simon, J.P. Peres, A. Guibert, M. Broussely, J.M. Bodet, F. Perton, J. Power Sources 81–82 (1999) 906–912.
[13] J. Jiang, J.R. Dahn, Electrochem. Solid-State Lett. 6 (2003) A180–A182.
[14] M. Galinski, A. Lewandowski, I. Stepniak, Electrochim. Acta 51 (2006) 5567–5580.
[15] Y. Wang, K. Zaghib, A. Guerfi, F.C. Bazito, R.M. Torresi, J.R. Dahn, Electrochim. Acta 52 (2007) 6346–6352.
[16] M. Taggougui, M. Diaw, B. Carre, P. Willmann, D. Lemordant, Electrochim. Acta 53 (2008) 5496–5502.

[17] M. Holzapfel, C. Jost, A. Prodi-Schwab, F. Krumeich, A. Wursig, H. Buqa, P. Novak, Carbon 43 (2005) 1488–1498.
[18] T. Sato, T. Maruo, S. Marukane, K. Takagi, J. Power Sources 138 (2004) 253–261.
[19] H. Nakagava, Y. Fujino, S. Kozono, Y. Katayama, T. Nukuda, H. Sakaebe, H. Matsumoto, K. Tatsumi, J. Power Sources 174 (2007) 1021–1026.
[20] N.S. Choi, I.A. Profatilova, S.S. Kim, E.H. Song, Thermochim. Acta 480 (2008) 10–14.
[21] A.M. Andersson, M. Herstedt, A.G. Bishop, K. Edstrom, Electrochim. Acta 47 (2002) 1885–1898.
[22] M. Holzapfel, F. Alloin, R. Yazami, Electrochim. Acta 49 (2004) 581–589.
[23] M. Herstedt, H. Rensmo, H. Siegbahn, K. Edstrom, Electrochim. Acta 49 (2004) 2351–2359.
[24] R. Mogi, M. Inaba, Y. Iriyama, T. Abe, Z. Ogumi, Langmuir 19 (2003) 814–821.
[25] I.A. Profatilova, S.S. Kim, N.S. Choi, Electrochim. Acta, doi:10.1016/j.electacta.2009.03.032, in press.