**Improved High-Temperature Performance and Surface Chemistry of
Graphite/LiMn₂O₄ Li-Ion Cells by Fluorosilane-Based Electrolyte Additive**

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Abstract

For graphite/LiMn₂O₄ based lithium-ion batteries, we have successfully improved the charge/discharge capacity retention during high temperature cycling at 60 °C by addition of proper amount of 1,2-bis(difluoromethylsilyl)ethane (FSE) into the electrolyte as an additive. In addition, the additive also suppresses self-discharge in a storage test at 60 °C for 7 days. Detailed surface analyses of graphite negative electrodes by electron microscopy, synchrotron X-ray photoelectron spectroscopy, and time of flight secondary ion spectroscopy, indicate that silicon and fluorine-containing thin layer is formed by FSE decomposition and deposited on the graphite negative electrode surface, which effectively protects the graphite negative electrode during the high temperature cycling and storage. The silicon- and fluorine-containing surface layer suppresses the degradation of the negative electrode caused by deposition of manganese, resulting from Mn²⁺ dissolution from LiMn₂O₄, and prevents self-discharge due to excess decomposition of electrolyte on the surface.

Keywords: Li-ion battery, Fluorosilane-based electrolyte additive, Solid electrolyte interphase,

LiMn₂O₄

1. Introduction

Lithium-ion batteries (LIBs) [1-3] are widely used as a power source for mobile electronic devices and electric vehicles due to their higher energy density and better cycle

performance compared with other secondary batteries, such as Ni-MH battery and Ni-Cd battery.

In LIBs system, lithium transition metal oxides, such as LiCoO_2 [3], and graphite are employed as active materials for the positive and negative electrodes, respectively, and Li^+ ions shuttle between the two electrodes with electrochemical lithation/delithiation processes.

It is known that the performance of LIBs depends on stability and functionality of thin passivation layer on graphite negative electrodes, so-called solid electrolyte interphase (SEI) [4], which is electrically an insulator but provides significant ionic conductivity. SEI formation mainly occurs by reductive decomposition of electrolyte solution on the electrode surface during initial charge process. SEI can prevent further electrolyte decomposition of solvent and electrolyte salt and bring stable long-term cycle performance. For further improvement on the performance in LIBs, a small amount of electrolyte additives is often used to obtain thinner and better conductive layers, including vinylene carbonate (VC) [5-8] and fluoroethylene carbonate (FEC) [9-11]. Some elements contained in additives are involved in the SEI formation during the electrochemical cycle and they effectively act as one of the factors for better SEI configuration.

The spinel LiMn_2O_4 has advantages as a positive active material for large-format LIBs because of its good rate performance and reasonable material cost compared with other materials used for LIBs systems [12-15]. However, it also has serious problem with electrode degradation during high temperature cycling or storage, e.g., hydrogen fluoride generated by reaction of LiPF_6 as electrolyte salt and H_2O as impurity, which accelerates dissolution of Mn^{2+} ions from the $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$

positive electrode [16, 17], resulting in Mn-containing deposition on the graphite negative electrodes to lead huge capacity fade because of undesirable electrolyte decomposition on the Mn deposited surface [8, 18]. To overcome this drawback and improve its performance, we have focused electrolyte additives for LIBs. Our group has reported 2-vinylpyridine as an efficient electrolyte additive, which suppressed degradation of the carbon negative electrode in C/LiMn₂O₄ cells [19]. Generally, amount of additive in electrolyte is less than 2 % in volume ratio (v/v), however, which often causes reduction of coulombic efficiency at first charge/discharge.

As reported previously, several silicon-containing compounds have been studied as effective electrolyte additives for LIBs [20-26]. In this study, we employed 1,2-bis(difluoromethylsilyl)ethane (FSE) [27] as a fluorosilane-based electrolyte additive in graphite/LiMn₂O₄ cells for LIBs. It contains silicon and fluorine in the molecule structure as shown in Fig. 1. Effects of FSE additive in the electrolyte on electrochemical performance, particularly under high temperature (60 °C) conditions, are for the first time examined in graphite/LiMn₂O₄ cells.

Furthermore, we discuss SEI formation mechanism involving FSE as the electrolyte additive and explain the origin of the superior electrochemical performance during high temperature cycling and storage conditions.

2. Experimental

2.1. Chemicals

For synthesis of LiMn_2O_4 , Mn_2O_3 as the starting material was prepared from $\text{MnCO}_3 \cdot n\text{H}_2\text{O}$ (Kishida Chemical Co., Ltd.), and then LiMn_2O_4 powder was obtained by heating mixtures of Mn_2O_3 and Li_2CO_3 (KANTO CHEMICAL CO., INC.) ($\text{Li}_2\text{CO}_3 : \text{Mn}_2\text{O}_3 = 1.03 : 2.00$ (molar ratio)) at 700 °C for 12 h in air (see supporting information, Figure S1) [28, 29]. Natural graphite powder with averaged particle size of $\sim 20 \mu\text{m}$ was used as active materials for negative electrodes. $1 \text{ mol dm}^{-3} \text{LiPF}_6$ in mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC = 3:7 (v/v) Kishida Chemical Co., Ltd.) was used as electrolyte. 1,2-bis(difluoromethylsilyl)ethane (FSE, ADEKA Co. Ltd.), which is transparent liquid at room temperature and soluble in the LiPF_6 EC/DMC solution, was employed as the functional additive for the electrolyte.

2.2. Preparation of electrodes

Negative electrodes were prepared by casting slurry consisting of an aqueous mixture of graphite (97 % (w/w)) and styrene-butadiene rubber latex / carboxymethylcellulose, i.e., SBR/CMC (3 % (w/w)) binder on copper foil as a current collector. For preparation of positive electrodes, LiMn_2O_4 (80 % (w/w)), poly(vinylidene fluoride) (PVdF) binder (10 % (w/w), Polysciences, Inc.) and acetylene black (10 % (w/w), Strem Chemicals Inc.) as conductive agent were mixed and dispersed in *N*-methyl-2-pyrrolidone (NMP, Kanto Chemical Co., Inc.), and then, the obtained slurry was coated on aluminum foil as a current collector. FSE was added to $1 \text{ mol dm}^{-3} \text{LiPF}_6$ EC/DMC

(3:7 v/v) as the functional additive with a mass ratio of 0.5, 1 or 2 % (w/w). Polyolefin porous membrane, which is composed of layered polypropylene-polyethylene, was employed as separator.

2.3. Characterizations

Electrochemical measurements were performed by using 2032-type coin cells. The weight ratio of LiMn_2O_4 /graphite for full-cell assembly was adjusted to 2.2-2.4. The “charge” (lithium intercalation into graphite and deintercalation from LiMn_2O_4) and “discharge” (reverse reactions of the charge process) tests were carried out between 3.0 – 4.3 V (vs. Li/Li^+) at a rate of 10 mA ($\text{g of LiMn}_2\text{O}_4$)⁻¹, i.e., C-rate is approximately C/10. The protocol for charge and discharge measurement at high temperature is as follows: cells are cycled at room temperature (RT) for first 10 cycles and (i) at high temperature of 60 °C for subsequent 20 cycles, or (ii) stored at charge state in the 11th cycle at 60 °C for 7 days and re-cycled at RT from discharge. To examine electrochemical decomposition of the additive and electrolyte, cyclic voltammetry was performed at a slow sweep rate of 0.05 mV s⁻¹ at RT between 0 - 2 V (working electrode, WE: Cu) or 3 - 5 V (WE: Al) vs Li/Li^+ with Li metal as reference and counter electrodes. The surface morphology on the electrodes was observed by scanning electron microscope (SEM, JEOL JSM-7000 FSHL JEOL Inc.) equipped with an energy dispersive X-ray (EDX) microanalyzer. For surface analysis of the electrode, synchrotron hard X-ray photoelectron spectroscopy (HAXPES, BL46XU at Super Photon Ring 8 GeV; SPring-8, Japan) was utilized to analyze components of the electrode surface. The charged or

discharged electrodes were rinsed in DMC and set to the observation chamber without any exposure to air by using a laboratory-made transfer vessel. Time-of-flight secondary ion mass spectrometry (TOF-SIMS, PHI TRIFT V nanoTOF, Ulvac-Phi Inc.) was also performed. The targets were bombarded by the 30 keV Au_3^+ beams with a pulsed primary ion current varying. The amount of deposited manganese on the negative electrode, which is derived from the LiMn_2O_4 positive electrode, was estimated by using the inductive coupled plasma – atomic emission spectrometry (ICP-AES, SPS3520UV, SII nanotechnology Inc.).

To estimate electrochemical decomposition potential of the additive and electrolyte, relative energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of EC, DMC and FSE was calculated by the Gaussian 09W program. The structural optimizations were carried out by density functional theory (DFT) calculation.

3. Results and discussion

The estimation for decomposition potential of electrolyte [30, 31] is important because the functionality of SEI passivation layer on the electrode depends on its components and structures, which generally form during the first-charge process by electrochemical decomposition of solvent molecules. Based on the molecular orbital theory, electrochemical stability of electrolyte and additives is estimated by comparison of energy levels of the highest occupied molecular orbital (HOMO) with the lowest unoccupied molecular orbital (LUMO). The calculated frontier molecular

orbital energy levels (E_{HOMO} and E_{LUMO}) of EC, DMC and FSE molecules are shown in Table 1. The LUMO energy of FSE molecule ($E_{\text{LUMO}} = -1.3$ eV) is lower than those of EC (-1.2 eV) and DMC (-1.0 eV) molecules. FSE molecule would be, therefore, better electron acceptor than EC and DMC molecules and readily formed SEI before the EC and DMC decomposition on electrochemical reduction.

To examine influence of the FSE additive on electrochemical behaviors of the electrolyte solution, cyclic voltammetry (CV) was performed by using bare Cu and Al foils as electrode. Figure 2 shows cyclic voltammograms with or without 0.5% (w/w) FSE additive. With respect to the voltammograms without FSE (black line), several peaks assigned to reduction and oxidation of the electrolyte appeared. A strong reductive peak was observed at around 1.5 V (vs. Li/Li^+) in the FSE-added electrolyte (red line), indicating that reduction of FSE on Cu foil would mainly occur at 1.5 V vs Li/Li^+ (Fig. 2(a)). Regardless of the presence of FSE additive, there was no clear difference in the profiles of the voltammograms of Al foil (Fig. 2(b)). Because of no drastic change in potential window by the FSE additive, we employed FSE-added electrolyte in graphite/ LiMn_2O_4 cells.

Charge and discharge curves of the graphite/ LiMn_2O_4 cells with FSE-free or FSE-added electrolyte (0.5, 1 or 2 % (w/w)) under the room temperature (RT) are shown in Fig. 3. The each initial discharge capacity was $80\text{--}110 \text{ mAh (g of LiMn}_2\text{O}_4)^{-1}$ with less than $20 \text{ mAh (g of LiMn}_2\text{O}_4)^{-1}$ of irreversible capacity. As shown in Fig.3, the prominent capacity reduction was observed in the 1

1 and 2 % FSE-added cells with gradually-shifted cycling curves compared with that of the FSE-free
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4 and 0.5 % FSE-added cells. The successive shift of charge/discharge curves indicates continuous
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7 irreversible capacity on cycle. The addition of 1 and 2% FSE, therefore, interferes with
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10 charge/discharge processes by intensive reductive decomposition of FSE from discussion in Table 1
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13 and Fig. 2. On the other hand, when 0.5% FSE was added, no deterioration of battery performance
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16 for the LiMn_2O_4 /graphite cell was confirmed compared with that of the FSE-free cell, therefore we
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19 employed the FSE concentration of 0.5% to examine the following all electrochemical
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22 measurements.
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29 protocol (i): initial 10 cycles at RT (approximately 25°C) and following 20 cycles at elevated
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32 temperature of 60 °C are shown in Fig. 4(a) and (b). From the comparison of the curves,
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35 charge/discharge behavior was definitively changed by the FSE additive. While it appears to be no
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38 difference during the room temperature cycles, discharge capacity of the cell without FSE seriously
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41 decreased under the high temperature condition and it is mostly due to the manganese dissolution
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44 from LiMn_2O_4 positive electrode and subsequent manganese deposition on the graphite electrode.
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47 According to our previous report, manganese ions are dissolved during degradation of the LiMn_2O_4
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50 positive electrodes and electrochemically deposit on the graphite negative electrode, leading severe
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53 electrolyte decomposition by electrocatalytic effect of deposited manganese [15, 18]. In the case of
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56 the FSE-added cell, decrease of the discharge capacity was much smaller than that of the FSE-free
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cells in the cycling under the high temperature condition. These results prove that the addition of proper amount of FSE to electrolyte is efficient to suppress degradation of the graphite/LiMn₂O₄ cell operated at the elevated temperature. In addition, such a smaller amount of FSE addition (optimum amount: 0.5% (w/w)) compared with those of other known electrolyte additives [9-11] is attractive in terms of improvement of coulombic efficiency at first charge/discharge.

To quantitatively discuss the effects of FSE additive on the performance, the reversible (discharge) capacity and its coulombic efficiency (defined as discharge/charge capacity ratio for each cycle) of the graphite/LiMn₂O₄ cells were plotted and shown in Fig. 5(a) and (b), respectively. From the measurement during the initial room temperature condition (during the initial 10 cycles), both of the cells with and without FSE addition had almost the same electrochemical properties through the cycles. On the other hand, there was obvious difference on the profiles at elevated temperature condition (between 11th and 30th cycles). The cells with FSE exhibit more stable cycle performance than the cells with the FSE-free electrolyte (Fig. 5(a)); the FSE-free cell had serious capacity loss of approximately 57 % at the 30th cycle, while the cell containing 0.5 % FSE achieved more than 62 % of capacity retention, i.e. less than 38 % of capacity loss with higher coulombic efficiency (Fig. 5(b)) at the same cycle number. It is also noteworthy that the coulombic efficiency of the cell with FSE-added electrolyte immediately recovered at the charge of 11th cycle where the measurement temperature was changed from RT to 60 °C. The addition of FSE into the electrolyte resulted in much improved cycle performance of the graphite/LiMn₂O₄ cells under the

1 elevated temperature condition. Since the finer particles of LiMn_2O_4 (~100 nm in diameter) was
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3 used for the test (see Figure S1 in Supporting Information), the larger surface area of LiMn_2O_4
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5 accelerated the manganese dissolution and degradation. When we used commercially available
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10 Li-Mn spinel with larger particle size, the degradation was found to be much less significant due to
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13 relatively reduced degradation of the electrode.
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17 Figure 6 shows SEM images of the LiMn_2O_4 electrodes surface taken out from the cell
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19 after 10 cycles at RT (25°C) and after the following elevated temperature (60°C) cycles. Any
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22 apparent differences are not observed on their surface morphology among the electrodes in the
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25 FSE-free and FSE-added cells even in the samples after the elevated temperature cycling. This fact
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28 was well agreed with the result concerning the observation of the positive electrode in $\text{LiMn}_2\text{O}_4/\text{Li}$
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31 cell in the previous literature [32]. Therefore, we further studied the graphite negative electrode and
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39 SEM images of the graphite negative electrodes before and after the high temperature
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41 cycles are shown in Fig. 7. There is no distinctive morphological difference of the surface between
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44 the two electrodes from FSE-free and FSE added cell after the first 10 cycles at RT, as shown in Fig.
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47 7(a). However, we found obvious difference on the electrodes surface after the cycles at elevated
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50 temperature. A large amount of precipitations with diameter of 1-2 μm were observed only on the
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53 surface of the graphite electrode of the FSE-free cell (Fig. 7(b)). Figure 8(a) and (b) shows EDX
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57 spectra for the graphite electrodes after being cycled at the elevated temperature with or without FSE.
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From the EDX images, the intensity of peaks assigned to fluorine is relatively stronger in the FSE-free cells. The elemental mapping of the graphite surface of FSE-free system in Fig. 8(c)-(f) reveals that the precipitation seen in Fig. 7(b) was fluorine-containing compounds. Considering the increased peak intensity assigned to phosphorus and fluorine in the spectrum of Fig. 8(a) for the FSE-free system, the fluorine-containing compounds are regarded as decomposition products of PF_6^- anions. Hence, it is thought that FSE addition to the electrolyte suppresses resultant decomposition of PF_6^- in the elevated temperature condition. However we also compared the amount of Mn deposition on the graphite surface, the peak intensities (Mn K-level emission lines, around 6 keV) are too low to visualize and compare the Mn deposition by the elemental mapping.

Components and thickness of deposits and SEI derived from the electrolyte and/or FSE was further examined by comparison of photoemission spectroscopy by hard X-ray (7938.9 eV) excitation for the graphite electrodes before and after the elevated temperature cycles. Because of higher kinetic energy of photoelectron excited by hard X-ray, detection depth of photoelectron is ~10 nm in the case of HAXPES measurement, which differs from that of conventional X-ray photoelectron spectroscopy, ~2 nm [33]. Figure 9 shows the C 1s, Si 1s, and P 1s HAXPES spectra for the graphite electrodes. The C 1s spectra (Fig. 9(a)) could be divided into five individual peaks including sp^2 hybridized carbons in graphene structure (284.6 eV)[34, 35], -C-O- (286.1 eV), -C=O (288 eV), Li_2CO_3 (290 eV), and CF (291 eV) [35]. From the spectra, the intensity of peak assigned to graphene structure (284.6 eV) in the FSE-free cell is significantly small after cycles at 60 °C,

1 suggesting that the graphite surface is covered with relatively thick and/or uniform deposits (~10 nm)
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4 due to electrolyte decomposition during the high-temperature cycles. On the other hand, the
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7 graphite peak of the electrode in the FSE-added cell still remains even after cycles at 60°C, and
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10 therefore, graphite surface in the FSE-added cell is expected to be less covered with electrolyte
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13 decomposition products, compared to those of the FSE-free cell.
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17 In the Si 1s spectra of Fig. 9(b), the peak appeared around 1844 eV, which is assigned to
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20 SiO_x species [33], for graphite electrodes in the FSE-added cells, and the peak was still observed
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22 after the high-temperature cycles. This result reveals that FSE decomposition during the cycles
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25 results in SiO_x-containing species, and they are deposited on or covered the graphite surface. Since
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28 the FSE-derived layer is relatively stable under the elevated temperature, this functional passivation
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31 layer, similar to so-called SEI [4], protects the graphite surface [25] and suppresses direct contact
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34 with electrolyte solution which contains dissolved manganese ions, and consequently, it considerably
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37 suppresses the electrolyte decomposition during the cycling.
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42 As shown in the P 1s spectra of Fig. 9(c), for the electrode cycled in the FSE-free cell,
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45 the peak of Li_xPO_yF_z (2151 eV) is stronger than those of the electrode from FSE-added cell. The
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48 electrode in the FSE-free cell is covered with large amount of LiPF₆-derived decomposition products
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51 both before and after the cycles at 60 °C. These results well agree with those of EDX analysis
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54 shown in Fig 8 (a) and 8(b).
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58 Figure 10 shows TOF-SIMS spectra of the graphite electrodes taken out from the
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graphite/LiMn₂O₄ cell after the high temperature cycling. TOF-SIMS analysis brings semiquantitative information concerning fragments of surface components (molecules) with an ion beam exposure dose of $< 1 \times 10^{12}$ ions cm⁻², making it possible to characterize the most superficial components within several angstroms on the graphite electrode. Many peaks assigned to the fragments derived from electrolyte salt, solvent, and additive decomposition and binder were observed in the both spectra. With respect to Li_nF_m fragments in the spectra, it is known that lithium fluoride, LiF, is one of the well-known SEI components of graphite-type negative electrodes. We think that the detected Li_nF_m fragments are also components of the SEI generated on the graphite electrode surface.

Clearly, there are several characteristic peaks in Fig. 10(b) concerning the electrode from FSE-added cell. A small peak of mass/electron charge (m/z) = 23 (positive ion mode), assigned to Na contained in CMC binder used, appears only in the case of FSE added. This supports that the CMC-graphite electrode surface cycled in FSE-added cell was covered with thinner deposits, compared to that of the electrode in FSE-free cell, as is consistent with the findings from the HAXPES analyses described above. Peaks at m/z = 28 in positive ion mode and m/z = 103 in negative ion mode are assigned to the fragments of Si and C₂O₂FSi, respectively, which are derived from FSE. In addition, distinctive peak of m/z = 101 (negative ion mode) would be attributed to the fragment of PO₂F₂. Since the fragments of C₂O₂FSi and PO₂F₂ are observed when FSE was added into the electrolyte, we speculate that these Si- and F-containing fragments play an important role as

components of SEI for the electrode, e.g., the improvement of high temperature performance and suppression of manganese deposition. As other characteristic feature in the spectra of Fig. 10(b), peaks of $m/z = 55$ (positive ion mode) and 145 (negative ion mode) are assigned to the fragment of Mn and PF_6^- , respectively. It is thought that detected manganese originates from adsorbed manganese ion at the most superficial surface, which should not be metallic Mn^0 [18, 19]. We speculate that some of the characteristic ionically-charged component in the SEI, derived from FSE, probably have electrostatic interactions with manganese ion and PF_6^- dissolved in the electrolyte, leading adsorption of those species on the surface.

From the SEM-EDX, HAXPES, and TOF-SIMS analyses, the graphite electrode cycled without FSE is considered to be covered with a larger amount of deposits due to electrolyte decomposition on the precipitated manganese, resulting in significant capacity fade under the high temperature condition. Furthermore, the FSE-added electrolyte suppresses LiPF_6 decomposition to deliver good cycle performances.

High-temperature storage tests at 60 °C were also performed to discuss detailed mechanism of FSE additive of the graphite/ LiMn_2O_4 cell at the high-temperature condition under the protocol (ii). For the storage tests, charge/discharge cycle was transitory stopped at the 11th fully-charged state following the 10 initial cycles at RT, and then the cells at open circuit state were kept to be aged in the thermostat oven at 60 °C for 7 days, and the charge/discharge cycles (from the 11th discharge) restarted at RT again.

Figure 11 show the SEM images of the graphite electrodes after the high temperature storage. Precipitation with a diameter of ~100 nm similar to one in the SEM image of Fig. 7(b) were prominently observed on the surface in the case of the electrode from the FSE-free cell (Fig. 11(a)), indicating that the deposited particles could be formed due to the same reaction at high temperature even without electrochemical cycling.

The charge/discharge curves before and after the 7 day storage at 60 °C are shown in Fig. 12(a). Both of cells with or without FSE exhibited almost same electrochemical behavior during first 10 cycles at RT. When discharge at the 11th cycle was conducted after the storage, there is a remarkable difference between the two cells. The estimated self-discharge capacity during the high temperature storage of the FSE-free and FSE-added cell were 76 mAh (g of LiMn_2O_4)⁻¹ and 42 mAh (g of LiMn_2O_4)⁻¹, respectively, as seen in the figure. For the following cycle performance after the storage, the discharge capacity of FSE-free and FSE-added cells kept about 50 % and 67 % of that before the storage (ca. 90 mAh (g of LiMn_2O_4)⁻¹), as shown in Fig. 12(b). Therefore, the capacity fading during the storage was suppressed in the case of FSE-added cell, simultaneously, the decrease in coulombic efficiency is also suppressed in the 11th cycle (Fig. 12(c)). This capacity reduction would be responsible for unbalanced state of the capacity between the positive and negative electrodes during successive cycles which is mainly due to the manganese deposition and following decomposition reaction between manganese and electrolyte solution, resulting in self-discharge of the graphite negative electrode [18].

Besides the electrochemical measurements, the total amount of dissolved Mn in the electrolyte and resultant precipitated Mn on the negative electrode, which originates from the LiMn_2O_4 positive electrode [15], was simply estimated by use of $\text{LiMn}_2\text{O}_4/\text{Li}$ half-cells. The initial 10 cycles at RT and following high temperature storage process were conducted for the half-cell with or without FSE. The Li metal electrode, separator, and spacer (made by stainless steel) in the coin-type half-cell were taken out before and after the storage and immersed in HCl solution for the ICP-AES analysis. Figure 13 compares the Mn amounts dissolved from positive electrodes (% per total Mn amount in the positive electrode) in each analysis. The dissolved Mn amount increased during the high temperature storage in both cells, however, in the case of the FSE-added cell, the Mn dissolution from the LiMn_2O_4 electrode is notably reduced compared with that of the FSE-free cell. This result indicates that FSE additive brings not only protection effects of graphite electrode from Mn deposition but also suppression effects of fundamental Mn dissolution from LiMn_2O_4 electrode.

HAXPES analysis was performed for the LiMn_2O_4 electrodes taken out from the graphite/ LiMn_2O_4 full cell before and after the high-temperature storage test. The Si 1s spectrum of the LiMn_2O_4 electrodes tested in FSE added cell evidenced that Si-containing compounds exist in the outermost surface layer particularly after the storage test (see Figure S2 in Supporting Information). This result reveals that protective Si-containing surface layer originating from FSE additive would be also formed on the surface of the LiMn_2O_4 electrode.

To further examine which electrode mainly causes the self-discharge under high

temperature condition in the full cell, graphite/LiMn₂O₄ full-cells with and without 0.5 % FSE were kept at fully-charged state at 60 °C for 7 days after 10 cycles at RT and then, the electrodes in the FSE-added cells and FSE-free cells were taken out carefully without air exposure to individually re-fabricate half-cells with Li metal in the electrolyte with and without 0.5 % FSE (w/w), respectively. Thus re-fabricated cells were cycled again from charge (i.e. delithiation and lithiation for the spinel and graphite electrodes, respectively). The “charge capacity” observed here directly corresponds to “self-discharged capacity” during the elevated temperature storage. Figure 14 (a) shows the charge/discharge curves of the re-fabricated Li_{1-x}Mn₂O₄/Li half-cell using the positive electrodes taken out from the FSE-free and FSE-added full cell. Small and similar self-discharge capacity of ca. 10 mAh (g of LiMn₂O₄)⁻¹ was observed in both profiles regardless of the FSE addition. This observation indicates that the performance of LiMn₂O₄ after high temperature condition would not be affected so much by the presence or absence of FSE additive in the electrolyte. On the other hand, a clear dependency on FSE additive is noted from the measurements of the re-fabricated graphite/Li half-cell in Fig. 14 (b), i.e., relatively-large self-discharged capacity of 68 mAh (g of graphite)⁻¹ was observed in the electrode taken out from the FSE-free full cell, which is self-discharged capacity more than 13 times larger than that (5 mAh (g of graphite)⁻¹) of the electrode from FSE-added full cell. As a result, the behavior of self-discharge in the full cell during the elevated temperature storage mainly depends on the graphite negative electrode, and consequently, FSE addition in the electrolyte enables to suppress the self-discharge to lead better

1 cycle performance in the $\text{LiMn}_2\text{O}_4/\text{graphite}$ cell. The loss of $68 \text{ mAh (g of graphite)}^{-1}$ and 10 mAh
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4 $(\text{g of LiMn}_2\text{O}_4)^{-1}$ in the full cell without FSE clearly evidenced the unbalanced capacity and resultant
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7 capacity reduction as mentioned in Fig. 12.
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10 We finally suggest schematic diagrams of the difference in surface properties including
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12 SEI formation with or without FSE on the graphite negative electrode when manganese dissolution
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14 occurs in the full cell, as shown in Fig. 15. When the cell was cycled at RT and before the
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16 storage/cycle at 60°C , electrode surface is covered with SEI layer or FSE-derived SEI layer
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18 including the deposition of inorganic compounds. The SEI formation should be completed almost
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20 at the first charge process due to the irreversible reaction. From the surface analysis described
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22 above, FSE-derived layer consists of Si- and F-containing compound and it would be thinner than
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24 SEI in the FSE-free system. During the high temperature state, it is speculated that the SEI layer is
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26 gradually and partly dissolved in the electrolyte [8], leading exposure of the graphite surface directly
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28 to electrolyte solution, resulting in loss of passivation layer formed at RT. As a result, the
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30 dissolution is followed by generation of manganese deposits on the graphite surface, originating from
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32 the released Mn^{2+} ions from $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ positive electrode at 60°C (Fig. 15(a)). It is believed that
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34 this manganese deposition brings intensive decomposition of electrolyte salt, LiPF_6 , as observed in
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36 the SEM-EDX analysis of Fig. 8, which results in a considerable self-discharge of the cell. On the
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38 other hand, the FSE-derived thin layer would be stable even at the elevated temperature and prevent
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40 the negative electrode from being degraded by the manganese deposition as well as self-discharge as
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described. Namely, the FSE-modified SEI layer is capable to protect the graphite surface against the Mn^{2+} attack without hindrance of lithium intercalation as illustrated Fig. 15(b). We believe that silicon element with fluorine element in the fluorosilane molecules is effective in stabilizing and improving the SEI passivation performance of the graphite/spinel cells as the SEI formation is definitively modified by the electrochemical decomposition of FSE additive as described in Table 1 and Fig. 2. Detailed mechanisms of electrochemical decomposition reactions of FSE and actual chemical compounds included in the resultant SEI formation are still required to further design new functional additives for achieving high-performance lithium-ion batteries.

4. Conclusions

The electrochemical performance of the graphite/ LiMn_2O_4 cell under the elevated temperature condition is greatly improved with the FSE additive. The proper amount of FSE additive brings relatively thin and stable layers on the graphite surface and suppresses self-discharge at the elevated temperature. The FSE-derived layer, which includes Si- and F-containing compounds, effectively protects the graphite surface even under the high temperature condition. Consequently, it suppresses accumulation of Mn deposits on the graphite and prevents following electrolyte decomposition as well as self-discharge in the cell. In addition, it is speculated that the surface of LiMn_2O_4 electrode is also covered with FSE-derived thin layer, which would suppress dissolution of Mn from the surface. Note that the smaller amount of FSE addition (optimum

amount: 0.5 %), compared with those of other known electrolyte additives, is attractive in terms of improvement of coulombic efficiency at first charge/discharge. It is believed that FSE and its analogues having silyl group will be promising electrolyte additives for LIBs and bring superior battery performance under severe operating conditions such as high temperature, high voltage and high capacity conditions.

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Table and Figure Captions

Table 1. Calculated E_{HOMO} and E_{LUMO} of EC, DMC, and FSE.

Figure 1. Structural formula of 1,2-bis(difluoromethylsilyl)ethane (FSE).

Figure 2. Cyclic voltammograms of (a) Cu foil electrode at a scan rate of 0.05 mV s^{-1} , and (b) Al foil electrode at 0.1 mV s^{-1} vs Li/Li^+ in $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ EC/DMC (3:7) with 0.5 % (w/w) FSE addition (red curves) and without FSE (black curves).

Figure 3. Galvanostatic charge-discharge curves ($10 \text{ mA (g of LiMn}_2\text{O}_4)^{-1}$, 30 cycle) of graphite/ LiMn_2O_4 cell at room temperature condition using (a) FSE-free, (b) 0.5 % (w/w) FSE-added, (c) 1 % (w/w) FSE-added, and (d) 2 % (w/w) FSE-added $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ EC/ DMC (3:7).

Figure 4. Galvanostatic charge-discharge curves ($10 \text{ mA (g of LiMn}_2\text{O}_4)^{-1}$) of graphite/ LiMn_2O_4 cell with initial 10 cycles at room temperature and following 11th-30th cycles at high temperature (60°C) in (a) FSE-free and (b) 0.5 % (w/w) FSE-added $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ EC/ DMC (3:7).

Figure 5. (a) Discharge capacity and (b) coulombic efficiency of the graphite/ LiMn_2O_4 cell ($10 \text{ mA (g of LiMn}_2\text{O}_4)^{-1}$) in FSE-free (circular plots) and 0.5 % (w/w) FSE-added (quadrate plots) 1 mol

dm⁻³ LiPF₆ EC/ DMC (3:7) with initial 10 cycles at room temperature and following 11th-30th cycles at 60 °C.

Figure 6. SEM images of the LiMn₂O₄ positive electrodes of the cell (a) after 10 cycles at room temperature and (b) after the following high temperature (60 °C) cycles. [left column] the electrode from FSE-free cell and [right column] FSE-added cell.

Figure 7. SEM images of the graphite negative electrodes of the cell (a) after 10 cycles at room temperature and (b) after the following high temperature (60 °C) cycles. [left column] the electrode from FSE-free cell and [right column] FSE-added cell.

Figure 8. EDX spectra of the graphite electrodes retrieved from (a) FSE-free cell and (b) FSE-added cell after the cycles under the elevated temperature condition (60 °C). Concerning the spectrum of (a), (c) SEM image and corresponding EDX elementary mapping of (d) carbon, (e) fluorine, and (f) oxygen are also shown.

Figure 9. (a) C 1s, (b) Si 1s and (c) P 1s HAXPES spectra of the graphite electrodes retrieved from the (top row) FSE-free and (bottom row) FSE-added graphite/LiMn₂O₄ cell after the 10 cycles at room temperature (25°C) and following elevated temperature (60°C) cycles.

Figure 10. TOF-SIMS spectra of graphite electrode retrieved from the graphite/LiMn₂O₄ cell after the elevated temperature (60 °C) cycles: (a) the electrode from FSE-free cell and (b) FSE-added cell.

Conditions: 10 s sputtering before measurement, positive and negative ion mode.

Figure 11. SEM images of the graphite negative electrodes of the cell after the storage at elevated temperature (60 °C). The electrode was retrieved from (a) FSE-free cell and (b) FSE-added cell.

Figure 12. Charge and discharge performance of the graphite/LiMn₂O₄ cell with FSE-free and FSE-added electrolyte: (a) charge/discharge voltage curves, (b) discharge capacity, and (c) coulombic efficiency before and after the storage at full-charge state under elevated temperature condition (60 °C) after 10th charge.

Figure 13. Mn amount dissolved from the LiMn₂O₄ electrode in the LiMn₂O₄/Li half-cell before and after the high-temperature storage test by ICP-AES analysis.

Figure 14. Charge/discharge curves of (a) LiMn₂O₄ electrodes and (b) graphite electrodes in half-cell (counter electrode: Li metal) using the electrodes retrieved from the graphite/LiMn₂O₄ full-cell with [left column] FSE-free electrolyte and [right column] FSE-added electrolyte after the storage at full-charge state under elevated temperature condition (60 °C).

Figure 15. Schematic illustrations of graphite electrodes in (a) FSE-free and (b) FSE-added electrolyte before and after the elevated temperature storage or cycling.

Table 1

Molecule	E_{HOMO} / eV	E_{LUMO} / eV
EC	-8.5	-1.2
DMC	-8.4	-1.0
FSE	-8.3	-1.3

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

(a)

(b)

Figure 6

(a)

(b)

Figure 7

(a) FSE-free

(b) with FSE additive

Figure 8

Figure 9

(a) FSE-free

Positive ion mode

Negative ion mode

(b) FSE-Added

Positive ion mode

Negative ion mode

Figure 10

(a)

(b)

Figure 11

Figure 12

Figure 13

Figure 14

(a) FSE-free

(b) with FSE

Figure 15

Table of contents

Graphite electrodes (in graphite/LiMn₂O₄ cell)

FSE-free

FSE electrolyte additive effectively suppresses electrode degradation.

with FSE additive