Short communication

Ionic liquid electrolytes compatible with graphitized carbon negative without additive and their effects on interfacial properties[☆]

Toshinori Sugimoto[a], Manabu Kikuta[b], Eriko Ishiko[b], Michiyuki Kono[b], Masashi Ishikawa[a,c,*]

[a] Department of Applied Chemistry, Faculty of Engineering, Kansai University, 3-3-35 Yamate-cho, Suita 564-8680, Japan
[b] Dai-ichi Kogyo Seiyaku Co., Ltd., 55, Nishi-Shichijo, Higashikubo-cho, Shimogyo-ku, Kyoto 600-8873, Japan
[c] Research Center for Business Academia Collaboration, Kansai University, 3-3-35 Yamate-cho, Suita 564-8680, Japan

ABSTRACT

Introduction of bis(fluorosulfonyl)imide (FSI) as an anion to an ambient-temperature ionic liquid electrolyte based on 1-ethyl-3-methylimidazolium (EMI) as well as lithium (Li) cations can provide a reversible Li intercalation into a graphitized electrode, while such intercalation is completely irreversible without FSI. The surface-layer components on the graphitized electrodes, cycled in the ionic liquid electrolytes with and without FSI, were found to be chemically similar based on X-ray photoelectron spectroscopy. Ac impedance spectroscopy revealed that the resistance of the electrode charged with FSI was much lower even than that charged in a solvent electrolyte system containing ethylene carbonate (EC) and dimethyl carbonate (DMC). On the basis of these physicochemical analyses, the origins of cycleability in the presence of FSI are discussed.

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1. Introduction

Ambient-temperature ionic liquids as alternative electrolytes have recently attracted the attention of researchers because they have the advantages of non-flammability and non-volatility in a wide temperature range, will also maintaining a liquid phase as well as acceptable conductivity. Their desirable features have encouraged many investigators to apply them to energy storage devices, such as Li-ion secondary batteries [1–8]. To obtain an acceptable cycling efficiency for a graphitized negative electrode in ionic liquid electrolytes, the addition of some functional organic solvent to the ionic liquid electrolytes has been considered necessary. A stable organic solvent can stabilize and protect the interface between a carbon negative electrode and the ionic liquid phase against an undesirable irreversible reaction with the ionic liquid. Recently, Holzapfel et al. reported a reversible Li intercalation into an artificial graphite in a 1 M LiPF$_6$ solution of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI–TFSI)

containing 5 wt.% of vinylene carbonate (VC) as an organic solvent additive [4,5]. Zheng et al. reported the effect of various organic solvent additives, including VC, on the cycleability of a graphitized negative electrode in an ionic liquid [6]. As an important alternative work, Ui et al. demonstrated that an LiCl-saturated AlCl$_3$–EMI Cl + SOCl$_2$ melt can be used as a compatible electrolyte for various carbon electrodes without organic solvents [8]. That report suggests that ambient-temperature molten salt electrolytes composed of complex inorganic anions with a free halide such as chloride together with an inorganic solvent can act as an alternative electrolyte and provide reversible cycleability for carbon electrodes. In spite of many reports like theirs, however, there has been no report on ambient-temperature ionic liquids using neither a free halide nor a solvent.

Quite recently, we investigated the electrochemical properties and cycling compatibility of ambient-temperature ionic liquids composed of bis(fluorosulfonyl)imide (FSI) as a novel anion and EMI or N-methyl-N-propylpyrrolidinium cation [9]. The essential finding of that work was that EMI–FSI containing a Li salt could provide a theoretical reversible capacity for a graphitized negative electrode during repeated cycling, without any additives. In this report, we analyzed the interfacial physicochemistry of graphitized carbon electrodes cycled in ionic liquid electrolytes with and without FSI as well as in a typical solvent electrolyte by using X-ray photoelectron spectroscopy (XPS) and ac impedance spectroscopy. On the basis of our results, key factors governing the
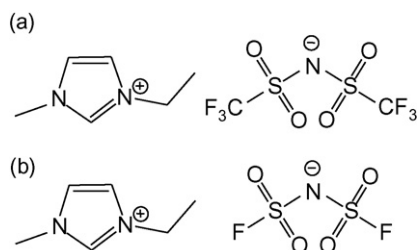

Fig. 1. Chemical structures of (a) EMI–TFSI and (b) EMI–FSI.

electrochemical performance of graphitized electrodes in the ionic liquids are discussed.

2. Experimental

The EMI–FSI and EMI–TFSI shown in Fig. 1 were produced by Dai-ichi Kogyo Seiyaku Co., Ltd. Ionic conductivities of EMI–FSI and EMI–TFSI are 15.5 and 8.1 mS cm^{-1} at 298 K, and their viscosities are 18 and 33 mPa s at 298 K, respectively. These ionic liquids contain less than 10 ppm (w/w) of moisture and 2 ppm (w/w) of halide and alkali metal-ion impurities. LiTFSI was purchased from Kishida Chemical Co., Ltd. and used without further purification.

The electrochemical behavior of a natural graphite electrode (HQB12: Hydro-Québec) was analyzed by cyclic voltammetry in EMI–TFSI and EMI–FSI as ionic liquid electrolytes as well as in ethylene carbonate mixed with the same volumetric amount of dimethyl carbonate (EC + DMC) as a common electrolyte; all of these electrolytes contain LiTFSI (0.8 M) as a lithium salt. The voltammograms were obtained between 0 and 1.2 V vs. Li/Li$^+$ at a scan rate of 0.1 mV s^{-1}; each cycling started from the respective OCV. Other experimental details of the electrochemical cycling, such as the cell configuration, are described in our recent paper [9].

For the XPS, after three galvanostatic cycles at a rate of 0.2 C between 0 and 1.2 V, each working electrode was removed from a coin cell inside a dry room and rinsed with DMC to remove the residual electrolyte and dried in a vacuum for 24 h. The sample electrodes were examined by an X-ray photoelectron spectrometer (ESCA-3400, Shimadzu Electron) with monochromatic Mg Kα radiation (1253.6 eV), which operated at 10 mA and 8 kV. The pressure during the experiment was kept below 7.5 × 10^{-9} Torr. Etching treatment was performed on the sample surface using an argon ion-beam gun operating at 10 mA and 1 kV. Ac impedance of the graphitized electrodes at open-circuit voltages was measured with an impedance analyzer (Solartron, S1 1280B) after a duration of 30 min following the first charging to 0 V at a rate of 0.1 C using a two-electrode cell with a Li sheet as a counter electrode. The scanned frequencies were from 20 kHz to 0.01 Hz, and the ac amplitude was 10 mV$_{p-p}$.

3. Results and discussion

3.1. Cyclic voltammetry for a natural graphite in ionic liquid electrolytes

Fig. 2(a) shows cyclic voltammograms for the graphite electrode in the LiTFSI/EMI–TFSI system. A significant irreversible reduction of EMI cations had taken place at ca. 0.6 V, especially during the first cycle. When the test cell was dismantled after the repeated cycles, it smelled like amines, indicating that the EMI cations decomposed via that irreversible reduction. On the other hand, in the LiTFSI/EMI–FSI system shown
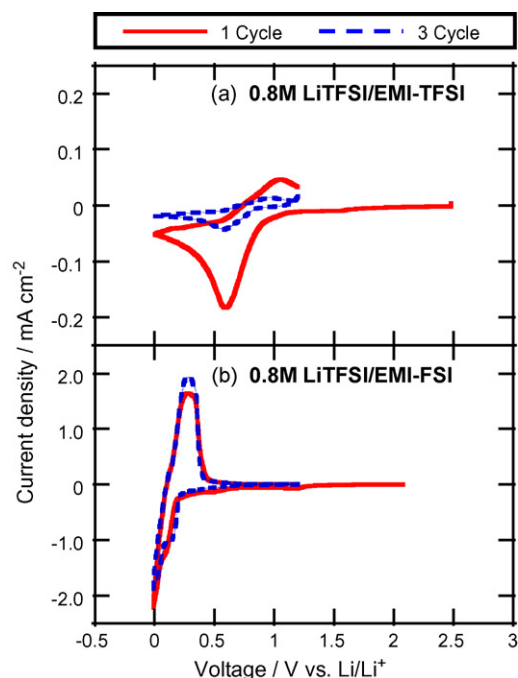

Fig. 2. Cyclic voltammograms of the graphitized electrodes in the ionic liquid electrolytes between 0 and 1.2 V at a scan rate of 0.1 mV s^{-1}; (a) LiTFSI/EMI–TFSI and (b) LiTFSI/EMI–FSI.

in Fig. 2(b), there is no cathodic peak above 0.5 V corresponding to the EMI response. Furthermore, Li intercalation was detected at around 0.2 and 0 V in a cathodic sweep, and the corresponding Li de-intercalation was also observed at around 0.25 V in an anodic sweep. We assume that such a desirable, reversible behavior was due to the presence of FSI anions because reversible Li cycling was observed in not only the EMI–FSI system but also the *N*-methyl-*N*-propylpyrrolidinium–FSI system [9].

3.2. Surface analysis by X-ray photoelectron spectroscopy

We applied XPS in the surface analysis of the natural graphite electrodes to elucidate the surface chemistry responding to a difference in electrolytes, i.e., LiTFSI/EMI–FSI and LiTFSI/EMI–TFSI ionic liquids as well as LiTFSI/EC + DMC as a common solvent electrolyte. Peaks observed in the high-resolution spectra were identified by reference to published articles related to electrode surfaces [10–14]; the data are summarized in Figs. 3 and 4.

Regarding the F 1s spectra (Fig. 3), peaks are identified as CF$_3$ at 689.0 eV and LiF at 685.5 eV. The amount of CF$_3$ present in the LiTFSI/EC + DMC system decreased significantly with the etching duration while there was a sharp increase in the quantity of LiF. In contrast, both the LITFSI/EMI–FSI and EMI–TFSI systems maintained considerable quantities of CF$_3$, while the amount of LiF only slightly increased with the etching duration. The CF$_3$ presence due to TFSI inside the electrode for both of the ionic liquid systems would indicate that their components were inserted relatively deeply into the graphite electrode, while a LiF surface layer on the electrode was relatively thin in the ionic liquid systems. In contrast, for the EC + DMC system, while there was a very small amount of residual components from this electrolyte, the LiF layer on the electrode was quite massive; such LiF layer formation has been widely known in common solvent electrolytes with an F-containing Li electrolytic salt [11].

As for the O 1s high-resolution spectra, peaks can be identified as CO$_3^{2-}$ or SO$_2^{2-}$ at 532.5 eV, Li$_2$CO$_3$ at 532.0 eV, and Li$_2$O at
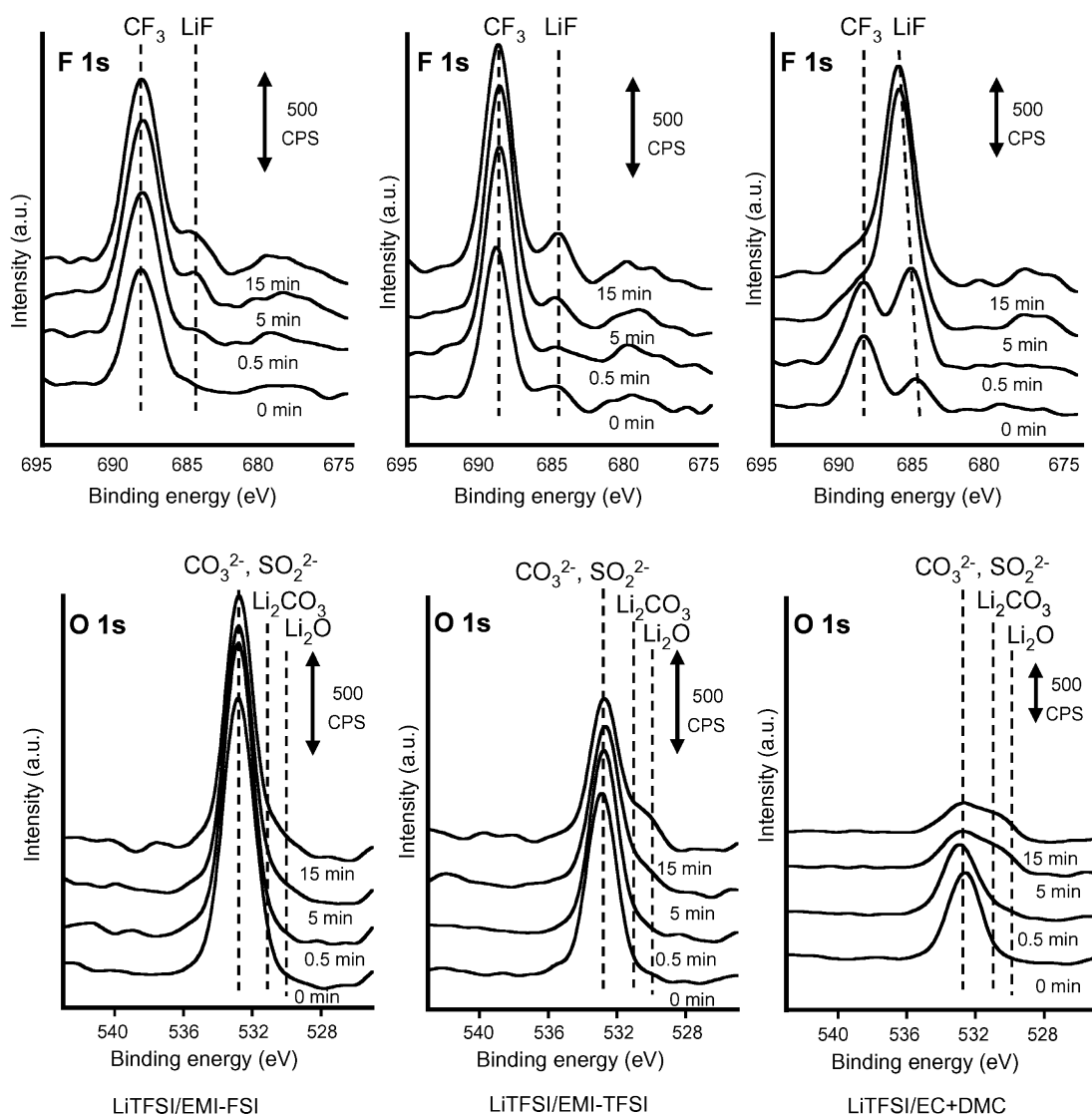
Fig. 3. High-resolution F 1s and O 1s photoelectron spectra for the graphitized electrodes charged at 0.2 C in LiTFSI/EMI–FSI, LiTFSI/EMI–TFSI and LiTFSI/EC + DMC with the etching duration.

528.5 eV (Fig. 3). The LiTFSI/EC + DMC system showed considerable quantities of Li_2O and Li_2CO_3, while the relevant responses in both the EMI–FSI and EMI–TFSI systems with LiTFSI were quite modest. A more notable feature in these ionic liquid systems is that a peak around 532.5 eV was very strong even with the etching duration, although the quantities of Li_2O and Li_2CO_3 were modest. Thus, the strong peak corresponds not to CO_3^{2-} but to SO_2^{2-}, which is due to the considerable amounts of TFSI or FSI inside the electrode; this interpretation is consistent with the above discussion for the F 1s spectra.

The reference binding energies in C 1s high-resolution spectra are 285.0 eV for C–C/C–H, 286.5 eV for C–N, 290.0 eV for CO_3^{2-}, and 293.0 eV for CF_3 (Fig. 4). Obvious CF_3 presence inside the electrode in EMI–FSI and in EMI–TFSI dissolving LiTFSI also suggests the ionic liquid components present inside the electrode in accordance with the above discussions. Furthermore, the main C–C/C–H peaks around 285 eV contained C–N responses that made the main peaks broaden to the left side, implying the presence of ionic liquid components inside the electrode as well. This characteristic was not observed, however, on the electrode in LiTFSI/EC + DMC.

In the Li 1s high-resolution spectra (Fig. 4), expected responses are identified as LiF at 56.0 eV, Li_2CO_3 at 55.3 eV and Li_2O at 54.0 eV. The separation of peaks was unclear in the EMI–FSI and EMI–TFSI systems, suggesting that the amounts of Li inorganic salts were small. On the other hand, the EC + DMC system more clearly showed the presence of LiF and Li_2O and they increased with the etching duration.

On the basis of the above XPS results, we can conclude that the inorganic solid-state interface, which is widely known in common solvent electrolyte systems, is very tiny or negligible on the graphite electrode in the present ionic liquid electrolyte systems. Instead of the layer, the components of ionic liquids can be detected even inside the electrode material. There was, however, no essential difference in any high-resolution XP spectrum between EMI–FSI and EMI–TFSI systems, although these ionic liquid systems provide crucially different performances in charge-discharge cycling as indicated in Fig. 2. Thus, the present XPS study suggests that the chemical components at the electrode interface would not be a critical factor governing the reversibility of the present ionic liquids/electrode systems.
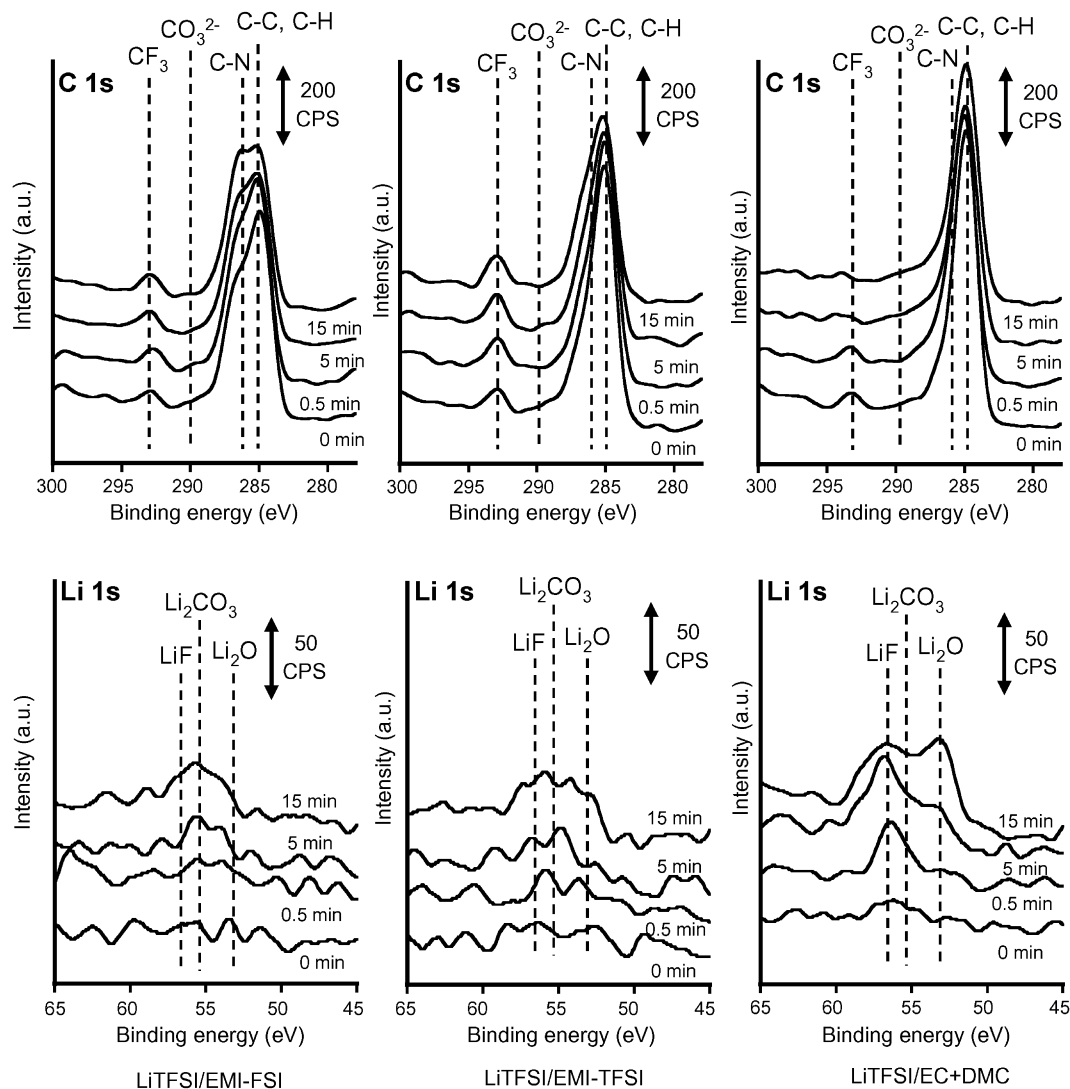
Fig. 4. High-resolution C 1s and Li 1s photoelectron spectra for the graphitized electrodes charged at 0.2 C in LiTFSI/EMI–FSI, LiTFSI/EMI–TFSI and LiTFSI/EC + DMC with the etching duration.

3.3. Electrochemical impedance spectroscopy (EIS)

As an alternative analysis for the present interfacial physicochemistry, EIS has been applied. Fig. 5 shows Nyquist plots after charging the graphite electrode to 0 V at 0.1 C in EMI–FSI and EC + DMC dissolving LiTFSI (0.8 M); the EMI–TFSI system was excluded from this analysis because charging in the system was essentially impossible so that we could not compare its impedance response with the others at the same charging status. The combination of a semicircle in the high frequencies and a small semicircle together with a short slope in the low frequencies was observed in the LiTFSI/EC + DMC system. The semicircle in the high frequencies can be attributed to the impedance of a surface chemical layer, and the low-frequency semicircle may be related to a charge-transfer resistance as a main charge process of the electrode [15].

On the other hand, the combination of a very small semicircle in the higher frequencies, compared to that observed in the solvent system, and another tiny semicircle together with a clear slope in the low frequencies was observed in the LiTFSI/EMI–FSI system. These results suggest that not only the resistance of an interface generated from the EMI–FSI system but also the reaction resis-

tance for the Li intercalation into the graphite in this ionic liquid was extremely low compared to the resistance levels in the solvent electrolyte.

3.4. Compressive interpretation of electrochemical and physicochemical analysis

We demonstrate that the electrode surface chemistry may not be a crucial factor governing the electrochemical performance in the present ionic liquid electrolyte. A possible critical factor would be energetics in the Li intercalation process. The XPS data suggest that charging draws the ionic liquid components into the electrode material, together with Li cations. In contrast, such charging draws only 'solvated' Li cations into the material in the conventional solvent systems, since the solvated Li cations have a much lower charge density and are thus energetically highly mobile. As for Li cations in ionic liquids, since Li cations are bound directly to a peripheral ionic cage without any salvation, Li cations are assumed to move together with a heavy ionic atmosphere even in an electrode; this can account for the XPS results. In this context, the Li charging reactivity would be derived from a facile Li transfer from an ionic liquid
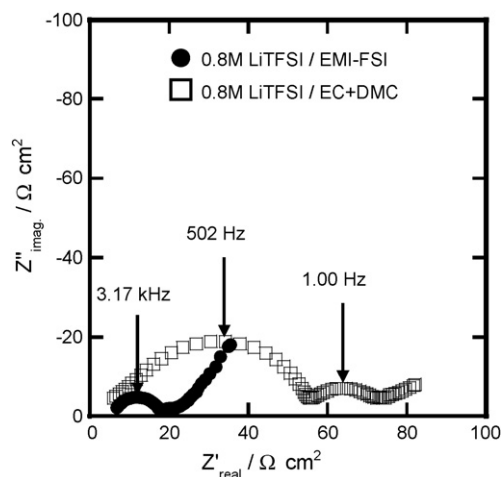
Fig. 5. Nyquist plots after charging the graphitized electrodes at 0.1 C in LiTFSI/EMI–FSI and LiTFSI/EC + DMC.

cage to a space between graphene multilayers by the prevailing electrostatic binding force in the cage.

Judging from our results of the potential cycling and EIS, the presence of FSI anions can effectively decrease the Li binding energy; the introduction of FSI obviously derives a low charge-transfer resistance (related to a small semicircle) and a weak diffusion limitation (as a short slope) even when compared to the solvent electrolyte system. This FSI effect can also be supported by the bulk properties, i.e., the viscosity and ionic conductivity of LiTFSI/EMI–FSI at 298 K were 8.7 mS cm^{-1} and 32 mPa s, which are 42 and 236% of the respective properties of LiTFSI/EMI–TFSI. Still, it is quite surprising that the introduction of FSI anion to ionic liquid electrolyte systems drastically changes the cycling reversibility of a graphitized carbon. This fortuitous finding encourages us to perform an extended study to realize a practical electrolyte system for rechargeable Li-ion batteries by utilizing the positive FSI effects.

4. Conclusions

A novel ionic liquid, LiTFSI/EMI–FSI, can provide reversible cycleability for a graphite negative electrode, while LiTFSI/EMI–TFSI leads to an irreversible cathodic current peak at ca. 0.6 V vs. Li/Li$^+$. From XPS results, we found that the surface layers on the graphitized electrodes cycled in the EMI–FSI and EMI–TFSI systems were chemically similar with penetrating ionic liquid components. Furthermore, the surface inorganic layer generated from both of the ionic liquid electrolytes was thinner than that derived from a typical organic solvent electrolyte. The impedance of the EMI–FSI system was much smaller than that of the LiTFSI/EC + DMC system, possibly due not only to a thinner surface layer generated from the EMI–FSI system but also to the low energies for Li migration as well as Li transfer to graphene interlayers from a peripheral ionic cage. Such interesting properties are promising for development of safe Li-ion batteries with a 'pure' ionic liquid.

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