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Short communication

Ionic liquid electrolyte systems based on bis(fluorosulfonyl)imide for lithium-ion batteries

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ABSTRACT

Ionic liquid electrolytes containing a certain amount of bis(fluorosulfonyl)imide (FSI) anion can provide reversible capacity for a graphitized negative electrode without any additives such as a solvent. Cyclic voltammetry for a graphitized negative electrode in ionic liquid electrolytes containing FSI with other anions suggests that the reversibility of Li intercalation correlates with the relative quantity (or concentration) of FSI in the electrolytes, and that the correlative tendency depends on the other kind of anion. On the basis of the present results, we discuss the effect of FSI in the ionic systems on a graphitized electrode interface.

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1. Introduction

Ambient-temperature ionic liquids have attracted increasing attention in many fields including batteries, electroplating, synthetic and catalytic chemistry because of their diverse properties such as a wide electrochemical potential window, acceptable ionic conductivity, high thermal stability and negligible vapor pressure. In particular, the application of these ionic liquids in lithium (Li)-ion secondary batteries has been considered in order to ensure safety by taking advantage of their lower flammability and lower reactivity than conventional organic electrolytes. However, the Li-ion batteries with ionic liquid electrolytes have some difficulties in their charge–discharge performance such as irreversibility of a carbon negative electrode [1–12].

Concerning this, some organic additives can stabilize and protect an interface between a carbon negative electrode and ionic liquid phase against an undesirable irreversible reaction of ionic liquid components. 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 [3,4]. Zheng et al. reported the effect of various organic solvent additives, including VC, on the cyclability of a graphitized negative electrode in an ionic liquid [5]. In spite of many reports like them, however, there had been for long time no report on ambient-temperature ionic liquids that can provide reversibility of a graphitized negative electrode without both a halide ion and a solvent.

We succeeded in finding novel electrolytes, bis(fluorosulfonyl) imide (FSI) anion-based ionic liquids, that provide a reversible capacity and high charge–discharge efficiency for a graphitized negative electrode without any additives [8,12]. To apply the FSI-based ionic liquids for practical purposes, however, it is necessary to clarify the effect and mechanism of the FSI anion on the negative electrode reactions.

The present work reports on the reversibility of a graphitized negative electrode in ionic liquid electrolytes containing binary anions based on FSI together with TFSI or tetrafluoroborate (BF_4). On the basis of the present results, we will discuss the effect of FSI in the ionic systems on the graphitized electrode interface.

2. Experimental

EMI-FSI and EMI-TFSI shown in Fig. 1 were produced by Daiichi Kogyo Seiyaku Co. Ionic conductivities of EMI-FSI and EMI-TFSI

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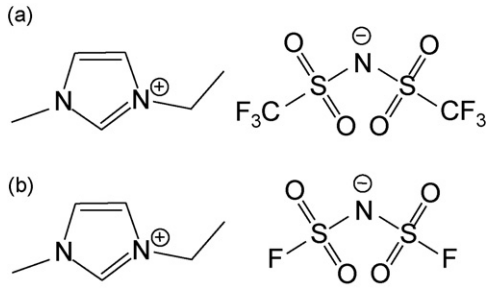

Fig. 1. Chemical structures of (a) EMI-TFSI and (b) EMI-FSI.

were 15.5 and 8.1 mS cm^{-1} at 298 K, and their viscosities were 18 and 33 mPa s at 298 K, respectively. These ionic liquids contain less than 20 ppm (w/w) of moisture and less than 2 ppm (w/w) of halide and alkali metal-ion impurities. EMI-BF_4, LiTFSI and $LiBF_4$ in battery grade were purchased from Kishida Chemical Co. and used without further purification.

To prepare negative electrode material for the charge/discharge cycling test, first we blended natural graphite (HQB12: Hydro-Québec) with carbon black (SFG6: Timcal Inc.), and then introduced PVdF as a binder into the mixture. After the mixture became homogenous paste in an agitated vessel, the paste was cast on a copper foil and smoothed by a knife blade designed to maintain a fixed distance from the copper foil. The resulting coated foil was dried at 363 K for 24 h in a vacuum to remove residual moisture, and then pressed with a roll press machine. The resulting electrode in this procedure was composed of 92 wt.% natural graphite, 3 wt.% carbon black and 5 wt.% binder. The foil electrode was cut in a circle of 1.13 cm^2 and its total thickness was 90 μm where the copper foil thickness was 20 μm. A two-electrode coin cell was used as a charge–discharge test cell. A separator film (Celgard 3501) was soaked into the ionic electrolyte solutions under vacuum before cell assembly. The cell fabrication processes were performed in a dry room with a dew point below 203 K.

The electrochemical behavior of a natural graphite electrode was analyzed by cyclic voltammetry in ionic liquid electrolytes. The voltammograms were obtained between 0 and 1.2 V at a scan rate of 0.1 mV s^{-1}; each cycling started from a respective open-circuit voltage.

3. Results and discussion

Fig. 2(a) shows cyclic voltammograms for the graphite electrode in EMI-FSI containing 0.32 mol kg^{-1} LiTFSI. The anion molar ratio was FSI:TFSI = 1.00:0.09. There was no cathodic peak at ca. 0.6 V corresponding to an EMI response: its intercalation or decomposition. Li intercalation was detected at ca. 0.2 and 0 V in a cathodic sweep, and the corresponding Li de-intercalation was also observed at ca. 0.25 V in an anodic sweep. Such a desirable, reversible behavior is due to the presence of the FSI anion [8,12].

Regarding EMI-FSI + EMI-TFSI (1:1, v/v) containing 0.32 mol kg^{-1} LiTFSI (the anion molar ratio was FSI:TFSI = 1:0.93), the current response was about half as large as that for the above EMI-TFSI-free systems, and a cathodic peak at ca. 0.6 V corresponding to the EMI response was not observed (Fig. 2(b)). Furthermore, as for EMI-FSI + EMI-TFSI (1:9, v/v) containing 0.32 mol kg^{-1} LiTFSI (the anion molar ratio was FSI:TFSI = 1.00:2.60) (Fig. 2(c)), an irreversible reduction of EMI cation appeared at ca. 0.6 V and then current response became lower in reversible cycling loops when compared to the foregoing EMI-FSI + EMI-TFSI (1:1, v/v) system.

On the basis of the above cyclic voltammetry results, we can suggest that the ratio of FSI to TFSI appears to correlate

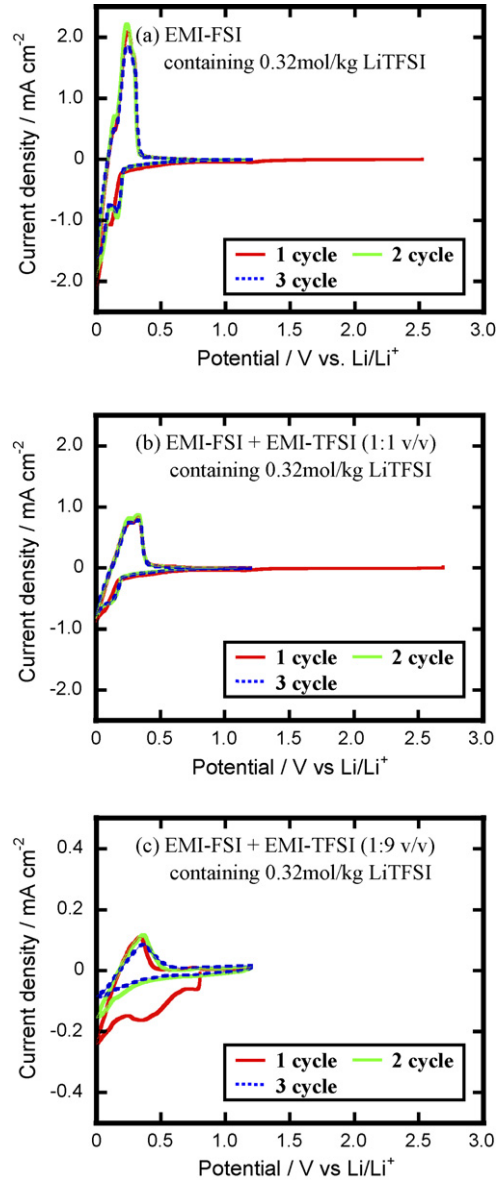

Fig. 2. Cyclic voltammograms of the graphitized electrode in the ionic liquid electrolytes containing 0.32 mol kg^{-1} LiTFSI between 0 and 1.2 V at a scan rate of 0.1 mV s^{-1}: (a) EMI-FSI only, (b) EMI-FSI + EMI-TFSI (1:1, v/v) and (c) EMI-FSI + EMI-TFSI (1:9, v/v).

with the magnitude of reversible currents on Li intercalation/de-intercalation; in other words, the reversibility of Li intercalation would be determined by the relative quantity (or concentration) of FSI in the ionic liquid electrolytes.

Next, we evaluated the relationship between the reversibility of Li intercalation and the relative quantity of FSI to BF_4 anion in ionic liquid electrolytes. Looking at cyclic voltammograms in EMI-FSI + EMI-BF_4 (9:1, v/v) containing 0.32 mol kg^{-1} $LiBF_4$ (the anion molar ratio was FSI:BF_4 = 1.00:0.27) (Fig. 3(a)), irreversible reduction of EMI cation occurred at ca. 0.6 and ca. 0.8 V in the initial cycle, and then the current response was markedly reduced when compared to the BF_4-free, reference system shown in Fig. 2(a), although the amount of FSI anion was about four times larger than that of BF_4 anion. As for cyclic voltammograms in EMI-FSI + EMI-BF_4 (3:1, v/v) containing 0.32 mol kg^{-1} $LiBF_4$ (the anion molar ratio was FSI:BF_4 = 1.00:0.61) (Fig. 3(b)), current response became lower in reversible cycling loops while an irreversible

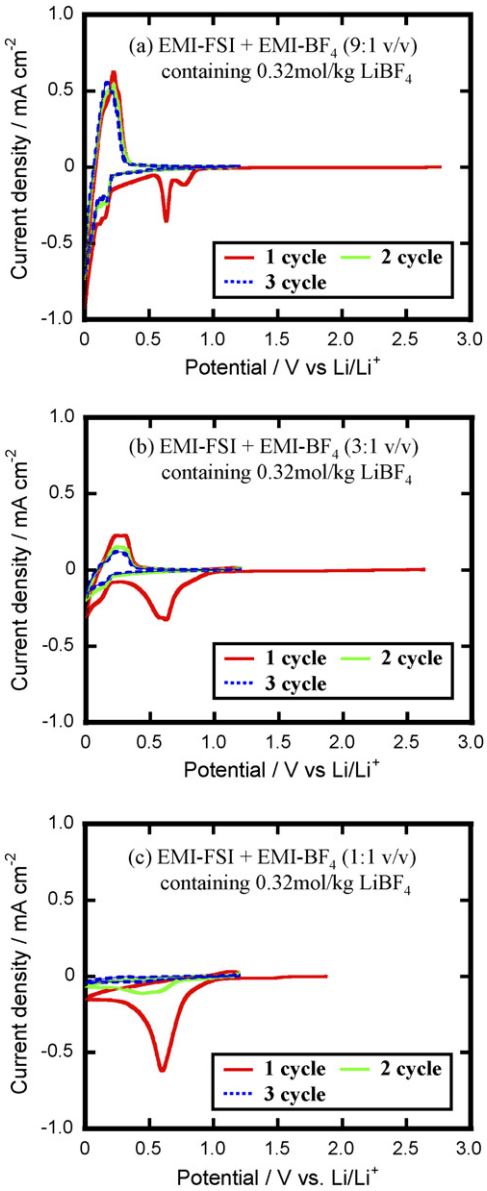

Fig. 3. Cyclic voltammograms of the graphitized electrode in the ionic liquid electrolytes containing 0.32 mol kg^{-1} $LiBF_4$ between 0 and 1.2 V at a scan rate of 0.1 mV s^{-1}: (a) EMI-FSI + EMI-BF_4 (9:1, v/v), (b) EMI-FSI + EMI-BF_4 (3:1, v/v) and (c) EMI-FSI + EMI-BF_4 (1:1, v/v).

peak at 0.6 V became more evident when compared to the above EMI-FSI + EMI-BF_4 (9:1, v/v) system. Furthermore, concerning EMI-FSI + EMI-BF_4 (1:1, v/v) with 0.32 mol kg^{-1} $LiBF_4$, (the anion molar ratio was FSI:BF_4 = 1.00:1.65), a significant irreversible reduction of EMI cation had taken place at ca. 0.6 V at the first cycle, and then no reversible current response was observed at all as shown in Fig. 3(c). When the test cell was dismantled after the repeated cycles, there was evidence of the decomposition of EMI cation via that irreversible reduction.

Generally, additives improving reversibility of negative electrodes for rechargeable Li batteries have been known to function above their critical concentration, which is typically below 10 vol.%, e.g. 3–5 vol.% for VC [4,5]. Because known additives work mainly on an electrode–electrolyte interface to give a thin solid–electrolyte interface (SEI) layer, the sufficient amount for their function is quite low [12]. Moreover, once additive amount reaches the critical concentration, no evident change is observed any longer in the reversibility above the critical concentration.

In contrast, the present results suggest that a sufficient ratio of FSI to the other anion for the reversible Li intercalation is quite subject to change with the kind of other anion. Rather, looking at the concomitance of reversible and irreversible responses in Fig. 3(a) and (b), there seems to be no "critical" ratio of FSI to BF_4 for the reversible reaction. Furthermore, concerning the EMI-FSI + EMI-TFSI systems in Fig. 2, the ratio of FSI to TFSI appears to correlate rather with the magnitude of reversible currents on Li intercalation/de-intercalation without the presence of obvious critical FSI ratio to generate the reversibility. These characteristics observed in Figs. 2 and 3 seem to be contradictory to the typical SEI mechanism known in common additives.

Thus we suggest that the effect of FSI on the reversibility would essentially correlate with the ionic structure of the present ionic liquid electrolytes. Recently, some papers reported on specific interactions between EMI^+, BF_4^-, and Li^+ [13–15]. They demonstrated that there should be a well-defined structure of ionic atmosphere in ionic liquid bulk, and especially suggested the existence of strong interaction between Li^+ and BF_4^- as well as the resulting ion cluster. Judging from our results of the potential cycling, the presence of FSI can promote Li cation migration into a carbon electrode and, at the same moment, can prevent EMI decomposition at ca. 0.6 V. This effect implies that FSI anion can mobilize Li cation escaping from the electrostatic inter-ionic cage, and in consequence, EMI cation alternatively recedes from the electrode interface, hence avoiding its reductive decomposition, although such possibility has not fully been confirmable. We will continue to investigate the origin of the FSI effect. Nonetheless, it is quite surprising that the introduction of FSI anion to ionic liquid electrolyte systems drastically changes the cycling reversibility of a graphitized carbon.

4. Conclusions

Cyclic voltammetry of the graphitized electrode in the ionic liquid electrolytes containing FSI with another anion, TFSI or BF_4, suggests that the magnitude of reversible current for Li intercalation correlates with the relative quantity of FSI to the other anion in the electrolytes without an evident critical concentration of FSI for its function, and that the correlative tendency much differs between TFSI and BF_4 as coexistent anion. Moreover, even the concomitance of reversible and irreversible responses was observed in the FSI-based ionic liquids containing BF_4. These characteristics appear to be contradictory to a typical SEI mechanism involving common additives. Then there is a possibility that FSI can energetically mobilize Li cation from an electrostatic inter-ionic cage into the electrode while EMI cation alternatively recedes from the electrode interface, hence avoiding its reductive decomposition.

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References

[1] H. Nakagawa, S. Izuchi, K. Kuwana, Y. Aihara, J. Electrochem. Soc. 150 (2003) A695.

[2] Y. Katayama, M. Yukumoto, T. Miura, Electrochem. Solid-State Lett. 6 (2003) A96.
[3] M. Holzapfel, C. Jost, P. Novak, Chem. Commun. 10 (2004) 2098.
[4] M. Holzapfel, C. Jost, A. Prodi-Schwab, F. Krumeich, A. Wursig, H. Bupa, Carbon 43 (2005) 1488.
[5] H. Zheng, K. Jiang, T. Abe, Z. Ogumi, Carbon 44 (2006) 203.
[6] K. Ui, T. Minami, K. Ishikawa, Y. Idemoto, N. Koura, J. Power Sources 146 (2005) 698.
[7] H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kikuta, E. Ishiko, M. Kono, J. Power Sources 160 (2006) 1308.
[8] M. Ishikawa, T. Sugimoto, M. Kikuta, E. Ishiko, M. Kono, J. Power Sources 162 (2006) 658.
[9] H. Nakagawa, Y. Fujino, S. Kozono, Y. Katayama, T. Nukuda, H. Sakaebe, H. Matsumoto, K. Tatsumi, J. Power Sources 174 (2007) 1021.
[10] A. Guerfi, S. Duchesne, Y. Kobayashi, A. Vijh, K. Zaghib, J. Power Sources 175 (2008) 866.
[11] E. Markevich, V. Baranchugov, G. Salitra, D. Aurbach, M.A. Schmidt, J. Electrochem. Soc. 155 (2008) A132.
[12] T. Sugimoto, M. Kikuta, E. Ishiko, M. Kono, M. Ishikawa, J. Power Sources 183 (2008) 436.
[13] C.G. Hanke, S.L. Price, R.M. Lynden-bell, Mol. Phys. 99 (2001) 801.
[14] K. Hayamizu, Y. Aihara, H. Nakagawa, T. Nukuda, W.S. Price, J. Phys. Chem. B 108 (2004) 19527.
[15] Y. Fukuda, R. Tanaka, M. Ishikawa, Electrochemistry 75 (2007) 589.