

Short communication

Pure ionic liquid electrolytes compatible with a graphitized carbon negative electrode in rechargeable lithium-ion batteries

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Abstract

Ambient temperature ionic liquids composed of bis(fluorosulfonyl)imide (FSI) as an anion and 1-ethyl-3-methylimidazolium (EMI) or *N*-methyl-*N*-propylpyrrolidinium (P-13) as a cation have the following desirable physicochemical properties, particularly for a battery electrolyte: a high ionic conductivity, low viscosity, and a low melting point. While an irreversible cationic intercalation into graphene interlayers at ca. 0.5 V versus Li/Li⁺ has been a significant and common problem with usual ionic liquids, we found that ionic liquids containing FSI with the Li cation can prevent such an irreversible reaction and provide reversible Li intercalation into graphene interlayers. Our experimental results found the reversible capacity of a graphite negative electrode, in a half-cell with EMI-FSI containing the Li cation as an electrolyte, to be a stable value of approximately 360 mAh g⁻¹ during 30 cycles at a charge/discharge rate of 0.2 C. The present paper may be the first report that a “pure” ionic liquid can provide a stable, reversible capacity for a graphitized negative electrode at an ambient temperature without any additives or solvents when an appropriate counter anion, e.g., FSI, is selected.

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1. Introduction

Lithium (Li)-ion secondary batteries have desirable characteristics such as a high energy density, less self-discharge, and a negligible memory effect when compared with other secondary batteries. Consequently, they have been applied to not only small electronic devices but also to relatively large power-source systems. Although Li-ion batteries are considered to be promising rechargeable power sources for next-generation HEVs, their reliability, especially regarding a safety function to inhibit combustion, must be improved to realize large, high-power, and high-voltage Li-ion batteries applicable to commercial or public vehicles.

Focusing on general aspects of material technology for Li-ion batteries, graphitized carbon has been used as a major

negative electrode material in commercial Li-ion batteries. Natural graphite and its derivatives have been regarded as especially desirable due to their high specific capacity, low operational potential, as well as their superior cycling behavior [1,2]. The electrochemical behavior of natural graphite negative electrodes has been widely known to depend strongly on the applied electrolyte's composition. Although, in general, organic binary or ternary electrolytes with a wide potential window have been used, Li-ion batteries with such conventional organic electrolytes feature some particularly risky aspects due to the volatile and inflammable properties of organic solvents when they encounter an accident or abuse: short-circuiting, overcharging, and stinging in destruction.

In this context, 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 across a wide temperature range, maintaining a liquid phase as well as acceptable conductivity. Their desirable features have encouraged many investigators to

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attempt to apply them to energy storage devices such as Li-ion secondary batteries [3–11] and electric double-layer capacitors [12–16]. Fung et al. examined electrochemical properties of an ionic liquid as an electrolyte in a cell system comprising Li–Al (as a Li-alloy negative)/1-ethyl-3-methylimidazolium chloride (EMI-Cl) + C₆H₅SO₂Cl (as an ionic-liquid electrolyte) / LiCoO₂ (as a positive) [3]. Nakagawa et al. reported on Li-ion batteries with ionic liquids such as EMI-BF₄, choosing Li₄Ti₅O₁₂ as the negative electrode material to avoid cathodic decomposition of the ionic-liquid electrolytes during charge–discharge cycles [5]. A grave shortcoming of ionic liquid electrolytes has been their poor charge–discharge efficiency at the graphitized negative electrode. This is an essential reason why the above researchers had to use the Li-alloy and metal oxide negative electrode instead of graphitized carbon, even though the alternative negative electrodes have a higher operational potential and lower cycling efficiency than those of a graphitized negative.

To obtain an acceptable cycling efficiency for a graphitized negative electrode in ionic liquid electrolytes, the addition of some functional solvent to ionic liquid electrolytes has been considered necessary. The addition of a suitable 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 component. Recently, for example, Holzapfel et al. reported a reversible Li intercalation into an artificial graphite in a 1 M LiPF₆ solution of EMI-bis(trifluoromethylsulfonyl)imide (EMI-TFSI) containing 5 wt.% of vinylene carbonate (VC) as a solvent additive [8,9]. Furthermore, Zheng et al. reported the effect of various solvent additives, including VC, on the cycleability of a graphitized negative electrode in an ionic liquid [10].

Despite many attempts to produce one, there have been no reports to date of a “pure” ionic liquid that provides reversible charging–discharging of a graphitized negative electrode at ambient temperature without any additives. In response, in the present study we focus on the electrochemical properties and cycle performance of ambient-temperature ionic liquids containing bis(fluorosulfonyl)imide (FSI) as an anion. In particular, we wish to report herein our findings that EMI-FSI containing a Li salt can provide a theoretical reversible capacity for a graphitized negative electrode during repeated cycling, without any additives.

2. Experimental

EMI-FSI, *N*-methyl-*N*-propylpyrrolidinium (P13)-FSI, indicated in Fig. 1, and EMI-TFSI were produced by Dai-ichi Kogyo

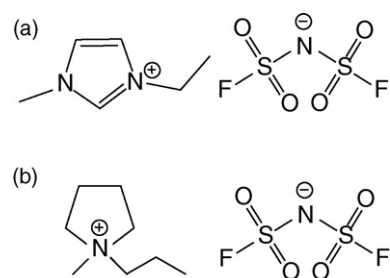


Fig. 1. Chemical structures of (a) EMI-FSI and (b) P13-FSI.

Seiyaku Co., Ltd. The ionic liquids contain less than 10 ppm (w/w) of moisture and less than 2 ppm (w/w) of halide and alkali metal-ion impurities. Li salts, LiTFSI and LiPF₆, were purchased from Kishida Chemical Co., Ltd. and used without further purification.

To prepare the negative electrode material for charge/discharge cycling tests, first we blended natural graphite (HQB12: Hydro-Québec) with carbon black (SFG6: Timcal Inc.), and introduced them to water, adding a 40 wt.% aqueous suspension of styrene butadiene rubber (BM400-B: Nihon Zeon Co., Ltd.) as a binder precursor and carboxymethyl cellulose (mean molecular weight: ca. 130,000) as a dispersant. After the mixture became a homogenous paste in an agitated vessel, the paste was cast onto 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 electrode resulting from this procedure comprised 95 wt.% of natural graphite, 3 wt.% of carbon black, 1 wt.% of binder, and 1 wt.% of dispersant. The foil electrode was cut into a disk of 1.13 cm² in area, with a total thickness of 90 μm—including the copper foil thickness of 20 μm.

A two-electrode coin cell was used as a charge–discharge test cell. Lithium ion-containing ionic liquid electrolytes were prepared by dissolving LiTFSI in EMI-TFSI, EMI-FSI, or P13-FSI, where the LiTFSI concentration was 0.8 M. A battery-grade Li foil was used as a counter electrode, and 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.

3. Results and discussion

Table 1 lists the melting point, viscosity, ionic conductivity, and temperature inducing 5% weight loss of EMI-FSI, P13-FSI, and EMI-TFSI. EMI-FSI and P13-FSI were found to be thermally stable below ca. 490 K, though this is lower than the

Table 1
Characteristics of EMI-FSI, P13-FSI, and EMI-TFSI

Ionic liquid	Melting point (K)	Viscosity (mPa s, 298 K)	Ionic conductivity (mS cm ⁻¹ , 298 K)	5% Weight loss temperature (K)
EMI-FSI	260.1	24.5	16.5	498
P13-FSI	255.5	52.7	8.3	490
EMI-TFSI	256.8	45.9	8.4	647

corresponding temperature for EMI-TFSI, 647 K. The FSI anion should obviously contribute to a low viscosity and high ionic conductivity of EMI-FSI when compared to the corresponding properties of EMI-TFSI, probably due to its being smaller than the TFSI anion while maintaining effective negative-charge delocalization similar to that of the TFSI anion. Generally, the application of small ions can enhance the carrier density per unit volume of ionic liquid bulk, and hence produce high ionic conductivity [17]. An excessively small ion should, however, have a high charge density that tends to increase the liquid's bulk viscosity and sometimes even its melting point. Nevertheless, EMI-FSI has a lower viscosity and maintains a liquid state even at ambient temperature. EMI-FSI has a high ionic conductivity of 16.5 mS cm^{-1} , a value that may be the highest among all ionic liquid conductivities ever reported. Furthermore, both EMI-FSI and P13-FSI have very favorable solubility for an additional Li salt, which encouraged us to apply Li salt/both FSI systems to Li-ion battery electrolytes.

The electrochemical behavior of a natural graphite electrode in EMI-TFSI, EMI-FSI and P13-FSI dissolving LiTFSI (0.8 M) was investigated using cyclic voltammetry. The voltammograms in Fig. 2 were obtained between 0 and 1.2 V versus Li/Li⁺ at a scan rate of 0.1 mV s^{-1} , with each cycling starting from respective open-circuit voltages. In the LiTFSI/EMI-TFSI system shown in Fig. 2(a), EMI intercalation was observed at ca. 0.6 V with a slight response of EMI de-intercalation at 1.0 V at the first cycle. Both peaks almost disappeared, however, in the second cycle, suggesting that a significant irreversible reduction had taken place, 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 mainly during the first charge. On the other hand, looking at the LiTFSI/EMI-FSI system shown in Fig. 2(b), there is no cathodic peak present 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. Such a desirable, reversible behavior is likely to be due to the presence of FSI anions because reversible Li cycling was observed in not only the EMI-FSI system but also the P13-FSI system, as Fig. 2(c) shows.

Figs. 3 and 4 respectively show the charge–discharge voltage profiles and the discharge capacities, at a rate of 0.2 C, for the natural graphite negative electrode with a Li counter electrode in the various electrolytes. During the first charge of the natural graphite in the LiTFSI/EMI-TFSI electrolyte, there was no voltage plateau characteristic of Li intercalation, although we did observe a tiny pseudo-plateau (corresponding to only ca. 4 mAh g^{-1}) at around 0.5 V, which can be ascribed to an irreversible EMI intercalation as shown in Fig. 3(a). In accordance with this poor result, no discharge capacity was observed at all throughout the galvanostatic cycling for this system, as Fig. 4 illustrates. In contrast, the discharge capacity of natural graphite in the LiTFSI/EMI-FSI electrolyte was about 360 mAh g^{-1} even in 30 cycles; degradation in the cycling can hardly be observed at all. The system's voltage profile was quite smooth and almost identical to that for a typical common electrolyte system, ethy-

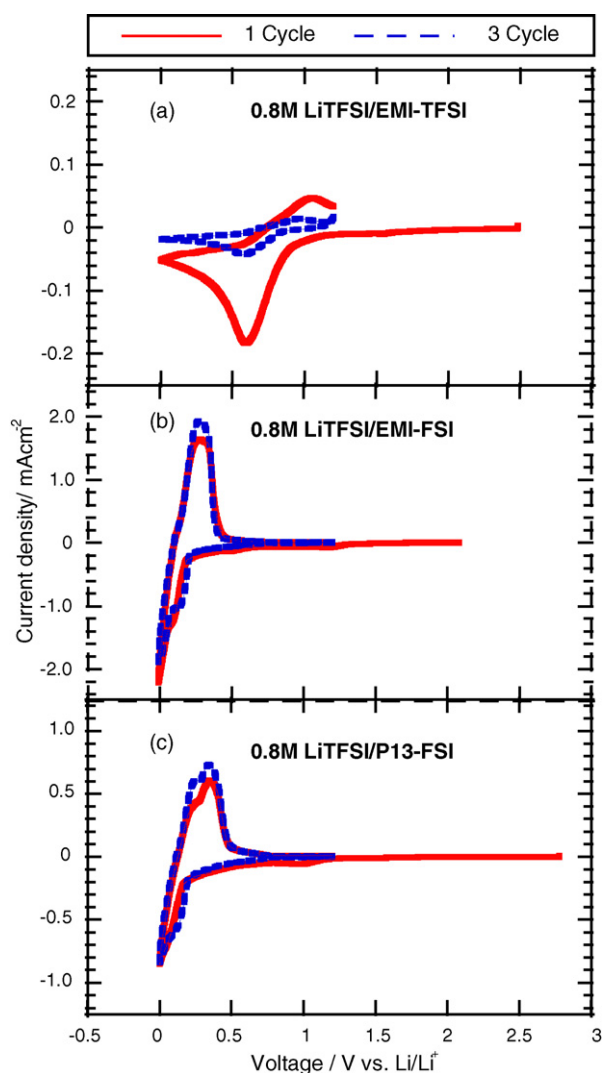


Fig. 2. Cyclic voltammograms of natural graphite in various ionic liquid electrolytes between 0 and 1.2 V at a scan rate 0.1 mV s^{-1} : (a) 0.8 M LiTFSI/EMI-TFSI, (b) 0.8 M LiTFSI/EMI-FSI, (c) 0.8 M LiTFSI/P13-FSI.

lene carbonate mixed with diethyl carbonate (EC + DEC) containing 1 M LiPF₆, as shown in Fig. 3(b). The stability of the LiTFSI/EMI-FSI system's discharge capacity favorably compares with that of the EC + DEC solvent system in Fig. 4. Judging from these results, the solid–electrolyte interface (SEI) formed in the electrolytes containing FSI in the first cycle would be stable. Furthermore, it would play a decisive role in protecting a carbon electrode against an undesirable irreversible reaction, especially the decomposition of the organic cation component, which has been a fatal problem yet to be solved in most ionic liquid electrolytes for Li-ion batteries. Although further investigation is essential to elucidate a reasonable FSI effect, it is quite surprising that only an exchange from TFSI to FSI as an anion species can drastically improve the cycling properties of a graphitized negative electrode.

Kasajima et al. reported successful Li intercalation/de-intercalation at a graphitized negative electrode in a LiBr–KBr–CsBr electrolyte (as a “pure” ionic liquid, with-

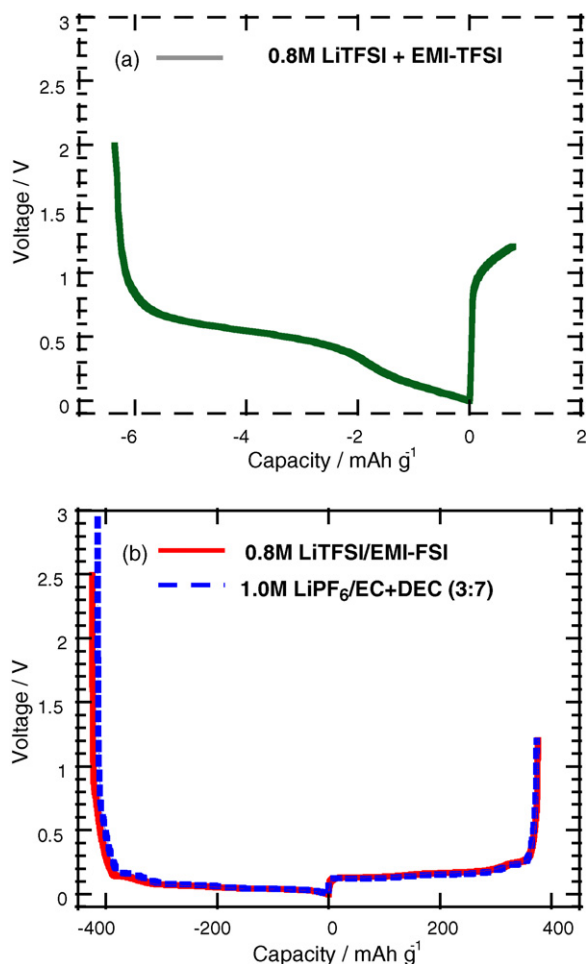


Fig. 3. Charge–discharge profiles of natural graphite during the first cycle, with various electrolytes at a charge–discharge rate of 0.2 C: (a) 0.8 M LiTFSI/EMI-TFSI, (b) 0.8 M LiTFSI/EMI-FSI and 1.0 M LiPF₆/EC + DEC (3:7 vol. ratio).

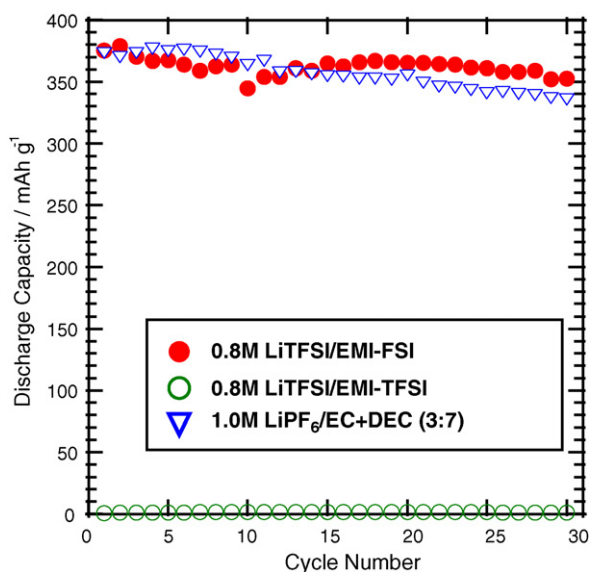


Fig. 4. Discharge capacities of natural graphite with various electrolytes during 30 cycles at a charge–discharge rate of 0.2 C.

out any solvent additives) [11]. Their cycling tests with the eutectic liquid were performed at 523 K; the ionic system is a solid state at ambient temperature. To the best of our knowledge, the present Li ionic liquid electrolytes containing the FSI anion are the first examples to provide good cycle performance with a carbon negative electrode at ambient temperature: an ideal reversible, stable capacity of 360 mAh g⁻¹, which is almost equal to the theoretical value without any solvents or additives.

4. Conclusions

One particular ionic liquid, EMI-FSI, has outstanding physicochemical properties particularly for a battery electrolyte: a high ionic conductivity, low viscosity, and a low melting point. The results from experiments on the FSI liquids revealed that no irreversible cathodic current peak on a graphite negative electrode, observed for LiTFSI/EMI-TFSI at ca. 0.6 V versus Li/Li⁺, could be seen for LiTFSI/EMI-FSI or LiTFSI/P13-FSI. Furthermore, the reversible capacity of a graphite negative electrode in a half-cell with LiTFSI/EMI-FSI as the electrolyte was stable at approximately 360 mAh g⁻¹ during 30 cycles at a rate of 0.2 C. This paper's results confirm that when FSI is selected as the counter anion, a “pure” ionic liquid can provide a stable, reversible capacity for a graphitized negative electrode without any additives or solvents at ambient temperature.

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