A New Prospect for Stabilization of Graphite Electrode/Electrolyte Interface in Bis(fluorosulfonyl)imide Anion-based Ionic Liquid Electrolyte

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ABSTRACT

We investigated effects of high lithium bis(fluorosulfonyl)imide (LiFSI) salt concentration or heat treatment before initial charge on charge-discharge performance of a graphite electrode in a 1-ethyl-3-methylimidazolium (EMImFSI)-based ionic liquid (IL) electrolyte. LiF was observed at the surface of graphite electrodes taken out from 2.00 mol kg$^{-1}$ LiFSI/EMImFSI system and from 0.32 mol kg$^{-1}$ LiFSI/EMImFSI system with pre-heat treatment before the initial charge. The surface LiF effectively suppresses the reductive decomposition of EMIm$^+$. As a result, the irreversible capacity of initial cycle was significantly suppressed and the coulombic efficiency of subsequent cycles was greatly improved.

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Keywords : FSI Anion Based Ionic Liquid, Graphite Electrode/Electrolyte Interface, SEI Film

1. Introduction

Improvement of the safety of Li-ion batteries has come to be considered the most important point along with upsizing Li-ion batteries. ILs are promising candidates for electrolyte components that can improve the safety of Li-ion batteries because of their non-flammability. Among various IL-based electrolytes, only FSI$^-$-based IL electrolytes can make a Li-ion battery operate without any electrolyte additives.1-3 The Li-ion batteries assembled with FSI$^-$-based IL electrolytes show quite good electrode/electrolyte interfacial performance.4-6 However, the control of electrochemical stability of EMImFSI-based IL electrolytes at a graphite electrode/electrolyte interface is quite difficult. The electrochemical instability of EMImFSI-based IL electrolytes at the graphite electrode/electrolyte interface would be attributed to EMIm$^+$ insertion into graphene interlayers and its reductive decomposition.7 Furthermore, the behavior of EMIm$^+$ insertion greatly depends on surface structure of graphite particles.8,9 The addition of Li bisoxalateborate is an effective method to form SEI film that can suppress the reductive decomposition of EMIm$^+$.10 However, the use of electrolyte additives leads to an increase in graphite electrode/electrolyte interfacial resistance.11 Therefore, we should consider a new method to form good SEI without any electrolyte additives.

In this study, we found that the slight decomposition of FSI$^-$, which undergoes no electrochemical process at a graphite electrode/electrolyte interface, is promoted by increasing LiFSI salt concentration or heat treatment before the initial charge process. Furthermore, the decomposition products derived from FSI$^-$, which is formed before the initial charge process, can effectively suppress the continuous decomposition of EMIm$^+$.  

2. Experimental

LiFSI salt (Kishida Chemical Co., Ltd.) was dissolved in EMImFSI (DKS Co., Ltd.) with concentrations of 0.32 or 2.0 mol kg$^{-1}$ in an argon-filled glove box with a dew point of $-70^\circ$C and these mixtures were used as IL electrolytes. These electrolyte components have sufficiently high purity (>99%) and their moisture content is sufficiently low (<30 ppm). Graphite particles (Nippon Carbon Co., Ltd., avg. 13.6 µm), acetylene black (Denka Co., Ltd., HS-100), sodium carboxymethyl cellulose (DKS Co., Ltd., F-A) and styrene-butadiene rubber (JSR Corp., TRD 2001) were dispersed in deionized water with a respective weight ratio of 95:3:1:1. The obtained electrode slurry was casted on copper foil (Furkawa electric Co., Ltd., NC-WS, 20 µm) and dried at 80°C in a vacuum oven. The prepared graphite electrode sheet was pressed and cut into 12 mm diameter disks for assembling test cells.

All the graphite electrode half-cells were assembled in an argon-filled glove box. These half-cells were composed of a graphite electrode, a Li foil (Honjo Metal Co., Ltd.) disk with 13 mm diameter as a counter electrode, an IL electrolyte with 0.32 or 2.0 mol kg$^{-1}$ salt concentration, and a highly porous polyolefin film coated with ceramic as a separator (represented as low- or high-concentration system). Some of low-concentration systems were heat-treated at 50°C (generally in an industrial process the temperature has been used for aging after the initial charge for stabilization Li-ion batteries) for 6 hours and returned to room temperature before the initial charge process (represented as low-concentration system with pre-HT).

The charge and discharge measurements were carried out using a charge/discharge unit (Intex Co., BTS2004W). At the initial cycle, the charge and discharge processes were carried out at 1/10 C-rate and the following cycles were conducted at 1 C-rate (= 372 mA g$^{-1}$) in a voltage range of 0.005–1.500 V. 

The chemical compositions of graphite electrode surface in respective graphite half-cells before the initial charge were analyzed by an X-ray photoelectron spectroscopy (XPS, JEOI Ltd., JPS-9010MC) with Mg K$\alpha$ radiation. The graphite electrodes taken out from the graphite half-cells just after assembling or after the heat treatment were carefully washed three times with dimethyl carbonate in an argon-filled glove box and dried for 12 hours in a vacuum. The dried graphite electrodes were transferred from the glove box to the vacuum chamber of XPS apparatus without air exposure. The spectra derived from N 1s (389–409 eV), and F 1s (686–696 eV) were measured as a depth profile with argon etching treatment.
shoulder caused by the reductive decomposition of EMIm$^+$ is observed at around 0.6 V in the low-concentration system. On the other hand, no shoulder at around 0.6 V is observed in the high-concentration system, suggesting that the reductive decomposition of EMIm$^+$ at the graphite surface is suppressed. Judging from these results only, one may speculate that the suppression of the reductive decomposition of EMIm$^+$ in the high-concentration system is attributed to a relative decrease in EMIm$^+$ concentration with an increase in Li$^+$. However, the above speculation is denied by a very interesting result that the reductive decomposition of EMIm$^+$ is suppressed even in the low-concentration system with pre-HT; the effect is the essentially same as what the high-concentration system shows. Since the low-concentration system with pre-HT was charged initially after it was cooled to room temperature, the activity of EMIm$^+$ at the initial charge process should be the same as that without heat treatment. Therefore, we consider that the suppression of the reductive decomposition of EMIm$^+$ in the low-concentration system with pre-HT is achieved by a specific non-electrochemical mechanism affecting the subsequent electrochemical reaction.

3. Results and Discussion

Figure 1 shows the initial charge and discharge curves of the graphite half-cells. Since we selected the graphite particles with edge-rich surface structure where the insertion and the reductive decomposition of EMIm$^+$ relatively tend to occur, a recognizable shoulder caused by the reductive decomposition of EMIm$^+$ is detected at the surface of the graphite electrode taken out from the respective cells before the initial charge process should be the same as that without heat treatment. Therefore, we consider that the suppression of the reductive decomposition of EMIm$^+$ in the low-concentration system with pre-HT is achieved by a specific non-electrochemical mechanism affecting the subsequent electrochemical reaction. Figure 2 shows the discharge capacities (a) and coulombic efficiency (b) vs. cycle number for the graphite half-cells. In the low-concentration system and the high-concentration system, the Coulombic efficiency and the low discharge capacity of the graphite half-cells were observed at the initial charge process.

To investigate what occurs at the graphite surface, the surface of the graphite electrode taken out from the respective cells before the initial charge was analyzed by XPS. Figure 3 shows the XPS spectra related to N 1s (a, b, c) and F 1s (d, e, f) at the graphite electrode surface and the argon etching time is displayed at the left end. Since two peaks at the slightly lower energy than 403 and 401 eV in the N 1s spectra can be also obtained from neat EMImFSI, the corresponding spectra with argon etching time 0 or 1 s in all charts would be derived from residual EMImFSI. Therefore, we discuss only the peaks observed with the etching time of 2–4 s. Although notable peaks are hardly observed in the low-concentration system, the large peaks attributed to LiF are observed in both the high-concentration system and the low-concentration system with pre-HT. These peaks indicate the decomposition of FSI$^-$ because FSI$^-$ is the only fluorine source in this study. It is interesting that LiF detected at the surface of the graphite electrode taken out from the cells before the initial charge; the open circuit voltage (OCV) of the graphite electrode half-cell containing the FSI-based IL electrolyte as just assembled is about 3.0 V, and the OCV does not change during the heat treatment. Furthermore, we found that LiF is similarly formed even when the graphite electrode is immersed in the high-concentration electrolyte or immersed and heat-treated in the low-concentration electrolyte in a sample bottle without a counter electrode. These important results mean that the decomposition of FSI$^-$ at graphite surface occurs without any electrochemical processes regardless of existence of a counter electrode. In other words, our study suggests the advantageous function; FSI$^-$ can form the initial SEI at graphite electrodes before any electrochemical processes. FSI$^-$-based ILs are not thermally decomposed at 50°C.
with or without Li⁺, and LiFSI is also thermally stable at 50°C regardless of moisture content. Therefore, we consider that LiF on the graphite electrode observed in this study is not derived from massive thermal decomposition or hydrolysis of FSI⁻ and that graphite electrode plays an important role in slight decomposition of FSI⁻. However, since the mechanism relating to the decomposition of FSI⁻ without any electrochemical processes has not been clarified sufficiently in this study, we have to elucidate it in our future study.

4. Conclusions

We applied high LiFSI salt concentration or heat treatment before the initial charge to the graphite half-cell assembled with the EMImFSI-based IL electrolyte and succeeded in significantly improving the initial and subsequent cycle efficiency. LiF was found at the surface of the graphite electrode taken out from the high-concentration system and low-concentration system with pre-HT. Furthermore, we found that the LiF formation is attributed to the LiFSI decomposition without any electrochemical process. Our results suggest the beneficial function that FSI⁻ can provide SEI at graphite electrodes before all electrochemical processes, leading to important knowledge for improving cycle stability of Li-ion batteries assembled with FSI-based IL electrolytes.

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