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Electrochemical and in-situ scanning tunneling microscopy studies of bis(fluorosulfonyl)imide and bis(trifluoromethanesulfonyl)imide based ionic liquids on graphite and gold electrodes and lithium salt influence

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HIGHLIGHTS

- In-situ STM is employed to understand compatibility between ILs and graphite.
- The decomposition of FSI forms film which suppresses the intercalation of Py_{13}.
- The decomposition of TFSI etches the surface which makes the intercalation easier.
- The addition of Li salt suppresses the intercalation and exfoliation, especially in $Py_{13}FSI$.
- The surface processes are different on HOPG and Au(111) electrodes.

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ABSTRACT

We report electrochemical and in-situ scanning tunneling microscopy (STM) studies of surface processes on graphite and Au(111) electrodes in N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)imide ($Py_{13}FSI$) and N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide ($Py_{13}TFSI$) ionic liquids in the absence and presence of LiTFSI salt. In both of neat ionic liquids, the intercalation of cations and exfoliation of HOPG layers occur during cathodic excursion. However, the surface decomposition of FSI anions can form an effective protection film on the surface, which suppresses the intercalation and exfoliation processes, while the surface decomposition of TFSI anions mainly causes etching of the surface, which makes the intercalation and exfoliation easier to proceed. The addition of Li salt can promote the formation of the protective film, especially in $Py_{13}FSI$, and thus significantly suppress the intercalation and exfoliation processes. The discrepancies between these two ionic liquids are caused by the different anion interactions with graphite. Additionally, comparisons of the behaviors on HOPG and on Au(111) confirm that the surface processes are crucially dependent on the nature of the electrode. Trace amounts of oxygen and water can cause the formation of a film-like structure on Au(111), but show no apparent influence on HOPG.

1. Introduction

Rechargeable lithium ion batteries are widely used as portable high energy density power sources. However, the safety problems caused by the flammable organic carbonates and the instability of interface between electrolyte and electrode are important issues [1,2]. Ionic liquids (ILs) as electrolytes for lithium ion batteries have attracted considerable attention due to their unique properties such as wide electrochemical window, non-flammability and thermal stability [3,4], which can lead to a great improvement in system safety. Understanding the interfacial property of electrode/IL interface is extremely important for successful applications of ionic liquids in electrochemical energy devices [5]. Ionic liquids containing pyrrolidinium (Py) and piperidinium (PP) cations and bis(trifluoromethanesulfonyl)imide (TFSI) anion show larger

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electrochemical cathodic windows than other types of ILs such as imidazolium based ILs. They also provide low viscosity and high conductivity, and are expected to have good performance when used as electrolytes for lithium batteries [6,7]. The solid electrolyte interphase (SEI) formed on graphite anode in ionic liquid media is mainly composed of the reduction products of the anions of ionic liquids [7–10]. However, the TFSI based ionic liquids are less facile in passivating graphite anode and the charge/discharge efficiency in these electrolytes is very poor. Good compatibility between ILs and graphite electrodes is achieved mostly by the addition of suitable additives which can stabilize and protect the interface between graphite electrodes and the electrolytes against undesirable irreversible reactions [11–18]. Raman investigations indicate that the intercalation of Py_{13} cations into the graphite anode during cathodic polarization is the main reason for the poor compatibility between the TFSI based ionic liquid electrolytes and graphite electrodes [19,20]. In recent years, it has been found that when bis(fluorosulfonyl)imide (FSI) anion is chosen to form ionic liquid with Py cation, the capacity associated with lithium intercalation/de-intercalation process on graphitized negative electrodes becomes more stable and reversible without any additives [21,22]. Moreover, FSI containing ionic liquids exhibit lower viscosities and higher conductivities [21,23–25], which are beneficial to the improvement of performance in lithium batteries [26].

Some studies have already been carried out to understand the interfacial behavior in the Py based ionic liquids formed with the two mentioned types of anions. Li salts can be dissociated in ILs and the released Li^+ ions can be solvated with three FSI anions or two TFSI anions at room temperature, which may promote Li^+ ion transport [27,28]. In addition, AC impedance spectroscopy measurements reveal that presence of FSI anions in ionic liquids can lower the charge transfer resistance of electrode reactions and relieve transport limitation through the surface film [29–31]. An explanation based on the chemistry of SEI is also proposed: The SEI structure formed in the FSI based ILs could ease the mineralization of the products during further reduction of the FSI anions, which suppresses the concurrent generation of organic radicals and gaseous products in side reactions [28].

Although ionic liquids formed with FSI have attractive properties in the interfacial processes of graphite electrode, studies on the influence of Li salt are still inadequate. In order to get deeper insight into the excellent performance of FSI based ionic liquids on graphite electrodes, further fundamental investigations on the interfacial electrochemistry of the systems are necessary.

In-situ scanning probe microscopy is a powerful technique used to characterize interfacial processes, such as morphology changes during a reaction process. Our group has been making efforts in the study of the interfacial electrochemistry in neat ionic liquids employing in-situ scanning probe microscopies [32–35]. Recently, our efforts have been extended to investigate the influence of Li salt on the interfacial process in ionic liquids [36]. In this article, we employ in-situ STM to investigate the surface processes of highly oriented pyrolytic graphite (HOPG) electrode in Py_{13}FSI and Py_{13}TFSI ionic liquids in the absence and presence of Li salt, to understand the discrepancies between these two ionic liquids in the compatibility with graphite as well as the influence of Li salt. The investigation on Au(111) electrode is also carried out to gain further insight into the possible mechanism of the surface processes.

2. Experimental

N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)imide (Py_{13}FSI), was purchased from Kanto Chemical Co., Inc, (Japan, grade for advanced material research), and N-methyl-N-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Py_{13}TFSI) was from IOLITEC (Germany, 99%). Before use, the neat ionic liquids or the liquids containing 0.5 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Aldrich, 99.95%) were dried under vacuum at 100 °C for 24 h to remove the remaining water.

HOPG (Shanghai NTI Co., Ltd, China, ZYB) was used as working electrode. Before use, the HOPG was cleaved freshly by adhesive tape. Graphite powder (expanded graphite) made by thermal expansion of flaky graphite was tested by using powder microelectrode technique [37]. A microcavity electrode was prepared by sealing a Pt wire (110 μm in diameter) into a glass tube and then electrochemical etching the tip of the Pt wire to form a microcavity. The powder was filled into the microcavity of the microelectrode by grinding the microcavity end on the weighting paper. A single crystal bead of Au was prepared according to Clavilier method [38], and one of the (111) facets was used as the electrode for in-situ STM measurements. Prior to each experiment, the Au(111) bead was subject to electrochemical polishing and flame annealing followed by quick transferring into the glove box. Silver wire and platinum ring were used as quasi-reference and counter electrode, respectively, in neat ionic liquids. In the presence of Li salt, the reference and counter electrodes were both lithium wires. The potential of the silver quasi-reference electrode was calibrated with respect to ferrocene and the potential was quoted versus Li^+/Li.

Cyclic voltammetric measurements were performed on a CHI631A electrochemical workstation. In-situ STM experiments were performed on a Nanoscope E (Digital Instrument, USA) under constant-current mode. STM tips were prepared by mechanically cutting a Pt–Ir wire (0.25 mm in diameter) and then insulating with thermosetting polyethylene to reduce the Faradaic current. All the measurements were carried out in an argon-filled glove box.

3. Results and discussion

3.1. Comparative study of HOPG/IL interfaces in Py_{13}FSI and Py_{13}TFSI

3.1.1. HOPG in neat ionic liquids

The electrochemical behaviors of HOPG electrode in neat Py_{13}FSI and Py_{13}TFSI are investigated using cyclic voltammetry (CV) as shown in Fig. 1. The CVs in a narrow range between 0.5 and 3.0 V are provided for detailed inspection, refer to the inset of

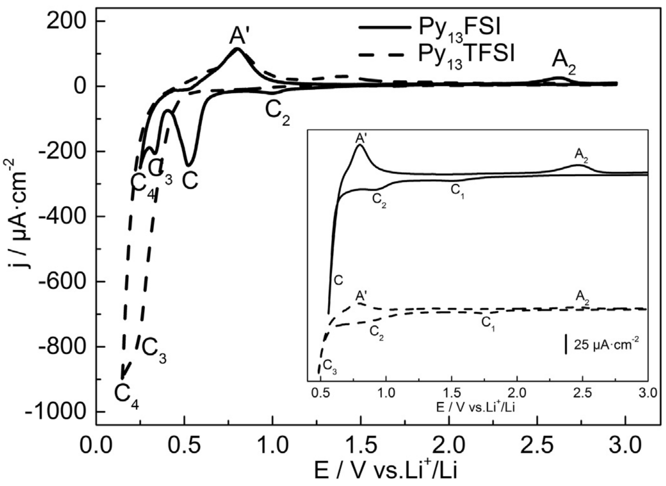

Fig. 1. Cyclic voltammograms of HOPG electrode recorded at a scan rate of 50 mV s^{-1} in Py_{13}FSI (solid line) and Py_{13}TFSI (dashed line).