Enabling bis(fluorosulfonyl)imide-based ionic liquid electrolytes for application in dual-ion batteries

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HIGHLIGHTS

- Evaluation of electrolyte additives in $Pyr_{14}FSI/LIFSI$-based dual-ion cell.
- Systematic study of anodic aluminum current collector dissolution.
- $LiPF_6$, $LiBF_4$ and MDFA additives significantly improve the dual-ion cell performance.
- FSI-based dual-ion cell with 91% capacity retention after 1000 cycles.

GRAPHICAL ABSTRACT
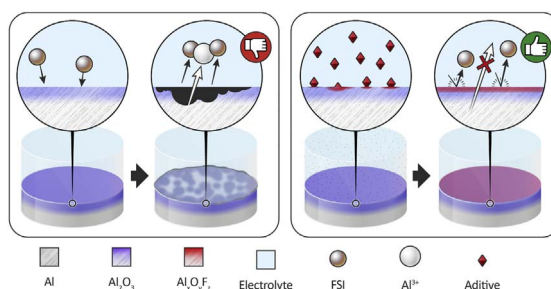
Al Al_2O_3 $Al_xO_yF_z$ Electrolyte   FSI Al^{3+} Aditive

ARTICLE INFO

ABSTRACT

In this work, we present a comprehensive study on the effect of adding different conductive salt additives including $LiPF_6$, $LiBF_4$ and LiDFOB, as well as the fluorinated solvent additive methyl difluoroacetate (MDFA) to a bis(fluorosulfonyl)imide (FSI)-based ionic liquid (IL) electrolyte, i.e. $Pyr_{14}FSI/LiFSI$, to protect the Al current collector (ACC) from anodic dissolution and, thus, enable reversible charge/discharge cycling in a high performance dual-ion cell. Chronocoulometry and scanning electron microscopy measurements were conducted to evaluate the specific ACC passivation ability of each electrolyte. Furthermore, the influence of these additives on anion intercalation behavior into the graphite positive electrode with special emphasis on the Coulombic efficiency (CE), reversible capacity, as well as capacity retention is presented. Overall, we can show that the addition of small amounts of $LiPF_6$, $LiBF_4$ and MDFA (0.5 wt%) into the FSI-based IL electrolyte significantly increases the overall cell performance, whereas LiDFOB as electrolyte additive deteriorates the dual-ion cell performance. In addition, an excellent cycling performance for 1000 cycles is obtained for the $Pyr_{14}FSI$ electrolyte having 5 wt% $LiPF_6$, displaying an average reversible capacity of 40 mAh g^{-1}, a CE exceeding 98% and a capacity retention of 91%, which has not been reported so far.

1. Introduction

Beside the lithium ion battery (LIB), which can be considered as state-of-the-art benchmark technology for various small-scale and large-scale applications [1–3], such as electro mobility or stationary energy storage, there is a large number of alternative and advanced battery technologies that have been intensively studied in the recent years. These commonly called "post-lithium ion" or "post-lithium" technologies include e.g. metal/sulfur and metal/air systems, all-solid-state batteries, batteries based on alternative single or multivalent ions

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(Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, etc.), dual-ion or dual-carbon batteries *etc.* [4–7]. The invention of an ultrafast rechargeable aluminum-ion battery in 2015, based on the electrochemical deposition and dissolution of aluminum at the anode, and intercalation/de-intercalation of chloroaluminate anions (AlCl$_4$$^-$) from an ionic liquid (IL)-based electrolyte into a graphite based cathode, attracted great attention in the research field of dual-ion batteries [8]. Against this backdrop, the utilization of an IL-based electrolyte for the application in dual-ion batteries (DIBs) is rooted in the unique and encouraging properties of this electrolyte class, first established by the works of Placke et al. in 2012 [9,10]. Due to the high cathode potentials during anion intercalation into graphite ($\approx$ 5 V *vs.* Li/Li$^+$), the high oxidative stability of selected ILs can sustainably improve the overall cell performance of this system, especially in terms of Coulombic efficiency (CE) and energy efficiency (EE) [11,12] as well as capacity retention and safety [13–22].

In previous studies, several imide-based ILs have been investigated in view of a potential application as electrolyte in dual-ion systems [7,10,13–15,19,23,24]. In further emphasis of the above statements, IL electrolytes based on the bis(fluorosulfonyl)imide (FSI) anion attracted great interest due to the manifold unique properties such as their low viscosity, comparatively high ionic conductivity, as well as the compatibility of these ILs with graphitic anodes [25–28]. Based on the work of Yamane et al. in 2012 [29], Fukutsuka et al. reported on the electrochemical formation of a stage-1 graphite intercalation compound (GIC) with a calculated composition of C$_{36}$FSI, using highly oriented pyrolytic graphite (HOPG) as model electrode [30]. Furthermore, Beltrop et al. confirmed the reversible electrochemical intercalation/de-intercalation of FSI anions into a graphitic host structure from a pyrrolidinium (Pyr$_{14}$)-based IL electrolyte [13]. However, the missing ability of FSI-based ILs to form an effective passivation layer at the aluminum current collector (ACC) surface leads to ongoing aluminum (Al) dissolution during anodic polarization (> 4.0 V *vs.* Li/Li$^+$), restricting their application as electrolyte solvent to low voltage energy storage systems so far [31,32]. In general, this anodic dissolution reaction is erroneously called "Al corrosion" in the literature [33]. Interestingly, Liu et al. confirmed the compatibility of piperidinium-FSI electrolyte with the ACC, however, merely at an upper cut-off potential of 4.2 V *vs.* Li/Li$^+$ [34]. Further studies commented on the missing ability of FSI-based ILs to form an effective passivation layer on Al, as reported by Kühnel et al. [31]. In contrast to TFSI-based ILs, it is assumed that the severe pit formation found at the ACC surface results from the increased solubility of the formed [Al(FSI)$_x$]$^{3-x}$ species in the specific IL electrolyte [32,35]. Moreover, halides such as chloride, as possible remaining impurities from the synthesis process were found to have a large impact on increasing Al dissolution [31,36]. Even though, the influence of halide impurities or even bulk halide electrolytes [8] on the electrochemical stability of the ACC has not been systematically investigated so far.

In general, there is a big difference between organic solvent and IL-based electrolytes in view of the compatibility of imide-based conductive salts with the ACC [37–40]. It is assumed that the different solubility of subsequently formed [Al (imide)$_x$]$^{3-x}$ species on the ACC by electrochemical oxidation in the specific electrolytes plays a crucial role in view of the stability of the Al passivation layer [41]. Recently, Meister et al. proposed a mechanism of anodic Al dissolution in imide-based electrolytes and figured out the importance of the attack of acidic species on the native Al$_2$O$_3$ layer in the first step and the influence of the electrolyte's dielectric constant on the dissolution of bare aluminum in the second step [39]. Several studies consider ways and means to protect the ACC from electrochemically induced Al dissolution in imide-based electrolytes, including the protection of the Al surface by coatings [42] as well as the application of nitrile, fluorinated or highly concentrated solvents, as well as the addition of liquid fluorine-containing electrolyte additives [33,43–50].

Another major attempt focuses on the approach of applying fluorine-containing conductive salts as electrolyte salt additives, such as

LiPF$_6$, LiDFOB or LiBF$_4$, to passivate the ACC from electrochemically induced Al dissolution [43,51–55]. For example, Cho et al. investigated the positive influence of the addition of the film forming conductive salt LiPF$_6$ on the Al dissolution in an FSI-based IL electrolyte [32]. Our work is influenced by this approach and presents a comprehensive study of the addition of different conductive salt additives including LiPF$_6$, LiBF$_4$, LiDFOB as well as an fluorinated solvent additive (MDFA) to an IL-based electrolyte consisting of Pyr$_{14}$FSI/LiFSI in order to protect the ACC from anodic Al dissolution. Chronocoulometry (CC) studies followed by SEM measurements were performed to evaluate the specific passivation ability of each additive on the Al working electrode. Furthermore, the influence of these electrolyte additives on the anion intercalation behavior of a series of IL-based electrolytes into the graphite positive electrode for the dual-ion system with special emphasis on the Coulombic efficiency, reversible capacity as well as capacity retention is presented.

2. Experimental

2.1. Electrode and electrolyte preparation

Electrode tapes for the positive electrode consist of 90 wt% KS6L graphite (Imerys Graphite & Carbon), 5 wt% of conductive carbon black agent C-nergy™ Super C65 (Imerys Graphite & Carbon) and 5 wt% of sodium carboxymethylcellulose (Na-CMC) as binder (Walocel CRT 2000 PPA 12, Dow Wolff Cellulosics). The preparation process of the electrodes was performed as reported in our previous publication [17]. The average mass loading of the electrodes was 2.0 $\pm$ 0.1 mg cm^{-2}. The electrode coating thickness resulted in $\approx$ 23 μm and the electrode porosity of the composite electrode was calculated to $\approx$ 61%. However, it was shown in previous publications that the electrode thickness, and most likely also the porosity of the graphite cathode, will change during reversible anion intercalation/de-intercalation [56,57].

For the preparation of the different electrolyte solutions, the following reagents and materials were used: *N*-butyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide (Pyr$_{14}$FSI; Solvionic; purity: 99.9%), lithium bis(fluorosulfonyl)imide (LiFSI; American Elements; purity: > 99%), lithium difluorooxalatoborate (LiDFOB; Sigma Aldrich), lithium hexafluorophosphate (LiPF$_6$; Sigma Aldrich; purity: > 99%), lithium tetrafluoroborate (LiBF$_4$; Sigma Aldrich; purity: > 99%) methyl difluoroacetate (MDFA; Sigma Aldrich; purity: > 96%) were purchased and used as received.

An electrolyte mixture of Pyr$_{14}$FSI with 0.3 M of the conductive and electroactive lithium salt LiFSI was used as baseline electrolyte. Furthermore, 0.5 wt% of the specific electrolyte additive (LiDFOB, MDFA, LiPF$_6$ or LiBF$_4$) was dissolved in the baseline electrolyte. The ratios of FSI$^-$: DFOB$^-$, FSI$^-$:PF$_6$$^-$ and FSI$^-$:BF$_4$$^-$ anions are 93:1, 98:1 and 61:1, respectively. The electrolyte preparation and storage as well as the cell manufacturing were carried out in an argon filled glove box (H$_2$O and O$_2$ < 0.1 ppm). Prior to use, the IL was dried, applying an ultra-high vacuum procedure (< 1·10^{-2} Pa). The water content of the IL was less than 10 ppm, as determined by Karl Fischer titration.

2.2. Cell preparation and electrochemical characterization

All electrochemical measurements were conducted in lab-scale Swagelok type T-cells with a three-electrode set-up, as described previously [9,10]. For both, the negative and the reference electrodes, high-purity metallic lithium foil (Albemarle Corporation) were applied. A glass microfiber filter (Whatman; grade GF/D) soaked with 120 μL of the corresponding electrolyte was used as separator. To ensure a sufficient wetting of the graphite electrodes by the viscous IL-based electrolyte, the assembled cells were equilibrated for 24 h at room temperature (20 °C) before electrochemical characterization.

The reductive and oxidative stability limits of various electrolyte compositions were obtained by means of linear sweep voltammetry