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Dual-Ion Cells based on the Electrochemical Intercalation of Asymmetric Fluorosulfonyl-(trifluoromethanesulfonyl) imide Anions into Graphite

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In this work, we investigate the electrochemical intercalation of the asymmetric fluorosulfonyl-(trifluoromethanesulfonyl) imide ($FTFSI^-$) anion into a graphite-based cathode for application in dual-ion cells. Since $FTFSI^-$ anions are smaller than bis(trifluoromethanesulfonyl) imide ($TFSI^-$) anions, a higher specific capacity can be expected as the decreased anion size should lead to an enhanced receptivity of the anions between the graphene sheets of graphite. The discharge capacity and the coulombic efficiency are studied at varying upper charging end potentials ranging from 4.8 V to 5.2 V vs. Li/Li$^+$. At these varying conditions a discharge capacity of 43 mAh g^{-1} to 99 mAh g^{-1} is obtained, respectively. However, the increase of the upper cut-off potential leads also to a decrease of the coulombic efficiency.

To gain a better insight into the influence of the anion size on the performance, $FTFSI^-$ and $TFSI^-$ intercalation is discussed on a comparative basis, with respect to the potential range for anion intercalation/de-intercalation, the discharge capacity and efficiency. We observed a lower coulombic efficiency, caused by the lower electrochemical stability, as well as an enhanced discharge capacity for all investigated upper cut-off potentials for the intercalation/de-intercalation of $FTFSI^-$ compared to $TFSI^-$ anion uptake/release.

1. Introduction

In 1938, Rüdorff and Hofmann introduced the concept of graphite oxidation by electrochemical intercalation of HSO_4^- anions from an aqueous electrolyte between graphite sheets. [1] In patents by McCullough [2–4] and the work by Carlin et al. [5] a new battery device has been presented, the so-called "dual-graphite cell" [6], in which graphite was used as both, the negative and the positive electrode material. In this electrochemical cell, not only the two graphite electrodes serve as the active materials but also the electrolyte. During the charging process, the cations are intercalated into the negative electrode, thus reducing the graphitic anode. Simultaneously, the anions are intercalated into the positive electrode accompanied by the oxidation of the graphitic cathode. The reverse reactions take place during the discharging process; the anions and cations are released back into the electrolyte. [5] This change in the salt concentration influences physical properties of the electrolyte, such as conductivity and viscosity. Hence, an increase of the state of charge yields a decreased conductivity. Further investigations on this concept have been conducted by Seel and Dahn and by Ishihara et al. [6–9] In their works, organic solvent-based electrolytes, such as sulfones or mixtures of carbonates with $LiPF_6$ as the electrolyte salt, were investigated.

However, the high oxidizing potentials for the anion uptake into the graphitic cathode (above 4.5 V vs. Li/Li$^+$) in combination with the limited stability of organic solvents resulted in an insufficient coulombic efficiency and strong electrolyte degradation. [7] In addition, the application of organic solvent-based electrolytes along with graphitic electrodes can lead to solvent co-intercalation reactions into graphite, which thus can result in graphite exfoliation. [10–14]

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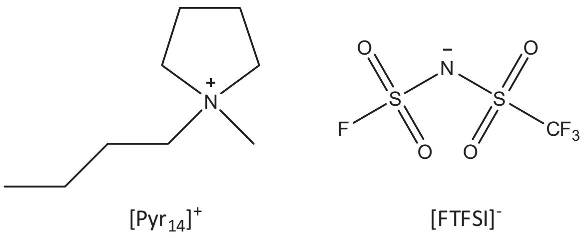

Fig. 1. Chemical structure of *N*-butyl-*N*-methylpyrrolidinium fluorosulfonyl-(trifluoromethanesulfonyl) imide ($Pyr_{14}FTFSI$).

Placke et al. [15–18] proposed a so-called "dual-ion cell", where metallic lithium is used as the negative electrode and graphite as the positive electrode. A mixture of lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) and *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ($Pyr_{14}TFSI$) was utilized as the electrolyte. In comparison to organic solvent-based electrolytes, there are several beneficial properties of ionic liquid-based electrolytes (ILs) in this cell concept. *N*-alkyl-*N*-methylpyrrolidinium bis(perfluoroalkylsulfonyl) imide ionic liquids provide a broad electrochemical stability window [19], a high stability against oxidative decomposition, a broad liquid range and high thermal stability. [16] Furthermore, the IL based electrolytes exhibit low safety hazards [19,20] (non-flammability as well as very low volatility) and a relatively good compatibility with existing lithium ion battery electrodes [21–25]. The issue of solvent co-intercalation into the graphitic cathode, as known for organic solvents [12,13,26–29], can be prevented by use of ILs, since these are only composed of ions. Besides, the anions of the IL can be also regarded as an additional source of active material. However, the application of ionic liquids in combination with graphitic anodes is in most cases problematic due to an ineffective solid electrolyte interphase (SEI) formation, compared to the SEI formation in organic solvent-based electrolytes. [30–33] For this reason, a co-intercalation of organic cations from the ionic liquid can occur, leading to graphite exfoliation. [34] Therefore, alternative anode materials have to be applied such as lithium titanate (LTO, $Li_4Ti_5O_{12}$) or metallic lithium, which are compatible with ionic liquids. [25,35,36]

For dual-ion cells employing 1 M LiTFSI–$Pyr_{14}TFSI$, a coulombic efficiency of ≥ 99% can be achieved displaying a highly reversible $TFSI^-$ anion intercalation/de-intercalation process. [16] Furthermore, a dependency of the discharge capacity as well as the coulombic efficiency on the upper cut-off potential was observed. With increasing the upper cut-off potential from 4.8 V up to 5.3 V vs. Li/Li^+ the coulombic efficiency drops from 99% to 90%, while the discharge capacity increases from 37 mAh g^{-1} to 97 mAh g^{-1}. Additionally, a temperature influence on the above mentioned parameters was also identifiable. [16]

In this work, a novel ionic liquid-based electrolyte, namely a mixture of lithium fluorosulfonyl-(trifluoromethanesulfonyl) imide (LiFTFSI) in *N*-butyl-*N*-methylpyrrolidinium fluorosulfonyl-(trifluoromethanesulfonyl) imide ($Pyr_{14}FTFSI$, Fig. 1) is evaluated for the dual-ion system. Ionic liquids based on the asymmetric fluorosulfonyl-(trifluoromethanesulfonyl) imide ($FTFSI^-$) anion with different cations, such as *N*-butyl-*N*-methyl-pyrrolidinium (PYR_{14}^+) or *N*-methoxyethyl-*N*-methylpyrrolidinium (PYR_{1201}^+) were investigated with respect to their chemical-physical properties, like their electrochemical and thermal stability. [37–39] These studies proved that ionic liquids based on $Pyr_{14}FTFSI$ show a relatively high anodic stability vs. oxidation (5.71 V vs. Li/Li^+) which is comparable to ILs based on *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ($Pyr_{14}TFSI$) (5.89 V vs. Li/Li^+). [37,39,40] Therefore, electrolytes based on the asymmetric fluorosulfonyl-(trifluoromethanesulfonyl) imide anion seem to be promising candidates for dual-ion cells. A comparison of the anion structures suggests that $FTFSI^-$ is smaller than $TFSI^-$. Estimated ion sizes of $FTFSI^-$ and $TFSI^-$ are given by model structures, depicted in Fig. 2. For this reason the intercalation capacity into graphite should be higher for $FTFSI^-$ than for $TFSI^-$. In addition, specific energy projections for dual-ion cells have shown a dependency of the specific energy on the mass of the applied electrolyte. [15] Hence, a lower mass of the utilized ionic liquid, as in the case of $FTFSI^-$ compared to the system applying $TFSI^-$ [16], should yield a higher specific energy.

In this work, the $Pyr_{14}FTFSI$ - LiFTFSI electrolyte solution will be investigated via DSC and TGA to examine the physical properties as well as thermal stability. In addition, this electrolyte will be evaluated with respect to the reversibility of anion uptake/release by means of coulombic efficiency and discharge capacity, both at different upper cut-off potentials. *Ex-situ* X-ray diffraction measurements were conducted to investigate the staging mechanism and to calculate the gallery height by $FTFSI^-$ anion intercalation. In order to gain a better insight into the influence of the anion size on performance, these results are compared with the $TFSI^-$ anion intercalation into graphite and discussed on a comparative basis.

2. Experimental

2.1. Electrode preparation

Electrode tapes for the positive electrode were composed of 90 wt.% KS6L graphite (TIMCAL®), 5 wt.% of conductive carbon black agent C-nergy™ Super C65 (TIMCAL®) and 5 wt.% of sodium carboxymethylcellulose (Na-CMC) as binder (Walocel CRT 2000 PPA 12, Dow Wolff Cellulosics®). For the preparation of the electrodes, at first the binder polymer was dissolved in de-ionized water to obtain a 2.5 wt.% solution. In the next step the corresponding amount of conductive agent Super C65 was added to the solution and further stirred to obtain a good distribution of the binder and the conductive agent. Thereafter, KS6L graphite was admixed into the slurry and dispersed for 1 hour at 5000 rpm (Ultra Turrax® T25 digital with an S25N-25F dispersion tool; Ika®-Werke GmbH & Co. KG) to get rid of agglomerates and to achieve a homogeneous paste. As current collector, freshly etched aluminum foil (30 µm, purity > 99.9%, etched with 5 wt.% KOH, 40 °C, 30 s) was used which was after the etching process carefully rinsed with de-ionized water and ethanol followed by drying in an atmosphere compartment dryer (Binder oven) at 80 °C prior to use. A standard lab-scale doctor-blade technique was employed to cast the paste on the aluminum foil. The gap of the doctor-blade technique was adjusted for a 120 µm wet film thickness yielding an average mass loading of approximately 2.5 mg cm^{-2}. Afterwards, the tapes were dried in air for 12 hours at 80 °C in a compartment dryer (Binder oven). Electrode discs with a diameter of 12 mm were cut out and dried under an oil-pump vacuum (< 10 Pa) at 170 °C for 24 hours (Büchi Glass Oven 585, Büchi). Thereafter, the electrodes were stored in an Argon filled glove box (UniLab, MBraun) with water and oxygen contents below 1 ppm.

2.2. Physical characterization of the $Pyr_{14}FTFSI$–1 M LiFTFSI electrolyte solution

Differential scanning calorimetry (DSC) was performed utilizing a DSC Q2000 (*TA Instruments, New Castle, USA*) with a liquid nitrogen cooling system. Starting from room temperature, the samples were cooled down to -150 °C and afterwards heated to 170 °C with a rate of 10 K min^{-1}.